RETENTION CHARACTERISTICS AND CONVECTIVE TRANSPORT OF PHOSPHORUS IN SOILS AMENDED WITH BIOSOLIDS, MANURES AND FERTILIZER

BY

BABASOLA AJIBOYE

A Thesis Submitted to the Faculty of Graduate Studies in Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

Department of Soil Science
University of Manitoba
Winnipeg, Manitoba

THE UNIVERSITY OF MANITOBA

FACULTY OF GRADUATE STUDIES

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ABSTRACT

Ajiboye, Babasola. M.Sc., The University of Manitoba, October, 2003. Retention Characteristics and Convective Transport of Phosphorus in Soils Amended with Biosolids, Manures and Fertilizer. Major Professor; Dr. O.O. Akinremi.

Three related studies were carried out in the laboratory to investigate the fate of phosphorus (P) from organic amendments when applied to the soil. The first study characterized forms of P in fresh and pre-treated (oven-dried) organic amendments to evaluate their potential environmental impact by comparing the magnitude of their labile P. The organic amendments were biosolids (BIO), dairy cattle (DAIRY) and hog (HOG) manures. The second study examined the impact of these organic amendments and monoammonium phosphate (MAP) fertilizer, on P sorption characteristics of two Manitoba soils, namely; Osborne clay (Gleysolic Humic Vertisol) and Lakeland silty clay loam (Rego Black Chernozerm) soils. Finally, the convective transport of P in soil amended with organic amendments and MAP was investigated to see if these amendments predispose the soil to rapid P movement. The labile P (sum of P extracted by H_2O and $NaHCO_3$) fraction ranged from 24% of biosolids P to 70% of cattle manure P. Labile P in hog manure from different barns was similar and comprised about 60% of total P. The residual P was about 10% in biosolids and cattle manures and 5-8% in hog manures. With oven drying, water extractable organic P (Po) was transformed to inorganic P (Pi) in hog manures, while in the dairy manure, $NaHCO_3$ -P was converted to H_2O-Pi. In the Osborne clay soil, the sorption maximum (S_{max}) ranged from 536 - 655 mg kg^{-1} with BIO, 559 - 650 mg kg^{-1} with MAP, 402 - 568 mg kg^{-1} with DAIRY, and 350 - 587 mg kg^{-1} with HOG. The S_{max} in the unamended soil was 660 mg kg^{-1}. The P saturation index (PSI) ranged from 7.5 - 15.4% with BIO, 7.5 - 16.8% with MAP, 10.5 - 44.7 % with DAIRY, and 16.4 - 55.2% with HOG depending on the rate of P addition. The PSI in the control soil was 2.6%. In the Lakeland silty clay loam, P sorption was significantly reduced by all the amendments except biosolids. The P sorption capacity estimated from one-point isotherms (P_{max}) ranged from 540-603 mg kg^{-1} with BIO, 454 - 596 mg kg^{-1} with MAP, 403 - 494 mg kg^{-1} with DAIRY, and 492 - 519 mg kg^{-1} with HOG. The P_{max} in the unamended soil was 630 mg kg^{-1}. The PSI values ranged from 14-24 % with BIO, through 20-52% and 19-70% with HOG and DAIRY, respectively, to 25-88% with MAP in the Lakeland soil. In the convective transport study, breakthrough of P from the soil column occurred in the unamended soil after 5 pore volumes (PV). At the low rates of all amendments, P breakthrough was similar to the unamended soil, occurring at about 5 PV except with MAP where breakthrough occurred around 4 PV. At the high rate, breakthrough of P from biosolids amended soil was still similar to the control soil, but P broke through earlier, around 4 and 3 pore volumes, with DAIRY and HOG, respectively. Detectable concentrations of P in the effluent prior to P breakthrough was approximately 0.7 mg P L^{-1}with BIO, 2.17 mg P L^{-1} with DAIRY, 2.5 mg P L^{-1} with HOG and 2.4 mg P L^{-1} with MAP. From an environmental point of view, results presented here suggest a lower risk of run-off and leaching loss of P with biosolids application than with hog and cattle manures at equal rates of P application.

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FOREWORD

This thesis was written in manuscript format outlined in *A Guide to Thesis Preparation for Graduate Students in the Department of Soil Science.* Each manuscript was written in journal article format according to ASA-CSSA-SSSA *Publication Handbook and Style Manual.* The first manuscript – *Laboratory Characterization of P in Fresh and Oven-Dried Organic Amendments* – submitted to Journal of Environmental Quality, is currently undergoing revision. Other manuscripts are planned to be published as notes or research papers. American English spelling was used throughout the thesis.

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LIST OF ABBREVIATIONS

BIO1– Biosolids sample collected from North-End Water Pollution Control Centre, Winnipeg, MB Canada in Feb., 2001.

BIO2 – Biosolids collected from same location as BIO1 in June 2001

OLD-HOG – Liquid hog manure collected from Elite Swine Inc.

HOG-SOW – Liquid hog manure collected from sow barn of University of Manitoba Experimental Farm, Glenlea MB. Canada.

HOG-NUR – Liquid hog manure from nursery barn of same location.

DAIRY– Solid manure from dairy cattle barn

BEEF– Solid manure from beef cattle barn

Pi – Inorganic phosphorus

Po – Organic phosphorus

TP – Total phosphorus

TPi – Total inorganic phosphorus

TPo – Total organic phosphorus

MAP – Monoammonium phosphate fertilizer

S_{max} – P sorption maximum from Langmuir isotherm

P_{max} – P sorption capacity from one point isotherm

DPS – Degree of P saturation

PSI – P saturation index

Psi – P sorption index

BTC – Breakthrough curve

R_1 – P retardation factor estimated using CXTFIT

R_2 – P retardation calculated as pore volume when $C/C_o = 0.5$

$P_{retained}$ – P sorbed in the miscible displacement experiments

CDE – Convective-dispersive equation

1. INTRODUCTION

Organic amendments like manures and biosolids (processed municipal sewage) are applied to agricultural lands to take advantage of their nutrient contents. In addition to supplying nutrient to crops, land application of organic amendments provides a viable means of disposal. There are logistical, economical, and environmental problems associated with manure storage, handling, transport, and adoption of alternative end-uses such as incinerations, composting, re-feeding to other animals, enrichment and pelletizing with mineral fertilizers (Sims, 1995). Continuous application of these organic amendments to agricultural land to meet nitrogen (N) requirements of crops, as currently practiced in most regions of Canada, has the potential to accumulate phosphorus (P) in the soil (Simard et al. 1995; Whalen and Chang, 2001). The subsequent build-up of P in the soil could be initially beneficial to crop growth, especially in Manitoba (Canada) soils that are often P deficient (Johnston and Roberts, 2001). P accumulation resulting from long term application of these amendments has been linked to P enrichment of water bodies, which has become a growing concern in many parts of the world (OECD, 1982; USEPA, 1986, 1996). A recent survey of Manitoba streams indicated an increasing trend in the phosphorus concentration with time (Jones and Armstrong, 2001). Since these streams empty into Lake Winnipeg and Lake Manitoba, there is the possibility of lake eutrophication if this trend continues. Some of the economic consequences of surface water eutrophication include costs of purification of drinking water, preservation of natural reserves, deterioration in recreational quality and damage to commercial fishing due to depletion of oxygen for aquatic life (Uunk, 1991).

Regulating the application of P from organic amendments to agricultural soils would be easy if the forms of P they contained were similar, but organic amendments vary in their contents and forms of P. It was hypothesized that the reaction of organic amendments P in soils and its environmental impact will depend on the forms of P in these amendments, and the mineral constituents of the soils. Therefore, separation of P in organic amendments into fractions with various physico-chemical reactivities can be useful in evaluating the potential for environmental impact of P from land application of these amendments.

Phosphorus interacts with the soil constituents, reducing its availability and mobility compared to other nutrients, except in sandy and poorly drained organic soils (Sharpley et al. 1994). The ability of a soil, with or without history of organic and inorganic P amendments, to retain P would depend on the sorption capacity of such soil. But, an improved understanding of the retention characteristics of P in soils is needed to develop management practices that mitigate P transport to surface waters (Dao, 2000). Determining the sorption characteristics of P in soils receiving organic or inorganic P sources can therefore provide a quantitative basis for comparing how the soils' P sorption capacity is affected by long-term application of these amendments, relative to unamended soils.

Subsurface transport of P is an important pathway for P loss, especially in parts of Manitoba with relatively flat landscape. Dissolved P at the soil surface can percolate with drainage water into lower horizons, and could get to surface water through groundwater discharge. Since the accumulation of P may influence the sorption capacity of the surface soil and subsequently, the potential for P movement, it is reasonable therefore to find out how previous applications of organic and inorganic amendment predispose the soil to rapid movement of P.

The main objectives of this research were to: (1) characterize the forms of P in organic amendments, (2) determine how the P retention characteristics of two soils is affected by organic and inorganic sources of P relative to unamended soils, and (3) examine the convective transport of P in a soil amended with organic and inorganic P sources.

2. GENERAL LITERATURE REVIEW

2.1 Organic Amendments in Agriculture

The current method of utilizing organic amendments, be it municipal biosolids, hog or cattle manure is to apply them to agricultural land, thereby taking advantage of their nutrients. Application of manures to agricultural land at P loading rates (based on plant N requirement) that exceeds crop export, as currently practiced on the Prairies, can result in the accumulation of P in soil (Simard et al. 1995; Whalen and Chang, 2001). The resulting build up of P in the soil could be initially beneficial to crop growth, especially in Manitoba soils that are often P deficient (Johnston and Roberts, 2001). Increased soil P levels could increase the concentration of dissolved P in surface runoff or lateral subsurface flow (Simard et al. 2001; Sharpley and Moyer 2000; Sharpley, 1996; Lennox et al. 1997; He et al. 1999), which could trigger eutrophication if the P gets to water bodies. Eutrophication of water bodies by P enrichment has been a growing concern in many parts of the world due to the impairment of water quality, depletion of oxygen for aquatic life and restriction of water for recreation, industries and drinking (OECD, 1982; Sharpley et al. 1994; Carpenter et al. 1998). Some countries in Europe and many US states have established P guidelines for maintaining surface water quality for recreational and drinking purposes, and for the protection of aquatic life. At the moment, there is no well-defined federal guideline for P in Canada, but P has been recently placed on Canada's list of priority pollutant (Fletcher, 2001).

Accumulation of P from manures in agricultural lands have been identified as a potential source of underground and surface water pollution (Beauchemin and Simard, 1999; Eghball et al. 1996; Whalen and Chang, 2001). Consequently, application of biosolids (digested sewage sludge) on land has also created concerns about the possibility of polluting nearby surface waters. A recent survey of Manitoba streams indicates an increasing trend in the phosphorus concentration with time (Jones and Armstrong, 2001). Since these streams empty into Lake Winnipeg and Lake Manitoba, there is the possibility of lake eutrophication if this trend continues. A possible strategy of P management in this region is to control land application of various organic amendments based solely on their P contents or P loadings. This would be plausible if the forms of P in the amendments were the same, with similar reactions, when added to soil. Hence, it is important to characterize the forms of P in organic amendments, which is essential in developing P regulations that is environmentally and agronomically sound.

2.2 P Forms and Contents in Organic Amendments

2.2.1 P forms in Animal Manures

Previous studies on manure P have shown that there is a wide variability in the forms of P in manures (Westerman et al. 1985; Barnett, 1994a; Lienweber, 1997; Dou et al. 2000). Most of these studies reported that the differences in the total amount and forms of P in manures depend on the animal species, the feed and feed supplements used, the age of animal, moisture content, type of bedding material and the duration of manure storage. However, not all P forms in manure are available to the plant or pose the same risk to surface water quality. For example, Kleinman et al. (2002a) found that the water soluble form of P in dairy, poultry and swine manure was highly correlated with dissolved P concentrations in runoff. Barnett (1994a), in a study to evaluate the P status from dairy, beef, hog and poultry (layers and broilers) manures, reported that total P was significantly higher in monogastric species than in ruminants. The percentage of inorganic P was highest in dairy manure (63%), and lowest in poultry manure (35%). The residual P was reported to be higher in hog and layer poultry manures, than in beef, dairy and broiler poultry manures. These differences were attributed to the diet and physiology of the animals. However, Lienweber (1997), in a study on the solubility and fractionation of manure P, reported higher total and labile P concentrations in poultry manure than in liquid hog manure. These results indicate that the forms of P in manures can be quite different.

2.2.2 P forms in Biosolids (Sewage Sludge)

Similar to manure, there is a great deal of variation in the P fractions in biosolids, depending on the biosolids treatments methods (either aerobic or anaerobic digestion) and nutrient removal (chemical versus biological) processes (Kyle and McClintock, 1995; Frossard et al. 1996: Maguire et al. 2001a; Penn and Sims, 2002). Penn and Sims (2002) reported that anaerobic treatment of municipal wastewater, followed by treatment in an aerobic zone during the biological nutrient removal process resulted in excessive P uptake by microbes. The chemical P removal process in biosolids usually entails the addition of Fe (as $FeSO_4$, $FeCl_3$ or $Fe(HClO_4)_3$) or Al (as alum - $Al_2(SO_4)_3.2H_2O$), or Ca (as lime - $Ca(OH)_2$) or organo-cationic polymers or combinations of these, as P removal agents or flocculants. It is not uncommon, however, to find a high Fe or Al content in biosolids that had not been treated with salts of these metals (Penn and Sims, 2002). This may be due to industrial sources of Fe and Al or residues from municipal drinking water treatment plant being discharged into the wastewater stream (Jenkins et al. 2000). It may also be due to storm runoff which contained Al and Fe from soil material. Maguire et al. (2001) investigated the relationship between biosolids treatment process and P availability in soils of different texture, organic matter content, cation exchange capacity and P status. They found that anaerobically digested biosolids with Fe additions produced a lower water-soluble P and FeO-P (i.e. P that easily desorbs from soils onto Fe oxide strip during 24-h equilibration) than anerobically digested sludge without Fe additions, and undigested sludge with or without Fe and lime additions. They concluded that P-based nutrient management to protect water quality should consider biosolids treatment process since P in biosolids treated with metal salts during processing was not the same as P in biosolids treated with no metal salts. They also recommended further research on comparison of biosolids P with a variety of animal manures. Frossard et al. (1996) in assessing P forms and exchangeability in different biosolids found that flocculated and heat-treated biosolids contained low amount of rapidly exchangeable P but high amount of slowly exchangeable P, which was related to the presence of precipitated P minerals in the biosolids. Penn and Sims (2002) also reported higher Mehlich-3 extractable P (29-68%) and water soluble P (10-45%) in biosolids that were not treated with Fe than in Fe or Al treated biosolids having 0.4-13% Mehlich-3 P and 0.4-5% water soluble P.

2.2.3 Fractionation Methods used in Characterizing P in Organic Amendments

Given the complex nature of organic amendments, it is easier to partition them into pools of available and non-available P than to identify individual P compounds. The classes of P compounds are usually defined by the extractant that removes them in a single or sequential extraction procedure. A review of some of the fractionation schemes that have been used to characterize manure P are included in the following sub-sections.

2.2.3.3 Single Chemical Extraction Methods. The first and earliest single chemical extraction method used in fractionating manure is the one developed by McAuliffe and Peech (1949). According to this method, manure P was characterized as lipid P, inorganic P (Pi), acid soluble organic P (Aso-P) and residual P. Lipid P was estimated as the P extracted by a mixture of ether and alcohol, Pi and Aso-P as P extracted by trichloroacetic acid (TCA) with and without activated carbon, respectively. Residual P was determined after acid digestion of the residue. Salomon and Gerriste (1981) also separated total P in runoff sediments into organic and inorganic P using a single extraction with a mixture of TCA and ethylenediaminetetraacetic acid (EDTA), or with 2.5M HCl. Organic P was estimated as the difference between total P and Pi in the extracts. A modification of McAuliffe and Peech (1949) fractionation scheme was used by Barnett (1994b) to characterize P as phospholipids, inorganic P, acid soluble organic P and residual P. Heating of ether was eliminated in this method because of its flammability. This was achieved by heating ethanol separately with manure, and then adding ether after cooling (AOAC, 1984). All of these fractionation methods were designed for estimating manure P availability for crops but may be inadequate to address the current concern on the potential impact of manure P on surface water quality.

2.2.3.2 Sequential Extraction Technique. This method was originally developed by Chang and Jackson (1957) to fractionate inorganic P in the soil. The underlying assumption in the sequential extraction technique is that; readily available P in soils is removed first with mild extractants, while less available P can only be extracted with stronger acids and alkali. For example, the Chang and Jackson fractionation scheme involved the extraction of 'soluble P' with 1M NH_4Cl, 'Al-P' with 0.5M NH_4F, 'Fe-P' with 0.1M NaOH, and 'Ca-P' with 0.5M H_2SO_4 in that order, from the same soil sub-sample. Another sequential fractionation technique proposed by Hedley et al. (1982), involved the separation of soil P into inorganic, organic and microbial P with various physico-chemical reactivity and plant related availability. The Hedley fractionation technique was modified to fractionate P in biosolids (Frossard et al. 1996; Sui et al. 1999; Penn and Sims, 2002), and different manures and composts (Sharpley and Moyer, 2000; Dou et al. 2000). This technique allows for the quantification of available and non-available P pool in the manure and can be used to predict the potential for loss of manure P when applied to land. Mild extractants like H_2O or anion exchange resin quantify manure P fractions that are easily available for crop uptake and susceptible to run-off loss. Labile P and Al- and Fe- bound organic and inorganic P are usually extracted by stronger extractants like $NaHCO_3$ and NaOH, and the recalcitrant P by a much stronger acid such as HCl. The recalcitrant P fractions, together with the residual P, are relatively stable and less likely to be carried away in run-off. Lienweber (1997) employed the sequential extraction procedure on freeze-dried poultry and hog manures and reported the distribution of total P among residual P (39-41%), recalcitrant H_2SO_4-P, (17-27%) labile P (24-39%) and NaOH-P (3-10%). Similarly, Dou et al. (2000) characterized P in dairy and poultry manures using the sequential extraction scheme involving multiple extractions with various extractants. They found that 70% of total P in dairy manure was extracted by water, 14% by $NaHCO_3$, 6% by NaOH, 5% by HCl and 5% as residual. In poultry manure, the P fractions extracted were: 49% by water, 19% by $NaHCO_3$, 5% by NaOH, 25% by HCl and 2% as residual. They concluded that dairy manure P, with a high concentration of labile P (sum of H_2O-P and $NaHCO_3$-P) may be more susceptible to runoff loss than poultry manure.

2.2.3.3 Isotope Exchange Technique. Isotope exchange has also been used to assess inorganic P availability in biosolids (Frossard et al. 1996) and in soils (Sinaj et al. 1992). Frossard et al. (1996) reported that the amount of biosolids P that was isotopically exchangeable within 1 day in the soil (corresponding to a period of active uptake of P by a single root or a root hair) was well correlated to the sum of water- plus $NaHCO_3$-extractable P from sequential extraction of the biosolids. The quantity of precipitated P, considered as the sum of HCl (Ca-P) and NaOH (Fe- and Al-P) extractable P in the sequential extraction was also highly correlated with isotopically exchangeable P after a 12-week period (corresponding to the active uptake of P by the complete root system of annual crops). Their results demonstrated that isotopic exchange of labeled P, just like the sequential extraction procedure, can be used to estimate the quantities of rapidly available P and of less available P in organic amendments like biosolids.

2.2.3.4 Nuclear Magnetic Resonance. Another method that has been used to characterize P compound in animal manure is the nuclear magnetic resonance (NMR) spectroscopy of ^{31}P. In this technique, manure is extracted with 0.5M NaOH and the intensity of the spectra lines in the extract is determined on NMR spectrometer (at 202.25MHz for ^{31}P). Leinweber et al. (1997) reported that the ^{31}P-NMR spectra showed differences in the forms of P in manures.

The P forms were identified as: orthophosphate, mono- and diester-P, teichoic acid-P and pyrophosphate. The ^{31}P-NMR spectra showed that the concentration of inorganic P in dry poultry manure was more than in hog manure, ranging from 84-95% of the total P. These researchers also obtained a significantly high correlation between NaOH-extracted P for ^{31}P-NMR spectroscopy and the sums of resin-P + $NaHCO_3$-P + NaOH-P in different arable soil of northwest Germany.

2.2.4 Pretreatment of Organic Amendments

Manures are known to be heterogenous materials and the high moisture content of fresh manures makes handling very difficult. To remove these limitations, manures are usually pretreated by freeze drying, air drying or oven drying prior to analysis (Dou et al. 2000; Sui et al. 1999). The effect of pretreatment methods was recently investigated by Akinremi et al. (2003) who found a significantly higher total P in fresh than in oven dried samples of hog and poultry manure and cautioned against the use of oven-drying where quantitative recovery of P is desired.

In investigating the fate of P in organic amendments, such as biosolids and manures, after land application, it is important to characterize the forms of P they contain since the forms of P in these amendments can possibly influence their reaction in soils. Most of the studies on P fractionation in organic amendments used either biosolids alone (Frossard et al. 1996; Sui et al. 1999; Penn and Sims, 2002) or manures (Sharpley and Moyer, 2000; Dou et al. 2000; Lienweber et al. 1997). Hence, fractionation of P in manures and biosolids as recommended by Maguire et al. (2001a) can be used as means of comparing these amendments with respect to the magnitude of their labile P and to evaluate their potential environmental impact.

Fractionations of manure and biosolids P will provide information on the proportion of total P in the organic or inorganic forms, which is important in assessing the reactivity of P in these amendments.

2.3 Retention of organic amendments P in the soil

Land application of organic amendments has the potential to stabilize the P from organic amendments in relatively immobile forms, because soils contain cations with high affinity for P. However, P accumulation in soils resulting from repeated applications of organic amendments, especially at loading rates that exceeds P removal, can lead to saturation of P sorption sites (Whalen and Chang, 2001, 2002), thereby increasing the risk of P transport to surface water though runoff and leaching. Previous studies on the mechanisms of P transfer have shown that the potential P loss to run-off depends on a soil's P content as well as the degree of saturation of P fixing sites (Lennox et al. 1997; Pote et al. 1999; Sharpley and Moyer 2000; Kleinman et al. 2002b). There is increasing awareness that runoff loss of P from agricultural land is a major non-point source pollutant causing accelerated eutrophication of aquatic system (OECD, 1982; USEPA, 1996; Carpenter et al. 1998). Since the application of amendments has the potential to modify soils' P sorption characteristics, an understanding of the changes in P sorption capacity of soils in the presence of organic and inorganic amendments is necessary.

2.3.1 P Sorption versus Precipitation

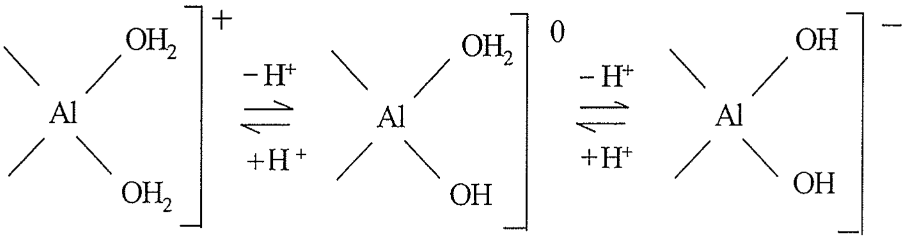
Retention of P either from organic or inorganic sources could be in the form of sorption and/or precipitation reactions. P sorption refers to both fast, almost instantaneous and slow long-term adsorption of P on the surface of soil minerals and organic compounds (Syers and Curtin, 1989; Barrow, 1985; McGechan and Lewis, 2002a). From the perspective of equilibrium chemistry, a rapid sorption of inorganic P to soil occurs when the aqueous concentration of P is greater than equilibrium permits. This is then followed by a slower time-dependent sorption process, which has been described by several authors as slow adsorption, slow reaction, deposition, fixation, solid-state diffusion, or precipitation (McGechan and Lewis, 2002a). However, some researchers believe that the sorption process should be regarded as a continuum with no separation between the slow and fast processes (Addiscott and Thomas, 2000). In most cases, there is a degree of irreversibility associated with sorption process causing hysteresis of P sorption-desorption in soils.

Similar to P sorption reactions is precipitation, which is a P fixation process describing the formation of discrete, solid material. Both sorption and precipitation reactions can occur simultaneously either at different points or on similar surfaces in the soil (Akinremi, 1990). The general consensus on the distinction between sorption and precipitation is that sorption predominates under a low concentration of P in soil solution whereas precipitation predominates at high P concentration. However, this distinction is only qualitative since there are no established threshold levels for either of these processes.

2.3.2 Mechanisms of P Sorption in Soils

Soil particles generally consist of net negative charge on their surfaces, yet they still retain anions like phosphates through the sorption process. The sorption of P involves specific soil constituents. Phosphate can be retained via specific sorption involving the formation of chemical bonds with the surface group of mineral oxides in the soil. It may also be retained via non-specific sorption, just like Cl^- and NO_3^-, on positively charged mineral surface by electrostatic attraction. The mechanism of P sorption onto various soil constituents is discussed in the following sub-sections.

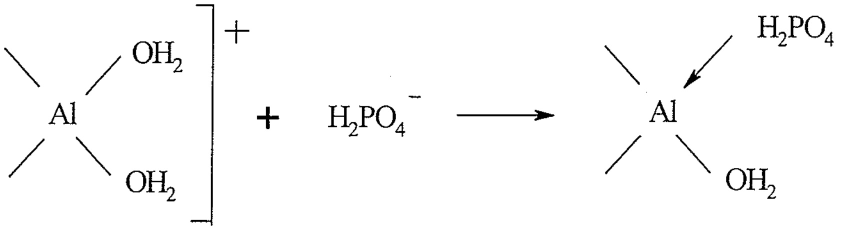
2.3.2.1 Sorption by Hydrous Oxides of Fe and Al. Mineral soils contain Al and Fe oxides as discrete particles, or as coatings on soil particles. Specific sorption of P by hydrous Al and Fe oxides was described by Hingston et al. (1968). In the presence of water, the surfaces of these oxides become hydroxylated, either as single hydroxyl or double hydroxyl groups. It is the H_2O or valence-unsatisfied OH^- ligands bound to the surface of Al or Fe that are sites of chemisorption. The surface charge of these hydroxyl and aquo groups, tetrahedrally coordinated with Fe or Al, is determined by the pH of the solution. The change in the surface charge of hydrouos oxides of Fe and Al with changing pH was depicted by Rajan et al. (1974) as shown below:



[2.1]

As the pH of the aqueous solution increases, H^+ dissociates from the aquo group thus forming the hydroxyl group and brings the surface to isoelectric point or Point of Zero Net Charge (PZNC). Further increase in pH (as in alkaline soils) leads to the formation of more hydroxyl groups and the charge on the surface becomes negative.

At low pH, the hydroxylated oxides of Fe and Al have a net positive surface charge due to the predominance of $Fe\text{-}OH_2^+$ or $Al\text{-}OH_2^+$. These charged surfaces can then retain $H_2PO_4^-$ by electrostatic attraction through a non-specific sorption. The electrostatic binding results in reversible sorption of P. The phosphate ion ($H_2PO_4^-$) can also penetrate the coordination shell of Fe and Al atom, exchanging with $-OH_2^+$ to form an inner sphere complex via covalent bonds. In this case, $H_2PO_4^-$ replaces an aquo group ($-OH_2^+$) to form a monodentate bond directly with Fe or Al atom as shown below:



[2.2]

At high pH, however, the specific sorption of P involves a ligand exchange reaction between two hydroxyl groups and HPO_4^{2-} to form bidentate bonding with Fe or Al. During the bonding process, HPO_4^{2-} loses a proton to form two bond to an Fe or Al atom or a bond to two adjacent atoms.

The low concentration of P, which can be related to pH, usually results in the replacement of aquo groups. However, as sorption increases, with increasing P concentration, more hydroxyl groups are replaced. Therefore at the sorption maximum, P will be mainly replacing hydroxyl groups.

2.3.2.2 Sorption by Alumino-Silicate Minerals. Wild (1950) proposed a mechanism for P sorption by silicate minerals similar to that by Al and Fe oxides. For example, P sorption by gibbsite involved: (1) an exchange of phosphate ions with the hydroxyl groups attached to the gibbsite layer and, (2) a non-specific sorption with a possible positive charge resulting from the adsorption of protons or hydroxyl groups of the gibbsite layer. However, P sorption onto kaolinite, at low concentrations, involved the replacement of aquo groups at the broken edge of the clay lattice (Kuo and Lotse, 1972). At high concentrations, P solutions will dissolve kaolinite to release Si and Al with possible precipitation as Al-P compounds.

2.3.2.3 Sorption by Soil Carbonates. Under an alkaline condition, P sorption onto the surface of $CaCO_3$ involves the replacement of $-OH_2$, HCO_3^-, or -OH on calcite surface by $H_2PO_4^-$ or HPO_4^{2-}, resulting in the formation of Ca-P (Morgan, 1997). The sorbed P on the calcite surface is held less firmly than P sorbed on Fe or Al oxides. There is limited information in the literature on P sorption by carbonate. One of the reasons for this is that, even at low P concentration, P reacts with calcite to form Ca-P, making it difficult to distinguish between sorption and precipitation.

2.3.3 P Sorption onto Colloidal Materials

The sorption of P onto mobile colloids, unlike P sorption onto ‘static’ soil components, has not received much attention until recently (McGechan and Lewis, 2002a, 2002b). Unlike the dissolved P that is readily available for algal uptake, particulate P and colloidal P were thought to be less effective in triggering surface water eutrophication because these particles settle to the bottom of water bodies (Fozzard et al. 1999). However, particulate and colloidal P can become soluble over time, especially during the course of transport. McGechan and Lewis (2002a) recently reviewed studies on P sorption onto mobile particulate and colloidal material by Stamm et al. (1998) and Haygarth et al. (1998). These researchers suggested that elevated P concentrations observed in drainage water during rainfall was probably due to colloidal P transport. They reasoned that a lower P concentration due to dilution of the soil solution by incoming rainfall would have occurred if colloidal P was not significant. Colloidal P, just like the dissolved P, has the potential to aggravate surface water pollution and its importance in P transport is now receiving attention.

2.3.4 Soil Factors Affecting Phosphorus Sorption

Many studies have identified the variables controlling sorption of P from organic and inorganic sources to include soil texture (Matthews et al. 1998), soil pH (Sharpley, 1983; Traina et al. 1986), $CaCO_3$ content (Akinremi, 1990; Morgan, 1997), hydrous oxides of Fe and Al (Torrent, 1987; Loganathan et al. 1987; Pena and Torrent, 1990; Borggaard et al. 1990; Agbenin, 2003), initial soil P levels (Sharpley, 1995) and, soil and manure-derived organic matter (Ohno and Crannell, 1996).

2.3.4.1 Soil Texture. Soil texture refers to the proportion of sand, silt and clay particles in the soil. The effectiveness of soil particles to retain any substance depends on their surface area to volume ratio, a property that is affected by texture. An increase in the proportion of clay (and sometimes silt) increases the surface area of the mineral particles. For example, a colloidal clay surface area ranges from about 10 to 1000 $m^2\ g^{-1}$, which is about 10,000 times greater than medium-sized sand of similar mass (Brady, 1990). Hence, finely divided particles such as clay will have high sorption capacity due to their small particle size and large surface area. Ryan et al. (1984) reported that P sorption increased with increasing clay content and decreased as CEC increased in several calcareous soils. The effect of CEC was ascribed to its correlation with degree of weathering and the surface area; the higher degree of weathering decreased CEC and increased the surface area available for sorption. Mozaffari and Sims (1994) also reported a strong correlation ($r^2 = 0.94$) between clay content and P sorption maxima in several Delaware soils. Similarly, Leclerc et al. (2001) reported that soil P sorption capacity of Gleysolic soils increased with increasing clay content. Campbell and Edwards (2001) also reported a high adsorption of P in weathered soils due to the relatively high clay content. In contrast, sandy soil with low amount of reactive constituents favored the occurrence of P in solution, as a result of their low sorption capacity.

2.3.4.2 Soil pH. The soil pH affects the surface charge on the Fe and Al oxides and on the broken edge of silicate minerals. At low pH, there is a net positive surface charge on the oxide surface. The charged oxide surface can then sorb HPO_4^- through a non-specific adsorption which is reversible since the ions are held by electrostatic attraction by the positively charged surface. However, the formation of inner sphere complexes at neutral and alkaline pH resulting from the ligand exchange reaction between one or two aquo groups ($-OH_2^+$) and phosphate may lead to irreversibility in P sorption. Leclerc et al. (2001) showed that P sorption decreased and water extractable P increased as the pH of soils with similar clay content increased from acidic to near neutral.

Frossard et al. (1995) reported that the effect of ionic composition of the solution on anion sorption varies with pH. Above a certain pH, sorption increases with increasing ionic strength and below this pH sorption decreases. The pH at which there is no effect of the electrolyte concentration is called Point of Zero Salt Effect (PZSE). For uniform surfaces such as those of synthetic oxides, the PZSE coincides with the PZNC.

2.3.4.3 Carbonate content. In P sorption study of Manitoba soils, Weir and Soper (1962) reported that neutral non-calcareous soils had greater P sorption maxima than calcareous soil. The higher P sorption in the non-calcareous than in the calcareous soils was attributed to their higher clay content. These researchers also reported that Ca-P was less soluble in the calcareous soil (with alkaline pH) compared to the neutral soils. Akinremi (1990) compared six Manitoba soils with similar texture but different $CaCO_3$ content and found that P sorption was higher in soils with higher $CaCO_3$ content. The calcareous soils, with $CaCO_3$ content ranging from 2-8 %, also had higher affinity for P than non-calcareous soils (<1 % Eq. $CaCO_3$). The only exception was the non-calcareous Portage clay loam that had an affinity constant similar to the calcareous McCreary soil.

2.3.4.4 Oxides of Fe and Al. The concentration of Al and Fe oxides are higher in acid than in calcareous soils. These oxides are the most important components controlling P sorption in acid soils, and to some extent in calcareous soils (Morgan, 1997). For example, Loganathan et al. (1987) reported that P sorption in tropical and sub-tropical soils was positively correlated with amorphous Fe and Al extracted by ammonium oxalate. For Mediterranean soils, Pena and Torrent (1990) found that P sorption was strongly related to crystalline Fe and Al, measured as the difference between citrate-dithionite-bicarbonate (CDB) and oxalate extractions. Similarly, Borggaard et al. (1990) reported that both crystalline and amorphous Fe and Al accounted for P sorption in a range of Danish soils. More recently, Agbenin (2003) reported that 73% of the variability in P sorption of acidic

Alfisol of northern Nigeria was explained by CDB extractable Fe and Al. The dominant effect of Fe and Al in P sorption in acid and neutral soils explains why the P sorption capacities of these soils are often estimated based on the amount of oxalate extractable Fe and Al (Pote et al. 1996; Beauchemin and Simard, 1999; McDowell and Sharpley, 2001).

2.3.4.5 Initial Soil P Levels. The influence of initial soil P level on P sorption (and leaching) has been investigated extensively by many researchers (Heckrath et al. 1995; Zhou and Li, 2001; Maguire and Sims, 2002a, 2000b). Heckrath et al. (1995) observed that below an agronomic soil test P of 60 mg Olsen P kg^{-1} in an acidic sandy soil, inorganic P was sorbed on high energy sites resulting in low P concentration in tile drain flow. Above this soil test value, regarded as a 'change point', P concentration in the drainage water increased rapidly due to reduction in P sorption and saturation of P fixing sites. Indiati et al. (1995) also reported a significant decrease in the amount of sorbed P with increasing rates of P fertilizer application to the soil. However, Anderson and Wu (2001) reported that P accumulation from 30 years of heavy fertilization of a clay loamy soil with pig and cow slurries had minimal effect on the P sorption capacity of the soil. Their finding was attributed to the degree of P saturation (DPS) in this soil, which varied between 37% and 53% after 30 years of fertilization. The DPS values indicate that the proportion of the overall sorption capacity of the soil occupied by P was low. Together with Fe and Al contents of the soil, initial soil P gives an indication of the degree of P saturation in acidic soils, depending on the mineral controlling P concentration in the soil and the extraction method for P. The concept of P saturation will be discussed later.

2.3.4.6 Soil Organic Matter. The decomposition of soil organic matter produces organic acids in the soil. These acids in turn undergo dissociation, usually at low pH, to produce organic anions that can undergo a ligand exchange reaction with hydroxyl-Al in soils (Traina et al. 1986). The formation of organic-Al complex can either increase or decrease P sorption. At low concentration of organic acids with weak affinity for Al, the exchange reactions increase the amount of exchangeable Al with subsequent increase in P sorption. The presence of organic acid can also increase P sorption by preventing the crystallization of amorphous oxides thereby increasing the specific surface area available for P sorption (Borggaard et al. 1990). On the other hand, the presence of high concentrations of organic acid with high affinity for Al results in the formation of soluble Al-organic complexes (chelates) and the release of previously sorbed P. The reduction of Al activity in the solution would favor the dissolution of more Al-P compounds, resulting in decreased P sorption. Sui and Thompson (2000) observed a very strong correlation between amount of P sorbed and the net amount of organic C desorbed from all samples of biosolids amended Mollisol. Their results confirmed that competition exists between organic anions and P for sorption sites during P sorption process. The formation of organic matter-oxide complexes can also reduce the affinity of the soil for P. For example, Dubus and Becquer (2001) reported that orthophosphate ions need to diffuse through the organo-mineral oxide complexes to reach sorption sites.

Organic molecules may also undergo specific sorption with the soil minerals, competing with P for sorption sites (Lopez-Hernandez et al. 1986; Hue, 1991). Hue (1991) in reviewing the effect of organic acid on P sorption cited the study by Moshi et al. (1974), in which the amount of P fertilizer required to attain a soil solution concentration of 0.2 mg P L^{-1}

decreased from 90 to 22 kg P/ha when the organic carbon level of the soil increased by 3%. Erich et al. (2002) observed that sorption of P in soils amended with manure and compost, and unamended soils resulted in an increase in dissolved organic carbon; indicating a competition between P and organic acid for sorption sites. Non-specific sorption of organic matter onto soil particles could increase the surface negative charge of the particle. In this case, the electrostatic attraction of P to the soil would be reduced, leaving more P in the solution (Iyamuremye and Dick, 1996). An indirect effect of organic matter on P sorption can occur as a result of anaerobic decomposition of organic matter, which causes Fe compounds to be dissolved and re-precipitated as amorphous minerals with strong P sorption abilities (Sah and Mikkelsen, 1989).

2.3.5 Organic Amendments and P Sorption by Soils.

Organic amendments like animal manures and biosolids have lower P content when compared to inorganic fertilizers. For example, Akinremi et al. (2003) reported that the total P contents of six organic amendments (biosolids, compost, poultry, hog, beef, and dairy cattle manures) ranged from 0.25 to 4.5% on a dry weight basis. But, granular P fertilizer such as monoammonium phosphate (MAP) contains about 21 to 24% P. Application of an organic amendment to supply equivalent amount of P as inorganic fertilizer will therefore result in the addition of large amount of organic matter to the soil. Zsolnay and Gorlits (1994) had earlier reported that the incorporation of C-rich organic amendments to soils increases the soluble soil organic matter content. Flaten et al. (2003) also showed that about 6700 kg ha^{-1} of dairy manure (containing 1.3g P kg^{-1} on a wet weight basis) will be needed to supply the same amount of P as MAP added at the rate of 40 kg P ha^{-1}.

The molecular weight of organic matter added to the soil by various organic amendments is important in P sorption. Ohno and Crannell (1996) reported that dissolved organic matter (DOM) derived from hog and poultry manure did not inhibit the ability of Al to sorb P probably due to its high molecular weights, but, the low-molecular-weight DOM from green manure (vetch and clover) inhibited P sorption. On the other hand, Sharpley and Sisak (1997) observed that P sorption increased in a soil receiving poultry manure. This was attributed to the low molecular weight of organic compounds contained in the manure, which formed complexes with Ca, Fe and Al, thereby increasing P sorption sites.

The P content of organic amendments also affects P sorption. Singh and Jones (1976) had earlier reported that organic residues (wheat straw, corn stalk and sawdust) that contained less than 0.3% total P increased P sorption, while those (especially poultry manure and barley straw) that had P content greater than 0.3% decreased P sorption. These authors then suggested that an increase or a decrease in P sorption is a function of P content of the organic amendments. In investigating the impact of biosolids amendments on P sorption, Sui and Thompson (2000) reported that biosolids decreased P sorption and binding intensity, and increased the equilibrium P concentration. They suggested that biosolids-derived P occupied the sorption sites to diminish P sorption in the soil. Another suggestion was that organic compounds added with biosolids, or produced after application, might have occupied some P fixing sites.

The quantity of cations and anions in organic amendments also plays an important role in P sorption. For example, Robinson and Sharpley (1996) observed that P sorption maxima and binding energies were greater in soil treated with poultry leachate than KH_2PO_4. The authors suggested that the addition of a significant quantity of Ca (31mg L^{-1}) to the soil, with poultry leachate, resulted in the formation stable Ca-P complexes which increased P sorption. In contrast, Iyamuremye et al. (1996) also reported that the presence of inorganic ligands such as SO_4^{2-} and /or F^- in manures can strongly complex exchangeable Al, preventing P from being fixed by Al. Addition of organic amendments to the soil could increase soil pH, minimizing the activity of Al and favors the production of OH^- that can compete with P for sorption sites. Other possible explanations for the effects of organic amendments on P sorption include the occupation of sorption sites with inorganic P dissolved from organic amendments or released by the mineralization of organic P fractions.

2.3.6 P Sorption Isotherms

The retention characteristics of P in soils are usually quantified by using P sorption isotherms, describing the relationship between the amount of P sorbed by the soil and the equilibrium concentration of P in solution at constant temperature. The P sorption isotherm technique was initially used to provide insight on the quantity and intensity of applied P that can be available for plant uptake. Isotherms are now used to determine the vulnerability of P applied as fertilizer or manure to loss in runoff and/or leaching, by considering the capacity factor (P sorption capacity) instead of quantity factor (Beauchemin and Simard, 1999). Some of the widely used sorption isotherm equations include: the Langmuir, Freundlich, Brunaeur-Emmett-Teller (BET), two-surface Langmuir, Gunary and Temkin (Sample et al. 1980; Akinremi, 1990). In general, the application of these isotherms to P sorption data is based on goodness-of-fit criteria to different model assumptions. Some of the common assumptions to sorption isotherms include; the existence of equilibrium conditions (Barrow and Shaw, 1975) and a reversible adsorption process (Sample et al. 1980). However, these assumptions rarely hold true for P sorption in soils. It is possible for these assumptions to be contradicted in soils even though the equations provide a good fit to the sorption data (Harter and Smith, 1981). Sposito (1989) cautioned that the conformity of P sorption data with any of the isotherms cannot explain the mechanism of sorption or ascertain whether sorption or precipitation has occurred. Despite these limitations, almost all investigations involving P sorption are summarized using these isotherms.

2.3.6.1 The Langmuir Isotherm. The Langmuir sorption isotherm was originally derived from the kinetic theory of gases, to describe the adsorption of gases onto solid (Akinremi, 1990). This isotherm is applicable to P sorption under a dilute equilibrium concentration of P. The underlying assumptions of the Langmuir model in describing P sorption are: (1) P sorption occurs on monolayer surface with same bonding energy; (2) there is a maximum sorption capacity that will not be exceeded regardless of increasing concentrations of P in the soil solution (Sample et al. 1980). The Langmuir equation is written as:

$$S = \frac{bS_{max}C}{1+bC} \qquad [2.4]$$

where S is the amount of P sorbed per unit mass of adsorbent (mg kg^{-1}), C is the equilibrium concentration of P (mg L^{-1}) in solution, b is a constant called the 'affinity factor', which reflects the relative rates of sorption and desorption at equilibrium and S_{max} is another constant , a 'capacity factor' (mg P kg^{-1}) which is regarded as the P sorption maximum. The S_{max} corresponds to complete monolayer coverage of the surface by P. Conformity of sorption data with Langmuir isotherm is checked by plotting the linearized form of equation [2.4] as shown below:

$$\frac{C}{S} = \frac{1}{bS_{max}} + \frac{C}{S_{max}} \qquad [2.5]$$

A plot of C/S against C should yield a straight line with slope $1/S_{max}$ and intercept $1/bS_{max}$, if the data conforms to the Langmuir isotherm. The S_{max} and b can be calculated from these regression coefficients. Some of the limitations of the Langmuir model includes: (1) the assumption of constant energy of sorption which contradicts observable pattern in the soil (Barrow, 1978); and (2) assumption that no interaction occurs between sorbed species is invalid, because the species involved in the sorption process are charged, and charges on the sorbing surface are variable. In spite of these limitations, the Langmuir equation is often used in describing P retention characteristics because the parameters obtained (S_{max} and b) can be related to various soil properties to provide information about the nature of reaction between the soil and P fertilizers (Akinremi, 1990).

2.3.6.2 Freundlich Isotherm. This isotherm is an empirical formulation, and as such, non-specific and applicable to a wide range of equilibrium P concentration, unlike the Langmuir equation. The Freundlich equation is written as:

$$S = KC^n \qquad [2.6]$$

where n is a constant related to the binding energy with which P is sorbed (usually < 1) and K is Freundlich sorption coefficient (L kg^{-1}), a measure of the soils' capacity to sorb P. Theoretically, K represents the amount of P sorbed when the equilibrium P concentration is 1 mg L^{-1}. The Freundlich equation implies that P sorption decreases exponentially with increasing saturation of sorption sites in the soil. This means that the higher the value of n, the lower is the affinity of the surface for P. Logarithmic transformation of Equation [2.6] is:

$$\ln S = \ln K + n \ln C \qquad [2.7]$$

A plot of lnS against lnC yields a straight line with lnK as the intercept and n as the slope, indicating conformity of the sorption data with the Freundlich isotherm.

2.3.6.3 The Brunaeur-Emmett-Teller (BET) Isotherm. The BET equation is an extension of the Langmuir equation to account for multilayer adsorption. It describes multilayer sorption by assuming that the first layer of adsorbate becomes a site for the second layer, the second layer for the third layer, and so forth. The BET equation in its linear form is given by:

$$\frac{C}{S(C_o - C)} = \frac{1}{kS_{max}} + \frac{(k-1)C}{kS_{max}C_o} \qquad [2.8]$$

where C_o is the maximum concentration of P that can exist in solution before precipitation occurs, k is a constant related to the free energy of transfer of P from solution to sorption sites (Griffin and Jurinak, 1973). Other parameters are as earlier defined. The monolayer capacity, S_{max}, in equation [2.8] can be used to calculate the surface area of adsorbent if the effective area occupied by each adsorbate molecule is known. Conformity of the sorption data with multilayer sorption is verified if a plot of $C/(C_o-C)S$ against C/C_o gives a straight line with slope $(k-1)/kS_{max}$ and intercept $1/kS_{max}$. This allows for the calculation of S_{max} from:

$$S_{max} = \frac{1}{\text{slope} + \text{intercept}} \qquad [2.9]$$

2.3.6.4 The 'Two-Surface' Langmuir Isotherm. Holford and Mattingly (1974) proposed the 'two-surface' Langmuir equation as a way of improving upon the failure of the traditional Langmuir isotherm to describe P sorption in 41 soils with varying physical and mineralogical properties. The underlying theorem is that if the distribution coefficient (ratio of S to C) of P sorbed by a soil is a finite, decreasing function of S, and extrapolates to zero at some finite value of S, the sorption isotherm can be represented mathematically by a two surface Langmuir equation (Sposito, 1982). The equation is:

$$S = \frac{k_1 S_{max1} C}{1+k_1 C} + \frac{k_2 S_{max2} C}{1+k_2 C} \qquad [2.10]$$

where S and C have the same meaning as in the traditional Langmuir equation. The parameters, k_1 and k_2, are related to high-and low-affinity binding energy of P, and S_{max1} and S_{max2} are the high and low affinity maxima of P sorption. Two straight lines can be obtained from a plot of S/C against S if the sorption data conforms to equation [2.10]. The P sorption parameters can then be calculated from the regression parameters of these lines.

2.3.6.5 The Gunary Sorption Isotherm. This isotherm is also a modification of the Langmuir isotherm and is given by:

$$C/S = A + BC + D\sqrt{C} \qquad [2.11]$$

where *A, B* and *D* are constant coefficients. The parameters C and S are solution P and adsorbed P concentrations, respectively. The presence of the square root was interpreted to indicate a diminishing affinity of the sites for P with increasing sorption, until a limiting value is reached. Although there was no theoretical justification for this modification, Gunary (1970) found that equation [2.11] gave a better fit in 24 soils than the Langmuir equation [2.5], accounting for 99.8% of the variation in P sorption.

2.3.6.6 The Temkin Isotherm. The Temkin equation was derived from the Langmuir equations by including the condition that the energy of sorption decreases linearly with increasing surface coverage. This equation is written as:

$$S = a + b \ln C \qquad [2.12a]$$

where

$$a = \frac{RT\, S_{max}}{B} \ln A \qquad [2.12b]$$

$$b = \frac{RT\, S_{max}}{B} \qquad [2.12c]$$

The parameter R is the universal gas constant, T is the absolute temperature, $A = e^{a/b}$ and B is a constant related to the energy of sorption. A plot of S against lnC should give a straight line if the sorption data conforms to the Temkin model. Equations [2.12b] and [2.12c] can be solved simultaneously to obtain S_{max} and B. This kind of plot, according to Bache and Williams (1971), is convenient because: (1) the wide range of P concentration in soils is better expressed on a logarithmic scale; (2) the intensity factor (equilibrium P concentration) in P sorption studies is a chemical potential, hence a logarithmic function of concentration (Bache, 1965).

2.3.6.7 The Single-Point Isotherms. Bache and Williams (1971) proposed a P sorption index (Psi) that can be used as a quick and simple single-point isotherm for estimating the P sorption capacity of soils:

$$Psi = S/\log C \qquad [2.13]$$

where S is the amount of P sorbed, expressed in mg/100g of adsorbent. C is the equilibrium P concentration, expressed in μmol P/L. These units were recommended because they give a convenient range of Psi values. Indiati et al. (1995) reported that Psi closely correlated with the P sorption maximum derived from a Langmuir sorption plot for a wide range of soils. This type of strong correlation between parameters from single and multi-point isotherms suggests the possibility of such a simple and inexpensive measurement to replace the multi-point sorption isotherms. Due to the time and effort involved with the use of the standard isotherm models for practical application, the one-point isotherm proposed by Bache and Williams (1971) is now used to quantify P retention potential of soils (Mozaffari and Sims 1994; Beauchemin and Simard, 1999).

Zhou and Li (2001) recently proposed another one-point isotherm measurement for estimating the P sorption capacity of calcareous soils. This method determined the amount of P sorbed with the addition of 400 mg P L^{-1} to the soil at a soil to solution ratio of 1:10.

2.3.6.8 Other Parameters Obtainable from P Sorption Isotherms. These parameters include: the equilibrium P concentration in the soil solution at which there is neither sorption nor desorption, EPC_o (Indiati et al. 1995; Sui and Thompson, 2000; Zhou and Li, 2001); the buffering capacity, defined as the change in the quantity of sorbed P per unit change in concentration of dissolved P (Holford and Mattingly, 1976) as cited by McGechan and Lewis (2002a), and the P equilibrium buffering capacity (PEBC) (Sui and Thompson, 2000), which describes the ability of the soil to modulate the effect of further P addition on P concentration of the solution. These parameters provide useful data to aid in explaining the potential loss of applied P in runoff and by leaching. For example, Zhou and Li (2001) showed that EPC_o was positively correlated to the degree of P saturation.

2.3.7 Degree of P Saturation of the Soil

The degree of P saturation (DPS) was introduced in recent times, as an environmental index to assess the potential release of P to runoff and leaching (Zhou and Li, 2001). By definition, the degree of P saturation refers to the extent to which the soil's capacity to retain P is affected by P accumulation. It is the ratio of extractable P to the soil P sorption capacity, expressed as a percentage (Van der Zee et al. 1987; Beauchemin and Simard, 1999; Khiari et al. 2000). The extractable P could be either oxalate-extractable P for non-calcareous soils (Pote et al. 1996), Mehlich-1 P for neutral soils (Sallade and Sims, 1997), Mehlich-3 extractable P for acid and calcareous soils (Sharpley, 1995; Khiari et al. 2000), or Olsen P for calcareous soil (Zhou and Li, 2001). The soil P sorption capacity (PSC) can be estimated from the oxalate-extractable Al and Fe of a wide variety of acidic, non-calcareous soils (Pote et al. 1996; Maguire et al. 2001b; Maguire and Sims 2002b, McDowell and Sharpley, 2001; Sims et al. 2002). The PSC could also be estimated from Mehlich-3 extractable Fe and Al (Sims et al. 2002), Mehlich-3 Al (Khiari et al. 1999, 2000) or from sorption maximum derived from Langmuir sorption isotherms (Sharpley, 1995). The degree of P saturation computation based on oxalate extraction of P, Al and Fe (DPS_{ox}) usually involves the expression of these elements in molar concentrations (mmol kg^{-1}). DPS_{M3} computed from Mehlich-3 extractable P and Al was reported to be well correlated with DPS_{ox} (Khiari et al. 2000). These authors reported that the critical DPS_{ox} value of 25% that resulted in an equilibrium P concentration of 0.1mg L^{-1} (Breeuwsma and Silva, 1992) is equilvalent to a DPS_{M3} value of 15%.

An important question is whether or not these parameters can be used to characterize P sorption of soils that have been amended with various rates of organic and inorganic P sources. The utility of these indices in reflecting the saturation of soil P retention capacity following the addition of organic amendments is unknown. This type of information can provide a quantitative basis for comparing how a soil's P sorption capacity is affected by long-term application of organic amendments and inorganic fertilizer relative to unamended soils.

2.4 Subsurface Transport of P in the soil

Phosphorus can be transported from agricultural land by surface runoff resulting from rainwater or snowmelt flowing overland into streams, and by subsurface flow (Sims et al. 1998). Subsurface P movement was considered an insignificant pathway for P loss because P is confined to the soil surface through sorption onto soil components like clays, Al and Fe oxides, carbonates and organic matter. However, the occurrence of P in the groundwater, in an environmentally significant quantity in organic, sandy and manured soils has changed the previously held view about P movement in the soil (Heckrath et al. 1995; Sims et al. 1998; Hooda et al. 1999). The amount of P moving down the soil profile in drainage water can vary widely, from negligible, almost undetectable amounts in soils with high sorption capacity, to a few mg P L^{-1} in organic soils with low sorption capacity (Sims et al. 1998).

Phosphorus loss in drainage water may not be significant economic loss from an agronomic point of view, but may pose an adverse environmental impact to surface water quality. For example, the minimum P concentration that can trigger eutrophication of surface waters ranges from 0.02 to 0.035 mg total P L^{-1} (OECD, 1982) or 0.01 - 0.05 mg dissolved inorganic P L^{-1} (USEPA, 1986). This threshold P level has prompted the establishment of various guidelines for water quality management in many countries. For example, the United States Environmental Protection Agency, (USEPA) established 0.05 mg dissolved P L^{-1} as the critical limit of P in streams entering lakes and/or reservoirs, and 0.025 mg dissolved P L^{-1} within the lakes. The Italian water quality guideline for P in multiple-use lake is between 0.01 and 0.1 mg total P L^{-1} (Chianudini and Premazzi, 1988; as cited by Heckrath et al. 1995). In the Netherlands, the critical limit of 0.1 mg dissolved P L^{-1} was set as the tolerable P concentration in ground water (Breeuwsma and Silva, 1992). In Manitoba (Canada) the upper limit of 0.05 mg P L^{-1} in surface waters was set by Manitoba Conservation to combat the eutrophication problem (Flaten et al. 2003).

There is increasing evidence that the accumulation of P in the soil profile with organic amendments contributes to losses of P in drainage water (Heckrath et al. 1995; Anderson and Xia, 2000). This may be attributed to the effect of these amendments on P retention as discussed earlier (section 2.2.5).

2.4.1 Mechanisms of P Movement in Soils

From the perspective of solute transport, phosphate is a relatively immobile and non-conservative ion (capable of being transformed within the soil matrix). It can interact with the soil matrix via sorption-desorption, precipitation-dissolution and ion exchange reactions. Phosphates, like any other solute can be transported via three main mechanisms, namely: diffusion, hydrodynamic dispersion and convection.

2.4.1.1 Diffusive Flux. Diffusion refers to the spreading out of solutes from regions of high concentration to regions of low concentration in the soil solution. Diffusive transport is due to the random thermal motion of solutes, ions and/or molecules. The random motion of the solute in all directions evens out any irregularity in the concentration of the solution. The diffusion process can be described by a simple empirical relation known as Fick's First Law. This law states that; the net amount of solute transversing through a unit area in unit time (flux density) is proportional to the concentration gradient across the area, and is given by:

$$J = -D\frac{\partial C}{\partial z} \qquad [2.14]$$

where J is the solute flux density (kg m^{-2} s^{-1}), D is the diffusion coefficient (m^2 s^{-1}). The parameters, C and z, are the solute concentration (kg m^{-3}) and distance (m), respectively. The quantity $\partial C/\partial z$ is the concentration gradient of the solute, which represents the driving force. For this reason, equation [2.14] is often called a flux-force relationship. The diffusion coefficient D, expresses the difficulty that the diffusing solutes experience in moving through the porous media. Some of the factors that affect the value of D includes the soil physical properties such as: soil moisture content, temperature and bulk density, and variables affecting sorption, such as, organic matter content, pH, salinity and clay content of the soil (Scott, 2001).

The flux-force relationship can only be used to describe ion movement under a steady-state condition. However, this condition rarely occurs in the soil, as transient state diffusion is the norm. The Fick's Second Law can be obtained by applying the law of continuity (conservation of mass) to the First Law. The continuity law states that the rate of change in the concentration of a solute accessing a unit volume of soil is equal to the gradient of the diffusive flux. In one dimension and without a chemical term, the continuity law is written:

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial z} \qquad [2.15]$$

Under a transient state, equations [2.14] and [2.15] are combined to give the general diffusion equation (involving a chemical reaction term, φ), as given below:

$$\frac{\partial C}{\partial t} = -D\frac{\partial^2 C}{\partial z^2} \pm \varphi \qquad [2.16]$$

The positive and negative chemical reaction term refers to source and sink of solute, respectively. In the case of phosphate, if sorption is considered as the only process responsible for P sink, the chemical term could be derived from a sorption isotherm through the local equilibrium assumption.

Diffusion is considered by many researchers as the most important pathway by which P is made available for plant uptake (Akinremi, 1990).

2.4.1.2 Hydrodynamic Dispersion (HD) or Dispersive Flux. Hydrodynamic dispersion occurs as a result of non-uniformity of flow velocity in the soil pores and is similar to diffusion in that it tends to even out concentration differences in the soil solution. Hydrodynamic dispersion or mixing can be visualized as occurring when a transition zone develops between two solutions of differing composition. One of the causes of dispersion is the distribution of solution velocity within the pore spaces. This boundary effect creates a velocity gradient in the solution, with the maximum velocity occurring at the centre of the pore. Another cause may be due to variation in pore sizes. For example, the average velocity in the large pores is often greater than in the small pores. The tortuous flow path through the pores could also be a cause of dispersion. The dispersion equation is similar to Fick's First Law, and is given by:

$$J_h = -D_h \frac{\partial C}{\partial z} \qquad [2.17]$$

where D_h is the dispersive coefficient and is a function of flow rate of the solute.

In general, HD increases with velocity because of the development of eddies as velocity increases. At high flow velocity, the effect of HD overwhelms that of diffusion. However, at low flow velocity, the effect of HD is negligible. Since the effects of both diffusion and dispersion on the distribution of solute concentration are similar (though with different mechanisms), they are usually combined in transport equations, with the implicit assumption that the two are additive.

2.4.1.3 Convective Flux. Convective flow refers to the physical transport of a solute with the soil solution. It is also know as mass flow or advection. Convective flux occurs as a result of differences in hydraulic head or matric potential of water in the soil, i.e. hydraulic gradient or gradient in matric potential. An idealized type of convective flux of a conservative (non-interacting) solute is piston flow. In piston flow, a known concentration of solute introduced at one end of the soil column travels through the soil without spreading. The concentration of the solute at the distal end of the column is zero until the front appears, and then the concentration becomes the same as that at the inflow end of the column. Piston flow can only occur under steady-state convection, when the solution is moving uniformly through the soil. The flow rate of the solute can be calculated using Darcy's equation:

$$J_x = qC \qquad [2.18]$$

where J_x is the solute flux density (kg m^{-2} s^{-1}) in the x direction, q is the macroscopic flow rate of the solution per unit area perpendicular to the x direction (m/s), and C is the concentration of the solute in the solution (kg m^{-3}). Under a steady state, the convective flux of a solute (J_c) in the soil can be expressed as:

$$J_c = v\theta_v C \qquad [2.19]$$

where v is the average water velocity in the soil pores (m/s) and θ_v is the average volumetric soil water content (m^3/m^3). Under a transient state, equations [2.19] and [2.15] are combined to give a one-dimensional equation (without a chemical reaction term) for convective flow:

$$\frac{\partial C}{\partial t} = -\frac{\partial (v\,\theta_v C)}{\partial z} \qquad [2.20]$$

The total solute flux in the soil is a combination of diffusive, dispersive and convective fluxes and is expressed as the convective-dispersive equation (CDE):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} - v\frac{\partial C}{\partial t} \pm \varphi \qquad [2.21]$$

2.4.2 Factors Affecting P Movement in the Soil

Some of the dominant factors affecting the movement of P in the soil are: soil texture and pore types, dominant flow type and soil P sorption capacity (Simard et al. 2000; Hooda et al. 1999).

2.4.2.1 Influence of Soil Texture and Aggregation on P movement. Soil texture and aggregation are related to the distribution of pores in the soil; macropres predominate in sandy soils while micropores predominate in clayey soils. Loamy soils have a combination of micro- and macro pores. Macropores can also occur in fine textured soils as a result of worm holes, channels created by dead plant roots, cracks in dry clay soil and inter-aggregates spaces in aggregated soils. The distribution of these pores determines the flow rate of water through the soil. Akhar et al. (2003), in a review of literature on the effect of flow rate on P retention, cited the observation of Simard et al. (2000), that "high pore-water velocities can override P sorption kinetics because the residence time of P can be too short to allow for P diffusion to reaction sites." Pore size distribution also affects the type of flow in the soil, i.e. matrix or preferential.

2.4.2.2 Matrix Flow and P Movement. By way of definition, matrix flow refers to the movement of water through the bulk soil. Therefore, matrix flow will be slow in fine textured soils devoid of macropores. The slow movement allows for intimate contact of dissolved P with the soil matrix, which may reduce significant P movement (Heathwaite et al. 2000). On the other hand, there could be high rate of matrix flow in soil with high conductivity, such as sandy soil, which may result in significant P movement. For example, Akhtar et al. (2003) observed little or no increase in P concentration of drainage water in a fine granular weakly structured soil when matrix type flow predominated. Similar result was reported in an earlier study by Sommers et al. (1979), who investigated the effect of long-term irrigation with municipal wastewaters on P leaching in clay loam and sandy loam soils. These researchers found a significant increase in the total P and extractable P (Bray 1) in the depth range of 30-60 cm in the sandy loam but little P leaching in the clay loam, with irrigation. They suggested that the slow matrix flow in the clay loamy soil increased P sorption and hence, reduced P leaching.

2.4.2.3 Preferential Flow and P Transport. Preferential flow describes the rapid water flow through cracks and biopores. Many studies on P transport have shown that a high amount of P occurs in leachate/drainage water shortly after P application under preferential flow conditions (Heckrath et al. 1995; Simard et al. 2000; Jensen et al. 2000). Heckrath et al. (1995) argued that the failure of a P-deficient sub-soil, with high P sorption capacity, to retain P when P concentration in the plough layer exceeded 60 mg Olsen-P kg^{-1} was due to preferential flow. Preferential flow was also suggested to be responsible for high amounts of particulate P that occurred in drainage water (Turtola and Jaakkola, 1995; Matthews et al. 1998). Jarvis et al. (1999), in modeling particle leaching in soil, suggested that preferential flow through macropores may be the only pathway by which colloidal and particulate P can move in unsaturated soil, since particles are retained by physical filtration processes when moving through the tortuous soil matrix pores. The higher proportion of P in tile-drainage water relative to surface runoff, observed by Simard et al. (2000) was also attributed to preferential flow. However, Jensen et al. (1998) believed that preferential flow through macropores (less than 3mm diameter) provided sufficient residence time for complete sorption of P within a 15cm soil column.

2.4.2.4 Influence of P sorption Capacity on P Movement. Reduction in the P sorption capacity and/or increased P saturation as mentioned earlier, can markedly increase P concentrations in drainage water. Hooda et al. (1999) reported that a change in the slope of sorption isotherms from high affinity to relatively low affinity, when the loading rates exceeded 100 mg P kg^{-1} corresponded to elevated P concentrations in the subsurface drainage. This was attributed to a reduced sorption capacity of the soil as the high energy sites decreased with increasing loading rates of P. Similar to Heckrath et al. (1995), these workers observed change point values of 38 and 47 mg Olsen P L^{-1} for two soils above which P concentration in the drainage water increased rapidly. The differences in the change point values led to the conclusion that the relationship between extractable P and losses in drainage may be soil, site, and management specific. McDowell and Sharpley (2001) also reported that dissolved reactive P (DRP) concentrations in subsurface flow after the applications of dairy manure at the recommended rate in the Unified National Strategy for Animal Feeding Operation (USDA-USEPA, 1999), exceeded those estimated to promote surface water eutrophication. This was attributed to saturation of the soils with P even before manure application, resulting in P movement when leaching occurred. Similarly, Schoumans and Groenendijk (2000) in modelling P leaching in noncalcareous sandy Dutch soil found an exponential increase in subsurface P concentration with increasing degree of P saturation (DPS). Lienweber et al. (1999) also reported a very strong correlation between leachate P concentrations and DPS, as well as P sorption capacity for soils with different management intensities. These authors also observed that a DPS value greater than 30% resulted in critical concentrations of P in ground water that could trigger eutrophication of surface waters.

2.4.3 Movement of P from Organic Amendments

The movement of P from an organic amendments is not as well understood as the movement of P added as inorganic P fertilizers. The forms of P in organic amendments and their cation and organic acid composition, may complicate the movement of P. For example, Hergert et al. (1981) reported that the application of dairy manure, at the recommended rates of 35 Mg ha^{-1} did not significantly contribute to P loss in drainage water (0.014 mg L^{-1}). However, excessive application at 200 Mg/ha increased the dissolved P concentrations in the tile drainage to 0.218 mg L^{-1}, a level that is above the limit normally associated with eutrophication of surface waters. This finding may reflect the reduction in P retention at higher application rate of dairy manure. Field et al. (1985) reported that the application of poultry manure to a loamy soil markedly decreased the P binding strength. Eghball et al. (1996), in a long term study of P movement and adsorption also found that P from manure moved deeper (up to 1.8m) in soil receiving P from cattle manure than in soil receiving commercial fertilizer. Eghball and co-workers attributed these findings to the movement of P in the organic form in manured soil. It is also possible that the application of organic amendments resulted in the occlusion of the P fixing sites and accelerated the downward movement of P in the soil. The studies reviewed above, though carried out in the field, are relevant as they tend to explain the movement of P in organically amended soil.

2.4.4 Methods of Measuring Convective Movement of P in the Soil

Phosphorus movement through the soil profile had been investigated in the field using lysimeters and artificial drainage systems (MacDowell and Sharpley, 2001; Simard et al.

2000), and in controlled laboratory and greenhouse column studies (Chen et al. 1996; Elliott et al. 2002). Akhtar et al. (2003) reported that convective flow of P can be better explained in a repacked soil column than in an intact soil column. These authors observed a huge variability in P breakthrough among treatment replicates of undisturbed soil columns relative to repacked columns, and an instantaneous P breakthrough in some soils with high P sorption capacity. They attributed the failure of the CDE to predict P transport in intact soil column to P movement via preferential flow path, and not to inadequate determination of sorption coefficients as earlier suggested by Ho and Notodarmojo (1995). This is due to the fact that preferential flow path in intact soil contradicts the convective flow assumption that water flows at an average velocity with only minor variations around the mean due to dispersion.

The convective flow of P can be used to estimate P movement, as well as the degree of P sorption in the soil. In estimating inorganic P sorption in soil, convective transport has advantages over the batch equilibration technique because the mechanical disturbances due to shaking and separation of the solution from the solids (filtration and centrifugation) are removed. In some cases, however, the flow rate may be too fast for equilibrium to occur between the P solution and the soil, therefore this technique is also applicable to fast sorption reaction of P with soils that are initially free of sorbed P (Van Riemsdijk and Van der Linden, 1984). Convective transport studies also provide a flexible way of expressing P movement. It is known that the residence time of P in the soil, as dictated by the flow rate, influences P breakthrough (Sakdinan, 1971) and based on this knowledge, correction can be made for the flow rate to normalize the breakthrough data for various treatments and replicates (Flaten, 1989).

Convective transport of P can be studied using the elution development and or the miscible displacement techniques (Sakdinan, 1971; Cho et al. 1970). The elution development involves the addition of P (pulse input) at the top of the soil column, followed by flushing with water until the outflow concentration of P becomes zero or negligible. In the miscible displacement approach, the resident soil solution is displaced by a known concentration of P (continuous input) and the breakthrough of the latter is monitored until the outflow concentration is equal to that of inflow. Cho et al. (1970) investigated the convective transport of labeled orthophosphates in different soil and reported that the rate of phosphate movement was greatly retarded by the interaction between soil and P. They also found that the retardation of P movement increased with an increase in the rate of P sorption in various soils. The rate of P movement was also a function of the mode of input. Pulse input (elution development) had a greater rate of movement than that obtained with continuous input (miscible displacement). The analytical solutions of the transport equation, using appropriate boundary conditions for the pulse and step inputs, revealed that the reversibility of the adsorption reaction did not affect the rate of P movement introduced as a pulse input, hence a higher rate of movement than P introduced as a continuous input. The differences in the rate of ^{32}P and ^{31}P movement in the soils, as measured by the miscible displacement, were attributed to isotopic exchange phenomena. Hence, ^{32}P isotopes, capable of exchanging with the unlabeled soil P cannot be used to accurately measure convective P movement.

3. LABORATORY CHARACTERIZATION OF PHOSPHORUS IN FRESH AND OVEN-DRIED ORGANIC AMENDMENTS

3.1 Abstract

The forms of P in different organic amendments and the effect of oven drying on forms of P were investigated. Biosolids collected at different times (from a wastewater treatment plant), cattle manures (from beef and dairy cattle barns) and hog manures (from sow and nursery barns) were selected. Both fresh and oven-dried amendments were analyzed for inorganic, organic and total P using a modification of the Hedley fractionation technique, starting with mild extractant and progressing to stronger extractants. Water extracted about 10% of biosolids P, and 30-40% of hog and cattle manure P. A large fraction of the water extractable P was in the inorganic form except for the beef cattle manure. There was less variation in the amount of P extracted by $NaHCO_3$ in all the amendments (range of 21-32% of total P) except in the dairy cattle manure (45% of total P). The labile P fraction (sum of water and $NaHCO_3$ extractable P) ranged from 24% of biosolids P to 70% of cattle manure P. Labile P in hog manure from different barns was similar and was about 60% of total P. The amount of P that could not be sequentially extracted was about 10% in biosolids and cattle manures and 5-8% in hog manures. Though oven dry manures and biosolids are easier to handle compared to fresh forms, results from this study indicate that oven drying caused transformation in forms of P in the organic amendments. In hog manures, water extractable organic P (Po) was transformed to Pi, while in the dairy manure $NaHCO_3$ -P was

converted to water extractable Pi with oven drying. Therefore, caution should be exercised in using pre-treatments, such as oven drying, for studies that evaluate forms of P in manures, biosolids and other organic amendments.

3.2 Introduction

A recent survey of streams in Manitoba indicated an increasing trend in the phosphorus concentration with time (Jones and Armstrong, 2001). Since these streams empty into Lake Winnipeg and Lake Manitoba, there is the possibility of lake eutrophication if this trend continues. A possible strategy for P management in this region is to control land application of various organic amendments based solely on their P contents or P loading. This would be plausible if the forms of P in the amendments were the same, with similar reactions when added to soil.

Studies have shown that there is a wide variability in the P content of manures (Westerman et al. 1985; Barnett, 1994a; Lienweber et al. 1997; Dou et al. 2000). Most of these studies indicated that the differences in the total amount and forms of P in manures depend on the animal species, the feed and feed supplements used, the age of animal, moisture content, type of bedding material and the duration of manure storage. Similarly, there is a large variation in the P contents and forms of P in biosolids, depending on the biosolids treatments methods (aerobic or anaerobic digestion) and nutrient removal (chemical versus biological) processes (Frossard et al. 1996: Maguire et al. 2001a; Penn and Sims, 2002). Our hypothesis was that the forms of P in these amendments influence the reaction between amendment P and the soil. Therefore, in assessing the fate of organic amendments P in the soil, it is essential to determine the forms of P in those amendments.

Most of the studies on P fractionation of organic amendments involved either biosolids (Frossard et al. 1996; Sui et al. 1999; Penn and Sims, 2002) or manures (Barnett, 1994a, b; Sharpley and Moyer, 2000; Dou et al. 2000; Lienweber et al. 1997) alone. A concurrent fractionation of P in manures and biosolids, as recommended by Maguire et al. (2001a), is an important step towards the proper management of organic sources of P.

The objective of this study was to characterize the forms of P in organic amendments, including biosolids, cattle and hog manures as a first step in determining the fate of organic amendments P in the soil. The effect of pre-treatment on organic amendments was also examined by comparing P fractions in fresh and oven-dried organic amendments, since dry manures are easier to handle than fresh forms during analysis. The result obtained from this fractionation study will provide a means of assessing the impact of organic amendment P on P retention and movement in the soil. The result will also be useful in comparing different organic amendments with respect to the magnitude of their labile P.

3.3 Materials And Methods

3.3.1 Collection and Pre-treatment of Organic Amendments

Samples of biosolids were collected from the North End Water Pollution Control Centre of the City of Winnipeg Water and Waste Department (Winnipeg, MB Canada) in February and June 2001 and labelled BIO1 and BIO2, respectively. The biosolids treatment involved anaerobic digestion and flocculation with organo-cationic polymers. Hog manures were collected from the storage lagoon of Elite Swine farm (OLD HOG), and from sow (HOG-SOW) and nursery (HOG-NUR) barns of the University of Manitoba Experimental Farm at Glenlea near Winnipeg, MB Canada. Manures from dairy (DAIRY) and beef (BEEF) cattle barns were also collected from the same location. All samples were frozen immediately upon collection (at -13°C) and thawed just prior to analysis. Portions of the thawed samples (FRESH) were oven-dried at 105°C for 24 hr to determine the moisture content of each amendment. The amendments were digested using the sulfuric acid-hydrogen peroxide method (Akinremi et al. 2003) and total P content determined colorimetrically. Total Al, Fe, Ca and Mg content of the digests was determined using inductively-coupled plasma atomic emission spectrometry (ICP-AES). The oven-dried samples (DRY) were kept in desiccators until sequentially analyzed.

3.3.2 Characterizing P in Organic Amendments

A modification of the sequential extraction procedure of Hedley et al. (1982) as described by Dou et al. (2001) was used. Extraction was performed sequentially using deionized water, 0.5M $NaHCO_3$ (pH 8.5), 0.1M NaOH and 1M HCl. According to this method, water-extractable P represents the most available form of P for biological uptake and run-off loss and, $NaHCO_3$ extracts the readily desorbable form of P from hydrous Al and Fe oxides, described as long-term bioavailable P (Kamprath and Watson, 1980). The less bioavailable P in the form of Al and Fe complexed P are extracted by NaOH, and HCl extracts the relatively stable and biologically unavailable P bound to Ca (Robinson and Sharpley, 1996). In the sequential extraction process, 30 mL of extractant, starting with water, was added to 0.3g (oven dry weight) of organic amendments in a 50 mL centrifuge tube. The suspension was shaken on an end-to-end shaker at 150 epm (excursions per minute) for 16 hr at room temperature. The sample was then centrifuged at 12500 × g for 15 minutes and vacuum-filtered using a 0.45 μm cellulose membrane. The phosphorus in the filtrate was determined colorimetrically using the molybdate-blue method (Murphy and Riley, 1962), on an Ultrospec 3100*pro* UV/Visible Spectrophotometer (Biochrom Ltd Cambridge, England) at a wavelength of 882 nm. This initial extract was regarded inorganic P (Pi). To measure the total P (Pt) in each extract, another portion of the filtrate was digested using the sulfuric acid-hydrogen peroxide method of Akinremi et al. (2003). The pH of the digested solution was adjusted to 6.5 - 7.0 and P measured using the same procedure described for Pi. Organic P (Po) in each extract was estimated as the difference between Pt and Pi. The residue in the centrifuge tube was added to the filter residue and then extracted by the next extractant in sequence. Both Pi and Po were measured in the extracts obtained with water, 0.5M $NaHCO_3$ (pH 8.5) and 0.1M NaOH, while 1M HCl extract was assumed to contain only Pi. Residual P was determined following sulfuric acid-hydrogen peroxide digestion of the residue remaining after all the extraction steps. The summary of this fractionation technique is shown in Figure 3.1. The same fractionation approach was used to characterize the oven-dried amendments.

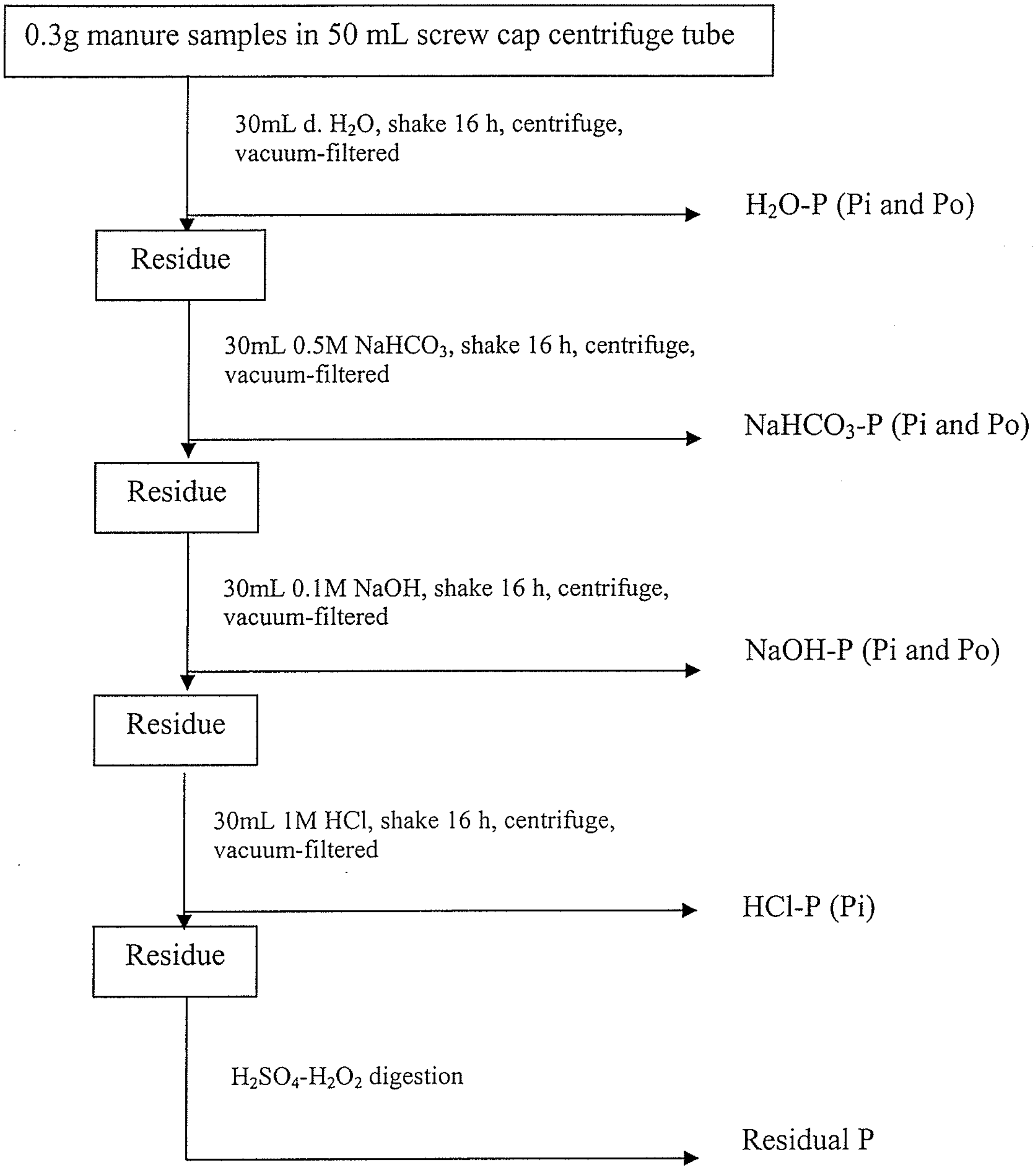


Figure 3.1 Flowchart of the sequential extraction procedure

The fractionation scheme was carried out on triplicate samples. The extracted P in each fraction was expressed as a percentage of total P in each amendment (Table 3.1) to provide a means of comparing the various P fractions in the organic amendments. The total inorganic fraction (TPi) was estimated as the sum of all Pi's including the HCl-P, while the total organic fraction (TPo) was estimated as the sum of all Po's plus the residual P. Unlike in soil, we assumed that the residue left after the extraction process contained only organic P, and as such, the residual P was classified as organic.

3.3.3 Statistical Analyses

The experiment was set up as a 2X7 factorial, carried out as a completely randomized design. The factors were types of amendments at seven levels (BIO1, BIO2, OLD-HOG, HOG-SOW, HOG-NUR, DAIRY and BEEF), and pre-treatment at two levels (FRESH and DRY). Statistical analysis was carried out using the GLM procedure of SAS (SAS Institute, 2001). Analysis of contrast was used to compare differences among organic amendments.

3.4 Results

3.4.1 P Fractions in Fresh Organic Amendments

The total P contents of the organic amendments used in this study varied significantly, ranging from a low of 0.25% in beef cattle manure to a high of 4.5% in hog manure from a sow barn (Table 3.1). There was variability in P contents, even between two biosolids samples collected at different times but from the same location (Table 3.1). There were also significant differences ($p < 0.05$) in the forms of P amongst the different amendments (Table 3.2).

Table 3.1 Selected characteristics of the organic amendments used

			Total			
Amendments	% Solids	Total P (%)	Fe	Al	Ca	Mg
			-----------(g kg^{-1} dry matter)-------------			
BIO1	24.06	1.84	10.35	20.94	48.27	19.48
BIO2	32.54	1.27	16.79	26.79	55.38	29.05
DAIRY	23.54	0.55	9.82	20.88	22.22	15.13
BEEF	30.71	0.25	2.73	3.78	47.61	22.49
OLD-HOG	4.20	3.34	2.58	1.57	24.93	13.28
HOG-SOW	12.44	4.50	2.52	1.73	38.41	15.03
HOG-NUR	2.99	2.14	1.73	1.30	18.63	13.51

In the fresh amendments, water extracted about 10% of total P in biosolids (BIO 1 and BIO 2), 20% in DAIRY and between 35-43% in BEEF and hog manures – OLD-HOG, HOG-SOW, and HOG-NUR (Figure 3.2a). $NaHCO_3$ extracted about 50% of the total P from DAIRY and 25% from the BEEF, complementing the amount previously extracted by water (Figure 3.2b). There was less variation in the amount of P extracted by $NaHCO_3$ from biosolids and hog manures (15-25%). A stronger extractant, NaOH, extracted a significantly higher percentage of total P from biosolids (38%) than from hog and cattle manures - DAIRY and BEEF (5-22%). HCl also extracted a significantly higher P (about 30% of total P) from biosolids and OLD-HOG, and less than 15% from cattle manures (Figure 3.2d). The residual P that could not be extracted by this procedure ranged from 5-8% in hog manures, 10-14% in cattle manures and about 11% in biosolids (Figure 3.2e). The amount of P accumulated with successive extraction of the fresh amendments is shown in Figure 3.3. The labile P fractions

(P accumulated up to the $NaHCO_3$ extraction) were significantly lower in biosolids (24%) compared to other amendments (55-70%).

3.4.2 Pre-Treatment Effects on P Fractions

There was a significant effect of pre-treatment on the P fractions (Table 3.2). The water-soluble P fractions in the DRY amendments were similar to those in FRESH amendments except in DAIRY, where 45% of the total P was extracted from oven dry sample compared to 20% in the FRESH DAIRY (Figure 3.2a). The effect of oven drying on H_2O-P in DAIRY that was not observed in other amendments was probably responsible for the significant pre-treatment by amendment interaction in the water Pi and Po (Table 3.2). The amount of P extracted by $NaHCO_3$ was significantly lower in oven dried DAIRY and hog manures compared to fresh form of these amendments (Figure 3.2b). Similar to $NaHCO_3$, P fractions extracted by NaOH were significantly lower in DRY biosolids and cattle manures compared to their fresh counterparts. In contrast, oven drying significantly increased NaOH-P in hog manures (Figure 3.2c). HCl-P in biosolids and cattle manures was also significantly increased by oven drying (Figure 3.2d). However, oven drying significantly decreased residual P in biosolids and cattle manures (Figure 3.2e).

3.4.3 Transformation of P Fractions with Oven Drying

There was a significant pre-treatment by amendment interaction on the entire P fraction in the organic amendments (Table 3.2). This was caused by a significant effect of oven drying on the forms of P in the organic amendments. Oven drying resulted in the transformation of one form of P to another. This transformation was expressed as the arithmetic difference between the P fractions extracted in the DRY and FRESH samples of these two manures.

Table 3.2 Mean squares values of the analysis of variance of the effects of amendments and pre-treatments on the P fractions

Source of variations	df	---------- Mean Squares ----------							
		Water-Pi	Water-Po	$NaHCO_3$ -Pi	$NaHCO_3$-Po	NaOH-Pi	NaOH-Po	HCl-P	Residual-P
Amendments	6	620***	201***	526***	61.5***	585***	131***	545***	12***
Pre-treatments	1	892**	381***	51***	48***	6.3**	85***	230***	10***
Pre-treat × Amend	6	242***	211***	59***	18.5***	9.2***	30***	48***	11***

Contrasts	df	---------- Mean Squares ----------				
		Water-P †	$NaHCO_3$-P ‡	NaOH-P §	HCl-P	Residual-P
BIO1 vs BIO2	1	29***	5.7ns	16***	0.26ns	0.25ns
Biosolids vs other Amend.	1	6472***	614***	3961***	1315***	36***
OLD-HOG vs other hogs	1	36***	0.95ns	67***	0.84ns	4.9***
HOG-SOW vs HOG-NUR	1	18***	34***	12***	183***	0.01ns
HOG-SOW vs other hogs	1	69***	38***	0.57ns	228***	1.95**
BEEF vs DAIRY	1	13***	609***	0.39ns	237***	25.5***

* significant at 5% level , ** significant at 1% level , *** significant at 0.1% level, and ^{ns} not significant

† Water-P = H_2O-Pi + H_2O-Po, ,

‡ $NaHCO_3$-P = $NaHCO_3$-Pi + $NaHCO_3$-Po

§ NaOH-P = NaOH-Pi + NaOH-Po

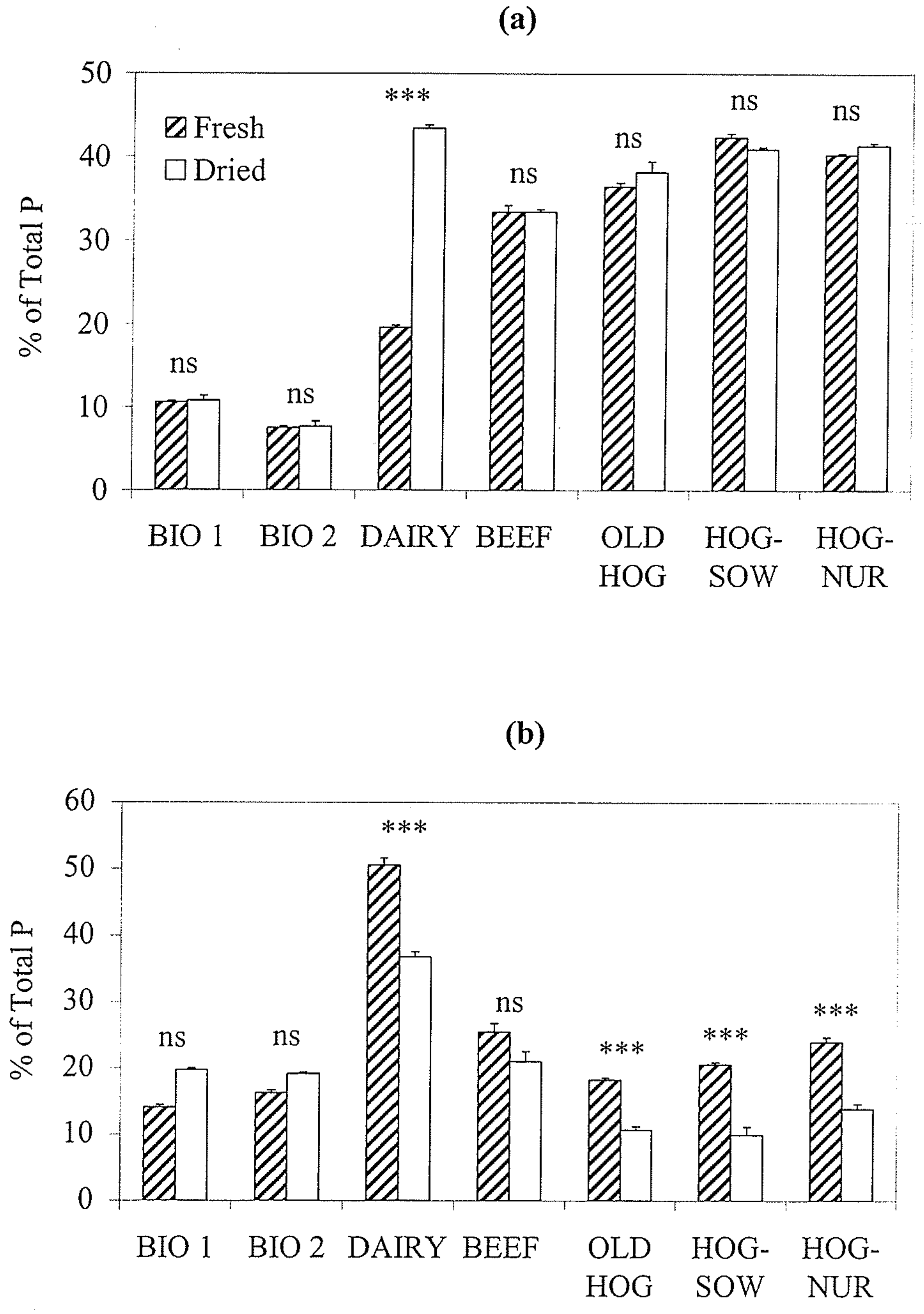


Figure 3.2 P fractions in fresh and oven-dried amendments (a) Water-P (b) 0.5M $NaHCO_3$-P ** significant difference between pre-treatments at 1% level , *** significance at 0.1% level, and ns not significant. The whiskers represent standard error of the means of three replicates.

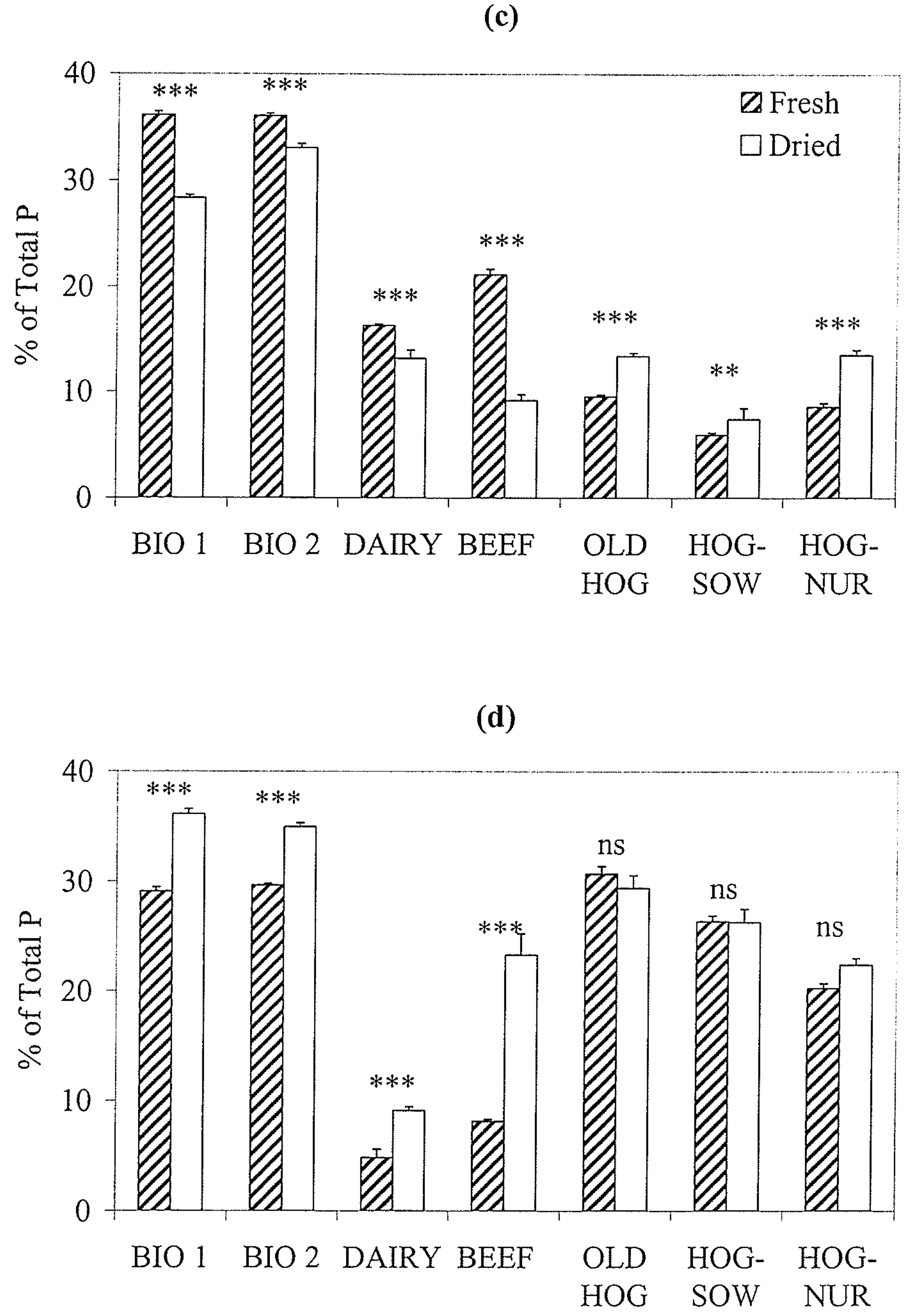


Figure 3.2 cont'd. P fractions in fresh and oven-dried amendments (c) 0.1M NaOH-P (d) 1M HCl-P

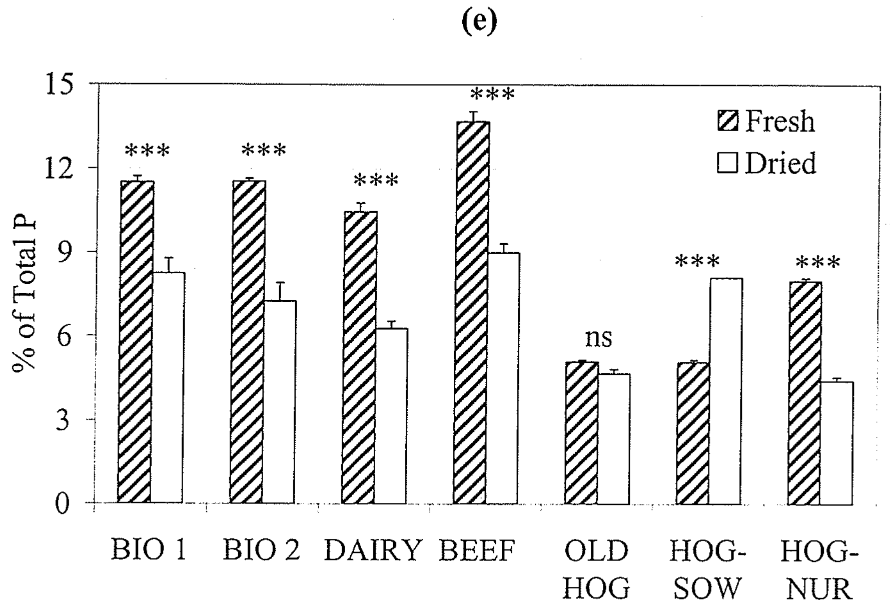


Figure 3.2 cont'd. P fractions in fresh and oven-dried amendments (e) Residual-P

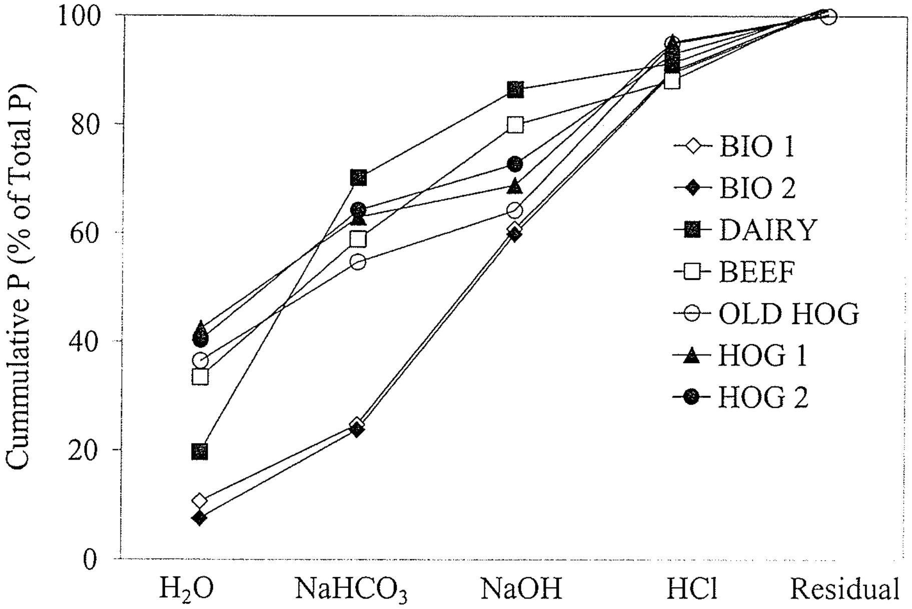


Figure 3.3 Cumulative P fractions extracted in the fresh organic amendments

In the hog manures, there was a significant transformation of P from Po into Pi within the water extract as a result of oven drying (Figures 3.4a - c). In DAIRY, however, $NaHCO_3$-Pi and Po were converted into water-soluble Pi following oven-drying (Figure 3.4d).

3.4.4 Organic and Inorganic P Fraction in the Amendments

Apart from BEEF, all organic amendments contained predominantly inorganic P (55-77% of total P). BEEF had the highest proportion of Po (50%) compared to other amendments (29-45%) (Table 3.3). The distribution of Pi differed among amendments (Table 3.3). For example, 6-8% of total P in biosolids was water-soluble Pi compared to 11-22% and 13-22% in cattle and hog manures, respectively. In contrast, most of the inorganic P in DAIRY (66%) was extracted by $NaHCO_3$. Similar proportions of Pi (33-38%) from biosolids were soluble in NaOH and HCl. However, HCl extracted a greater proportion of Pi in all hog manures but HOG-NUR. Most of the Po in hog manures was soluble in water (46-64% of TPo) and $NaHCO_3$ (24-32% of TPo). In cattle manures, NaOH extracted a relatively higher Po (30-37%) with the remainder being equally partitioned between H_2O, $NaHCO_3$ and HCl. The distribution of Po in biosolids was similar to that of Pi: least in water-soluble forms and most in NaOH- and HCl extractable forms.

Similar to the FRESH amendments, most of the P in DRY amendments was inorganic (Table 3.3). However, the proportion of total P in the Pi form was higher in DRY compared to FRESH amendment (55-77% for fresh versus 75-89% for oven-dried samples). There was a concomitant reduction in Po (11-24% of total P) in DRY manure compared to FRESH (Tables 3.3 and 3.4).

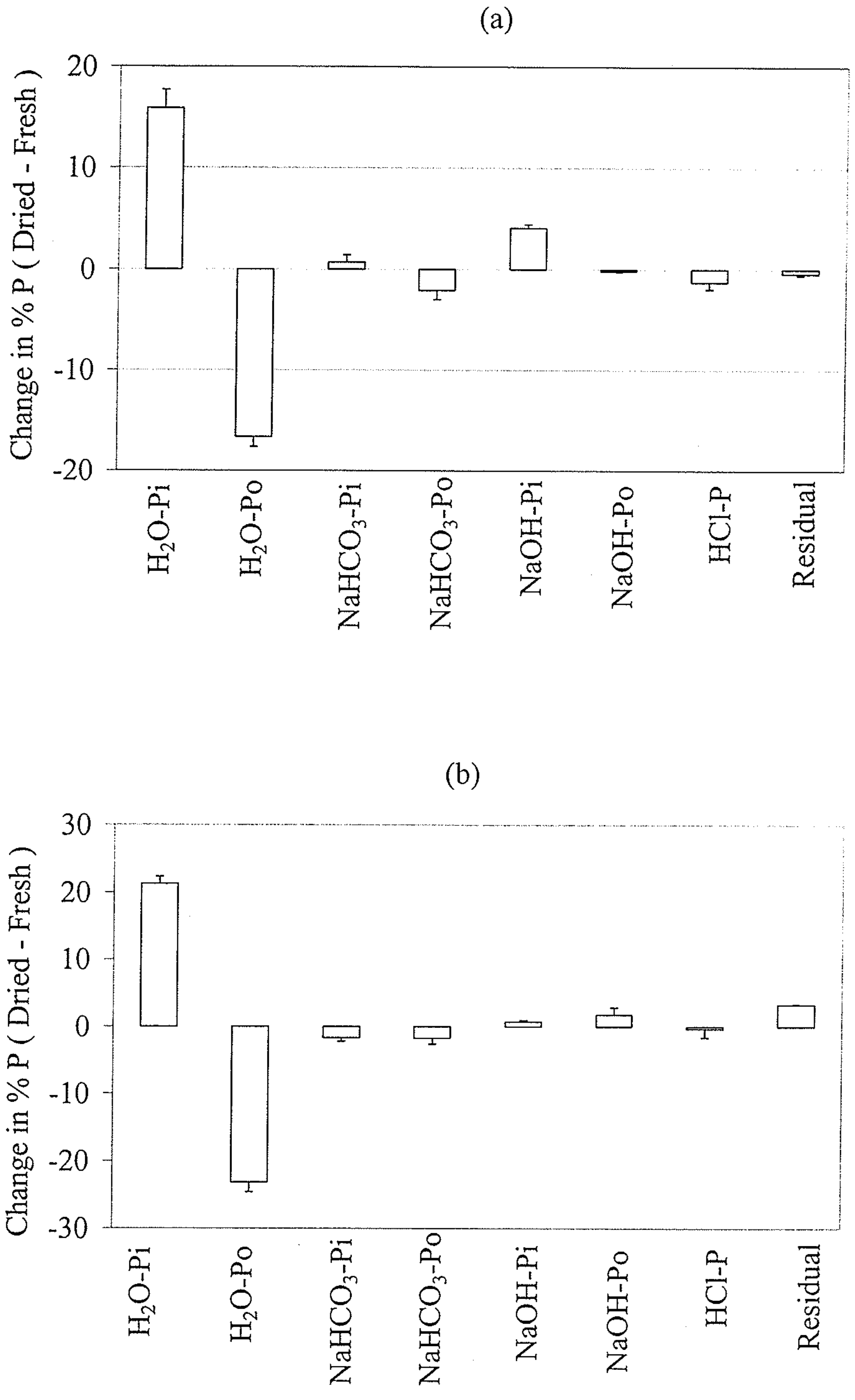
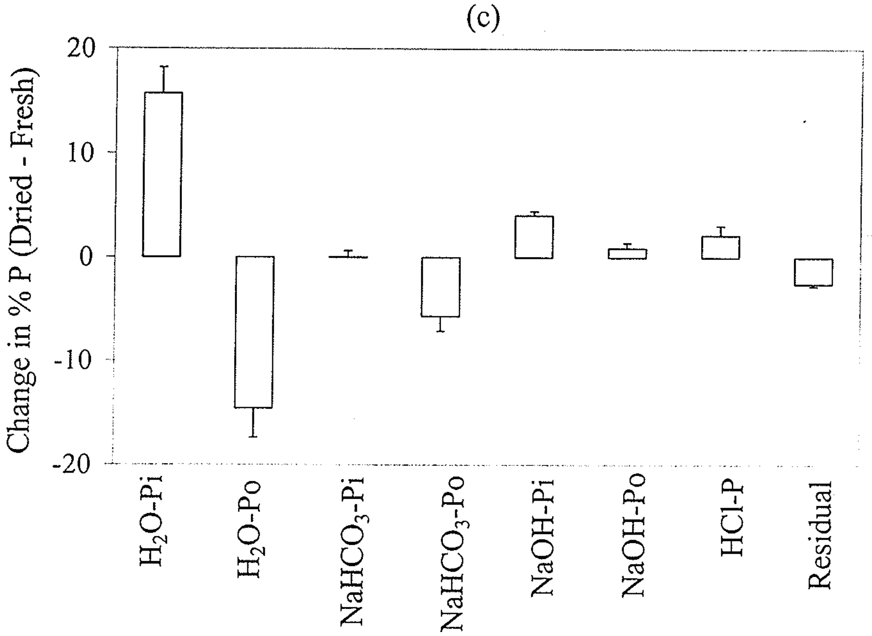


Figure 3.4 Transformation of P fractions with oven drying of the amendments (a) Hog manure from Elite Swine, OLD-HOG (b) Hog manure from sow barn, HOG-SOW. The whiskers represent standard error of the means of 3 replicates



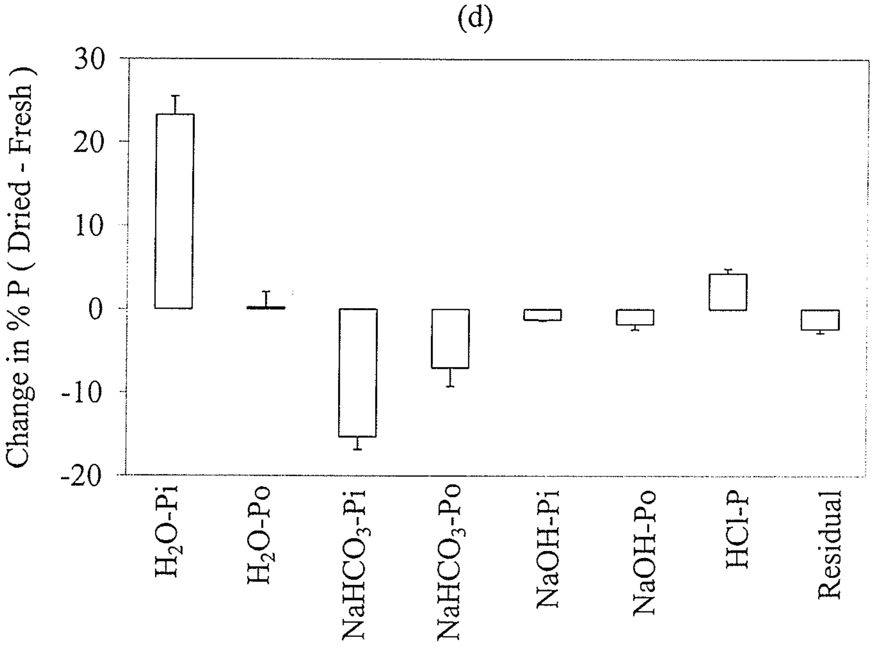


Figure 3.4 cont'd. Transformation of P fractions with oven drying of the amendments (c) Hog manure from nursery barn, HOG-NUR and (d) Manure from dairy barn, DAIRY.

Table 3.3 Organic and inorganic P in various sequential fractions of fresh amendments

P-fractions	P Contents (% of total P)						
	BIO1	BIO2	DAIRY	BEEF	OLD-HOG	HOG-SOW	HOG-NUR
Inorganic P							
Water-Pi	7.79	6.55	11.57	21.77	22.26	13.59	22.39
0.5M $NaHCO_3$-Pi	10.09	12.40	43.35	17.88	8.78	9.87	11.21
0.1M NaOH-Pi	23.66	27.98	5.54	2.54	8.09	4.97	6.89
1M HCl-Pi	29.08	29.65	4.84	8.13	30.68	26.31	20.25
Σ Pi fractions[†]	71^{b}	77^{a}	65^{c}	50^{f}	70^{b}	55^{e}	61^{d}
Organic P							
Water-Po	2.83	0.96	8.05	11.66	14.18	28.81	17.89
0.5M $NaHCO_3$-Po	3.99	3.84	7.24	7.59	9.46	10.70	12.71
0.1M NaOH-Po	12.46	8.09	10.73	18.59	1.45	0.97	1.69
Residual-P	10.10	10.52	8.68	11.85	5.10	4.77	6.96
Σ Po fractions[†]	29^{e}	23^{f}	35^{d}	50^{a}	30^{e}	45^{b}	39^{c}
Σ (Pi + Po)[‡]	2.01	1.37	0.62	0.23	2.95	3.19	2.32
Total P (%)[§]	1.84	1.27	0.55	0.25	3.34	3.95	2.33
% Recovery[¶]	109	108	113	92	88	81	100

[†] Values with same row followed by same letters are not significantly different based on Fisher's protected LSD (0.05) test

[‡] Absolute values (%)

[§] H_2SO_4-H_2O_2 digestion

[¶] (Σ (Pi + Po) / Total P)*100

Table 3.4 Organic and inorganic P in various sequential fractions of oven-dried amendments

P-fractions	P Contents (% of total P)						
	BIO1	BIO2	DAIRY	BEEF	OLD-HOG	HOG-SOW	HOG-NUR
Inorganic P							
Water-Pi	6.64	4.10	34.83	13.78	38.13	34.87	38.10
0.5M $NaHCO_3$ -Pi	12.84	14.91	27.99	13.51	9.47	8.16	11.24
0.1M NaOH-Pi	21.49	28.82	4.30	1.71	12.61	5.68	10.92
1M HCl-Pi	36.15	34.98	9.16	23.64	29.40	25.97	22.39
Σ Pi fractions [†]	77^c	83^b	76^c	52^d	89^a	75^c	83^b
Organic P							
Water-Po	4.17	3.59	8.29	19.68	-2.47	5.65	3.32
0.5M $NaHCO_3$ -Po	3.57	2.10	0.19	11.30	7.39	8.94	7.03
0.1M NaOH-Po	6.89	4.26	8.95	7.40	1.25	2.71	2.58
Residual-P	8.25	7.25	6.29	8.96	4.67	8.02	4.41
Σ Po fractions[†]	23^b	17^c	24^b	48^a	11^d	25^b	17^c
Σ (Pi + Po) [‡]	1.86	1.41	0.59	0.24	3.38	3.29	2.19
Total P[§]	1.84	1.27	0.55	0.25	3.34	3.95	2.33
% Recovery [¶]	101	111	107	96	101	83	94

[†] Values with same row followed by same letters are not significantly different based on Fisher's protected LSD (0.05) test

[‡] Absolute values (%)

[§] H_2SO_4-H_2O_2 digestion

[¶] (Σ (Pi + Po) / Total P)*100

3.5 Discussion

3.5.1 P Fractions and Solubilities

The variability in the P content of the organic amendments used in this study confirmed the results from previous studies (Barnett, 1994a; Dou et al. 2000). The water extractable P in the cattle manures was within the range of 15 to 47% reported by Sharpley and Moyer (2000) for several dairy and composted manures. The observed dominance of $NaHCO_3$-P in DAIRY is similar to the results obtained by Dou et al. (2000), with dairy and poultry manure. Qian and Schoenau (2000) also reported that 70% of the total P in liquid hog manure was in labile form. The total inorganic P fraction (TPi) in DAIRY and BEEF (Table 3.3) is similar to the values of 50 and 70% reported by Barnett (1994b) for beef and dairy cattle manures, respectively. The mild extractant, water, extracted a proportionally small fraction of P from biosolids compared to the strong extractant, HCl, indicating that biosolids P is in a more recalcitrant fraction compared to other amendments. The relatively low proportion of H_2O-P may be due to Fe, Al and Ca contents of biosolids (Table 3.1). The combined effect of anaerobic digestion and higher Fe, Al and Ca contents of biosolids may partly explain the lower labile P fractions in biosolids compared to other amendments (Table 3.2). Elliot et al. (2002) reported a reduction in the amount of labile P in activated and anaerobically digested sewage sludge with high levels of Fe and Al. Application of inorganic chemicals to wastewater and sludge was also reported to reduce labile P content (Häni et al. 1981; Kyle and McClintock, 1995). The treatment of the biosolids used in our study with a polymer for flocculation may be responsible for the higher contents of Fe, Al and Ca, hence the reduced labile P. As a result, the biosolids P may be less vulnerable to run-off loss compared to other amendments (Figure 3.3). The lower proportion of labile P in biosolids compared to other amendments also suggests that biosolids P may not be as readily plant available as P in hog and cattle manures.

The distribution of P in hog manures in this study may be due to P formulation in the animals' diet. Barnett (1994a) proposed that some hog manures had proportion of 'acid-soluble organic P' that were higher than the existing literature values because of diet. Sharpley and Moyer (2000) also suggested that the difference in the P fractions of swine manures in their study, compared to those obtained by Zhang et al. (1994) may be due to differences in mineral P supplementation of the animals' diet. Ebeling et al. (2002) reported that high P diet of dairy cattle achieved when supplemented with monosodium phosphate resulted in 2- to 3-fold increase in water soluble P, bioavailable P and total P concentrations in the manure compared to low dietary P.

3.5.2 P Transformation with Oven Drying

The transformation of the H_2O-Po into H_2O-Pi in the hog manures following oven drying (Figures 3.4a-c) indicated that hydrolysis of organic P fractions into inorganic P fractions was facilitated by high oven temperature and high water content of hog manures (Table 3.1). While the transformation of hog manures by oven drying was restricted to the forms of P within a given extract (water), the transformation of DAIRY by oven drying was from one extractant form to another, that is, $NaHCO_3$-P to H_2O-Pi. Similar effects of pre-treatment on P fractions were reported by Barnet (1994b) who observed that freeze-dried manure sieved with 2mm screen produced a higher lipid-P than finely ground (0.25 mm) material even though the fraction (lipid-P) constituted only 2% of the total P. Akinremi et al. (2003) also observed a higher total P in fresh than in oven dried poultry manure.

3.6 Summary and Conclusions

Results from this study clearly showed that most of the P in biosolids was in a recalcitrant form. However, P in hog and cattle manures was mainly in labile forms that are soluble in water and $NaHCO_3$. Inorganic P predominated in biosolids, hog and dairy cattle manures but not in beef cattle manure. The fact that a higher proportion of P in biosolids was soluble in strong extractants such as NaOH and HCl suggested that biosolids P may be less vulnerable to run-off loss compared to other amendments when applied to agricultural lands. Though oven dry manures are easier to handle compared to fresh forms, results from this study indicate that caution should be exercised in using pre-treatments, such as oven drying, for manure P studies.

4. RETENTION CHARACTERISTICS OF PHOSPHORUS IN MANURED AND FERTILIZED SOILS

4.1 Abstracts

This investigation was carried out to determine the effects of biosolids (BIO), dairy cattle (DAIRY) and hog (HOG) manures, and monoammonium phosphate (MAP) fertilizer on P sorption characteristics of two calcareous Manitoba soils, with differing texture. The Osborne clay soil was amended at the rates of 0, 230, 460 and 920 kg P ha^{-1} and the Lakeland silty clay loam, at 0, 248, 619 and 1238 kg P ha^{-1}, based on the total P content of the amendments. The P sorption process was studied with different initial concentrations of P ranging from 0 - 100 mg P L^{-1} as KH_2PO_4 in the presence of 0.01M KCl. The sorption data were fitted to Langmuir and Freundlich sorption isotherms. P sorption was also determined from a one-point isotherm. In the Osborne clay soil, the reduction in P sorption, relative to the unamended soil, was least with BIO and MAP compared to DAIRY and HOG. The sorption maximum (S_{max}) ranged from 536 - 655 mg kg^{-1} with BIO, 559 - 650 mg kg^{-1} with MAP, 402 - 568 mg kg^{-1} with DAIRY, and 350 - 587 mg kg^{-1} with HOG. The S_{max} in the unamended soil was 660 mg kg^{-1}. The P saturation index (PSI), a measure of the degree of P saturation in the soil, was higher in all of the amended soils than in the control soil (2.6%). Overall, the PSI ranged from 7.5 - 15.4% with BIO, 7.5 - 16.8% with MAP, 10.5 - 44.7 % with DAIRY, and 16.4 - 55.2% with HOG depending on the rate of P addition. In the

Lakeland silty clay loam, P sorption was significantly reduced by all the amendments except biosolids. The P sorption capacity, estimated from one-point isotherms (P_{max}), ranged from 540-603 mg kg^{-1} with BIO, 454 - 596 mg kg^{-1} with MAP, 403 - 494 mg kg^{-1} with DAIRY, and 492 - 519 mg kg^{-1} with HOG. The P_{max} in the unamended soil was 630 mg kg^{-1}. The PSI values ranged from 14-24 % with BIO, through 20-52% and 19-70% with HOG and DAIRY, respectively, to 25-88% with MAP. From an environmental point of view, the results presented here suggest a lower risk of P loss with biosolids application than with hog and cattle manure at equal rates of P applications.

4.2 Introduction

The movement of phosphorus from agricultural lands to surface water is a major cause of eutrophication, which has become a serious environmental concern in many parts of the world (OECD, 1982; USEPA, 1984). The potential movement of P depends on both source and transport factors. Among the source factors, the P retention characteristics in the soil play an important role. The retention of P and its potential release to runoff depend on the P sorption capacity of the soil as well as the degree of saturation of this capacity (Breeuwsma et al. 1995; Zhou and Li, 2001). Application of organic amendment to the soil based on N rather than P requirements can result in P accumulation (Simard et al. 1995; Sharpley et al. 1996; Sims et al. 2000), which can contribute to the over-saturation of the finite P sorption capacity of the soil. A better way of managing P, to avoid loss from agricultural lands, is to apply organic amendments based on crop requirement, which is usually described in terms of inorganic P. However, organic amendments contain lower total P compared to inorganic fertilizers. Therefore, application of organic amendment to supply equivalent amount of P as inorganic fertilizer requirement will result in the addition of large amount of organic matter to the soil (Flaten et al. 2003).

Organic matter that is added to the soil in organic amendments can interact with the soil matrix to either decrease or increase P sorption. Bumaya and Taylor (1988) reported that organic matter tends to promotes soil aggregation thereby increasing the surface available for sorption. The presence of organic acid can also increase P sorption by preventing the crystallization of amorphous Fe and Al oxides, thus increasing the specific surface area available for P sorption (Borggaard et al. 1990). On the other hand, organic anions may undergo specific sorption with the soil minerals (complex formation), competing with P for sorption sites (Hue, 1991; Dubus and Becquer, 2001). Non-specific sorption of organic matter onto soil particles could also increase the surface negative charge of the particle, causing a reduction in the electrostatic attraction of P to the soil. (Iyamuremye and Dick, 1996). Since organic amendments like biosolids and manures contain different amounts and forms of P (Ajiboye et al. 2002), we hypothesized that these amendments will supply different amounts of surface reactive P to the soil with different effects on the degree of P saturation and the ability of amended soil to sorb P. The evaluation of how different types and levels of organic amendments affect P sorption in the soil compared to inorganic fertilizer is essential in determining the potential environment impact of these amendments.

The objective of this study was to determine the effects of biosolids (anaerobically digested sewage sludge), hog and cattle manures, and phosphate fertilizer, applied at different rates, on the retention of P in two Manitoban soils. This type of information can provide a quantitative basis for comparing how a soil's P sorption capacity is affected by long-term application of organic amendments and inorganic fertilizer relative to unamended soil. Such information will also help to determine the likelihood for P movement in the soil.

4.3 Materials and Methods

4.3.1 Soil Samples

Surface horizon (0-15cm) of Osborne clay (Gleysolic Humic Vertisol) and Lakeland silty clay loam (Gleyed Rego Black Chernozerm) soils were collected from two locations around southern Manitoba, Canada in the Fall of 2001. The soils were dried, crushed and ground to pass through a 2-mm sieve on a roller-grinder and stored in plastic bags prior to incubation. Initial extractable P concentration in the soil was determined using the $NaHCO_3$ method (Olsen et al. 1954). Particle size analysis was carried out using the pipette analysis following dispersion with sodium hexametaphosphate and removal of organic matter with hydrogen peroxide (Sheldrick and Wang, 1993). The soil pH was measured with a glass electrode in a 1:2 soil-water suspension. Total C was determined on finely ground material (< 1.0mm) using an automated elemental analyzer (Carlo Erba, Milan, Italy). Total carbonate contents was determined by a modification of the volumetric calcimeter method (Loeppert and Suarez, 1996).

4.3.2 Soil Amendments and Incubation

Biosolids (BIO) from City of Winnipeg wastewater treatment facility, manures from hog sow (HOG) and dairy cattle (DAIRY) barns, and monoammonium phosphate (MAP) fertilizer were applied to 100 g of Osborne soil at the rates of 0, 230, 460 and 920 kg P ha^{-1} based on the total P content of the amendments. These rates were chosen so that the amount of P added at the highest rate corresponds to P addition with the current rate of a one-time application of biosolids by the City of Winnipeg Water and Waste Department. The rates of biosolids application (dry weight basis) for the Osborne soil were 0, 12.5, 25 and 50 Mg ha^{-1}. The Lakeland soil was amended at slightly higher rates of 0, 248, 619 and 1238 kg P ha^{-1}. The experiment was carried out in triplicate and the amended soil was aerobically incubated at 20°C for 16 weeks. The soil was maintained at field capacity water content throughout the incubation period. At the end of 16 wk, the amended soils were air-dried and stored for batch equilibration study.

4.3.3 Phosphorus Sorption Experiment

The amended soil (1.5g) was weighed into 50 mL centrifuge tube and 30 mL of 0.01M KCl solutions containing 0, 2.5, 5, 10, 15, 20 30, 40, 60, 75 and 100 mg P L^{-1} of oven dried (105°C) reagent grade KH_2PO_4 was added to each of the tube. A 0.01M KCl solution was used as the background electrolyte to maintain a constant ionic strength of the solution. Three drops of chloroform were added to each tube to inhibit microbial activities. Equilibration was achieved by shaking the tubes on a mechanical shaker at the speed of 104 epm (excursions per minute) and room temperature (~ 25°C) for 24 hours. This was followed by centrifugation at 12,500 x g for 10min. The supernatant was decanted and analyzed for P colorimetrically using the molybdate-blue method (Murphy and Riley, 1962). The sorbed P was obtained as the difference between the amount of P added to the soil and the P remaining in solution following 24-hr equilibration (Equation 4.1).

$$S = S_o + (C_o - C_{eq})\ Df \qquad [4.1]$$

where S (mg P kg^{-1} soil) is amount of P sorbed per unit mass of soil. S_o is the native sorbed P calculated as the y-intercept of a plot of S against C_{eq} at low equilibrium P concentrations on the unamended soil, C_o is the initial P concetration, C_{eq} is the equilibrium P concentration (mg P L^{-1}) and Df is the dilution factor - the soil to solution ratio.

Phosphorus sorption isotherms were generated by plotting S against equilibrium P concentrations over the range of initial P concentrations used. The sorption data for each amended soils were fitted to the Langmuir and Freundlich equations [Equations 2.5 and 2.7].

4.3.4 Sorption Isotherms Parameters and Saturation Index

The P sorption maximum (S_{max}) was calculated from the Langmuir equation (Equation 2.5) as the inverse of the slope of the regression line between C/S and C. The affinity factor was estimated as the quotient of slope and intercept of the same regression. Phosphorus equilibrium buffering capacity (PEBC) was calculated as the slope of linear regression between S (quantity factor) and C (intensity factor) at the low equilibrium concentrations. The equilibrium P concentration at zero sorption (EPC_o) was estimated as the x-intercept when S is zero (Sui and Thompson, 2000). The phosphorus sorption index (Psi) was estimated according to equation [4.2], using an initial concentration of 75 mg P L^{-1} and a soil to solution ratio of 1:20 (Bache and Williams, 1971).

$$Psi = S/\log C \qquad [4.2]$$

The soil P sorption capacity (P_{max}) was calculated as the amount of P sorbed from one-point isotherm according to (Zhou and Li, 2001), at the initial solution P concentration of 75mg L^{-1} (equivalent to $\sim 0.7\times 10^{-4}$M). The degree of P saturation (DPS) and P saturation index (PSI) were estimated as given in equations [4.3] and [4.4], repectively according to (Zhou and Li, 2001):

$$\text{DPS (\%)} = \frac{P_{\text{Olsen}}}{S_{\text{max}}} \times 100 \qquad [4.3]$$

$$\text{PSI (\%)} = \frac{P_{\text{Olsen}}}{P_{\text{max}}} \times 100 \qquad [4.4]$$

where P_{Olsen} is the Olsen P (mg kg^{-1}) in the amended soils obtained in a parallel experiment on P solubility in amended soils (Kashem et al. 2003).

4.3.5 Statistical Analyses

The sorption experiment was carried out as a completely randomized design (CRD) with thirteen treatments (comprising of four types of amendments at three rates and the control) and three replicates. Sorption parameters obtained from Langmuir, Freundlich and single point isotherms, and the saturation indices (DPS and PSI), for each replicated measurement, were analyzed statistically by one-way ANOVA using the proc GLM (SAS Institute, 2002). The parameters were compared among amended soils using Fisher's least significant difference (LSD) after analysis of variance indicated a significant treatment effect. Simple linear correlation analyses were carried out among the P sorption and saturation parameters from multi- and single-point isotherms.

4.4 Results and Discussion

4.4.1 Soil Characteristics

The soils used in this experiment were alkaline in reaction. The textural classes were silty clay loam for the Lakeland soil and clay for the Osborne soil. Extractable P, total C and, % CO_3-C were higher in the Lakeland than in the Osborne soil (Table 4.1). The organic C (difference between total C and CO_3-C) was 3.2% in Lakeland and 1.7% in Osborne soil.

Table 4.1 Selected properties of the soils used

Properties	Lakeland	Osborne
pH	8.0	7.6
Texture (g kg^{-1})		
Sand	78	83
Silt	613	326
Clay	297	590
Extractable P (mg kg^{-1})†	60	12
% CO_3-C	6.0	3.4
Total C (%)	9.22	5.12
P saturation index, PSI (%)‡	10.16	2.14

† Olsen P

‡ PSI = Olsen-P/P_{max} for unamended non-incubated soils

4.4.2 Phosphorus Sorption in Osborne Soil

4.4.2.1 Amendment Effects. The effects of different organic amendments on P sorption in the Osborne soil are shown by the sorption isotherms (Figure 4.1). Each point on the figures represents a mean of three replicates. The amounts of P adsorbed at the low rate of biosolids and MAP (230 kg P ha^{-1}) were similar to the unamended soils, but dairy and hog manures decreased the sorption of P at this rate (Figure 4.1a). The amendment effect of biosolids and MAP on P sorption by the soil was consistent at all rates of P. However, the ability of hog and dairy cattle manure to reduce P sorption was magnified at higher rates of P additions (Figure 4b and c). The trend in P sorption isotherms obtained in this study suggest that the recalcitrant biosolids-derived P (Ajiboye et al. 2002; section 3.5 of this thesis), was probably not available to occupy the P sorption sites. On the other hand, the highly labile P in dairy and hog might have occupied the sorption sites causing a decline in the sorption of the newly added inorganic P. Sui and Thomson (2001) attributed the diminishing ability of organically amended soil to sorb added P, primarily, to the occupation of sorption sites by P derived from these amendments. The reduction in the amount of P sorbed with DAIRY and HOG, relative to the control and biosolids amended soil, may also be due to the higher Po in these manures (45-50%) than biosolids (29%), which upon mineralization competed with P for sorption sites. Iyamuremye et al. (1996) also attributed the reduction in P sorption in the soil to the competition of organic acids produced during mineralization of organic amendments for the same fixation sites as P. The lack of reduction in P sorption with MAP may be due to differences in the retention mechanism of MAP-P compared to other amendments. High P concentrations from MAP granules probably resulted in precipitation as the main mechanism of P retention, leaving the P sorption sites unaffected in MAP amended Osborne soil.

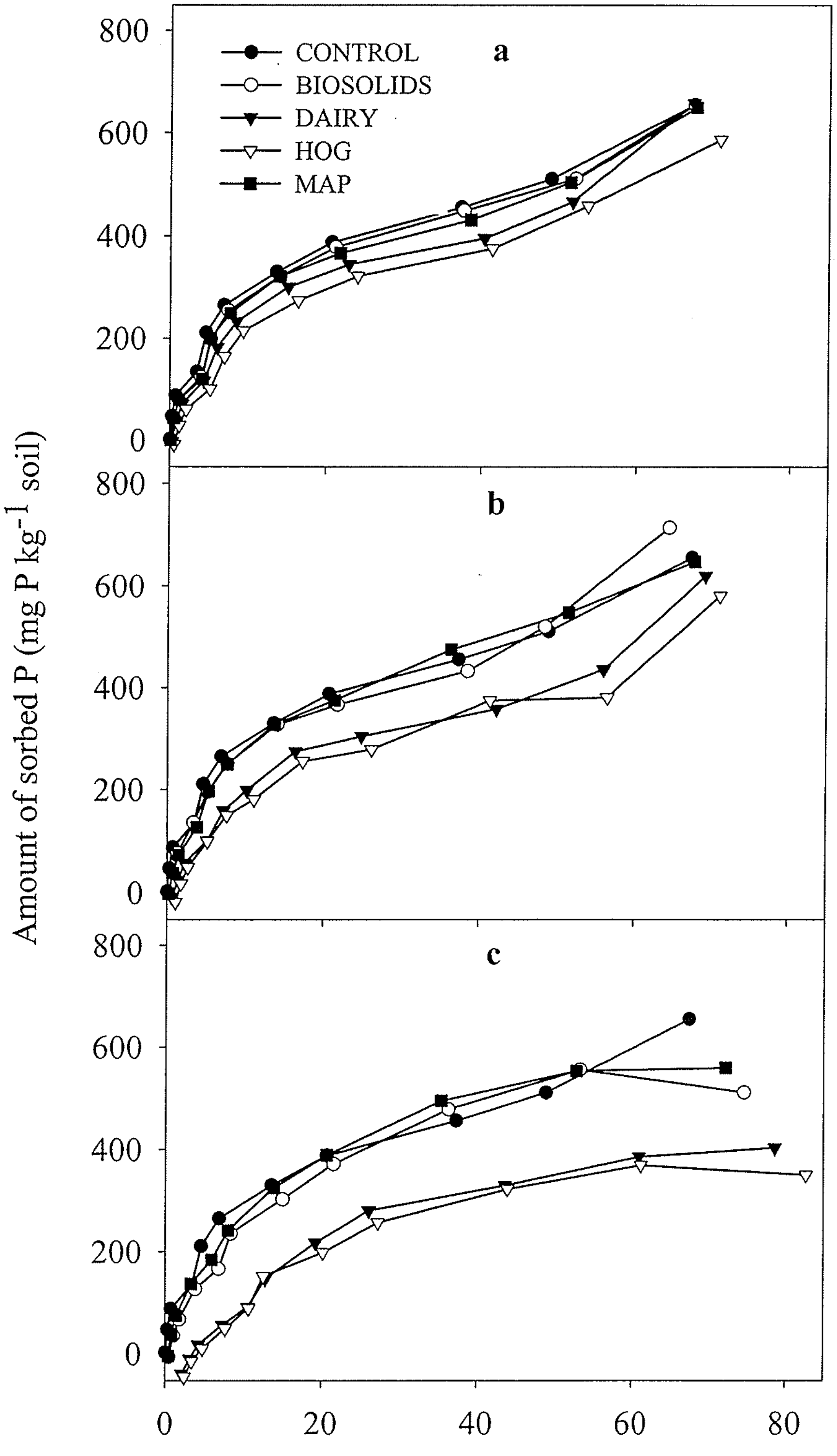


Figure 4.1. Amendment effect on P sorption in Osborne soil at different levels of P input (a) 230 kg ha^{-1}, (b) 460 kg ha^{-1} and (c) 920 kg ha^{-1}.

4.4.2.2 Rate Effects. The effects of rates of organic amendments on P sorption in the Osborne soil are shown in Figure 4.2. In the biosolids amended soil, P sorption isotherm was similar to the unamended soils at all rates, except at the highest rate of biosolids (920 kg P ha^{-1}) where the amount of P sorbed decreased relative to the control soil at the highest equilibrium P concentration (Figure 4.2a). Han and Thompson (1999) showed that soluble organic C increased by biosolids application to the soil. So, the highest rate of biosolids application, which is equivalent to 50 Mg ha^{-1}, could have added a substantial amount of organic C to the soil and in combination with the highest inorganic P addition of 100 mg P L^{-1} (equivalent to 2 g P kg^{-1} soil) overwhelmed the P sorption capacity of the soil. The effect of rate on P sorption in the soil amended with MAP fertilizer was similar to that in biosolids amended soil (Figure 4.2b). However, dairy cattle manure amendments showed a decrease in P sorption with increasing rate (Figure 4.2c). The rate effect of hog manure on P sorption was also similar to that of dairy cattle manure (results not shown).

4.4.3 Phosphorus Sorption in the Lakeland Soil

4.4.3.1 Amendment Effects. The P sorption isotherms obtained in the amended soils were different from that obtained in the Osborne soil. At the low rate of P amendments (248 kg P ha^{-1}), P sorption in the biosolids amended soil was similar to the control soil but declined at the high equilibrium P concentrations (Figure 4.3a). The magnitude of the reduction in P sorption was higher and occurred at a lower equilibrium P concentrations with dairy and hog manure than other amendments. At the medium rate (619 kg P ha^{-1}), DAIRY, HOG and MAP fertilizer reduced P sorption and the most pronounced reduction occurred in dairy manure amended soil (Figure 4.3b). At the high rate (1238 kg P ha^{-1}) of amendment, MAP and dairy cattle manure caused the greatest reduction in P sorption (Figure 4.3c).

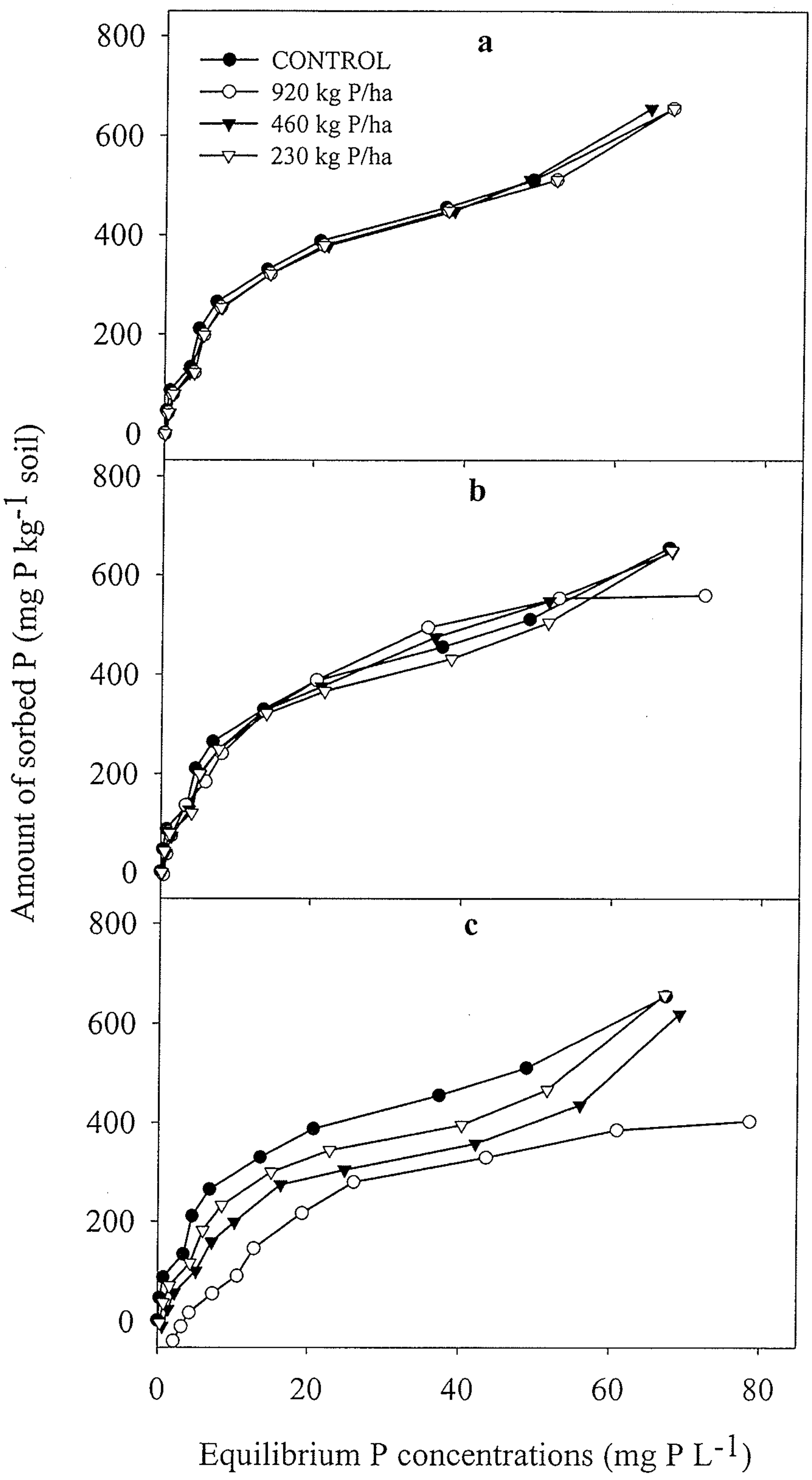


Figure 4.2. The rate rate effect of different organic amendments on P sorption in Osborne soil (a) Biosolids, (b) MAP fertilizer and (c) Dairy cattle manure

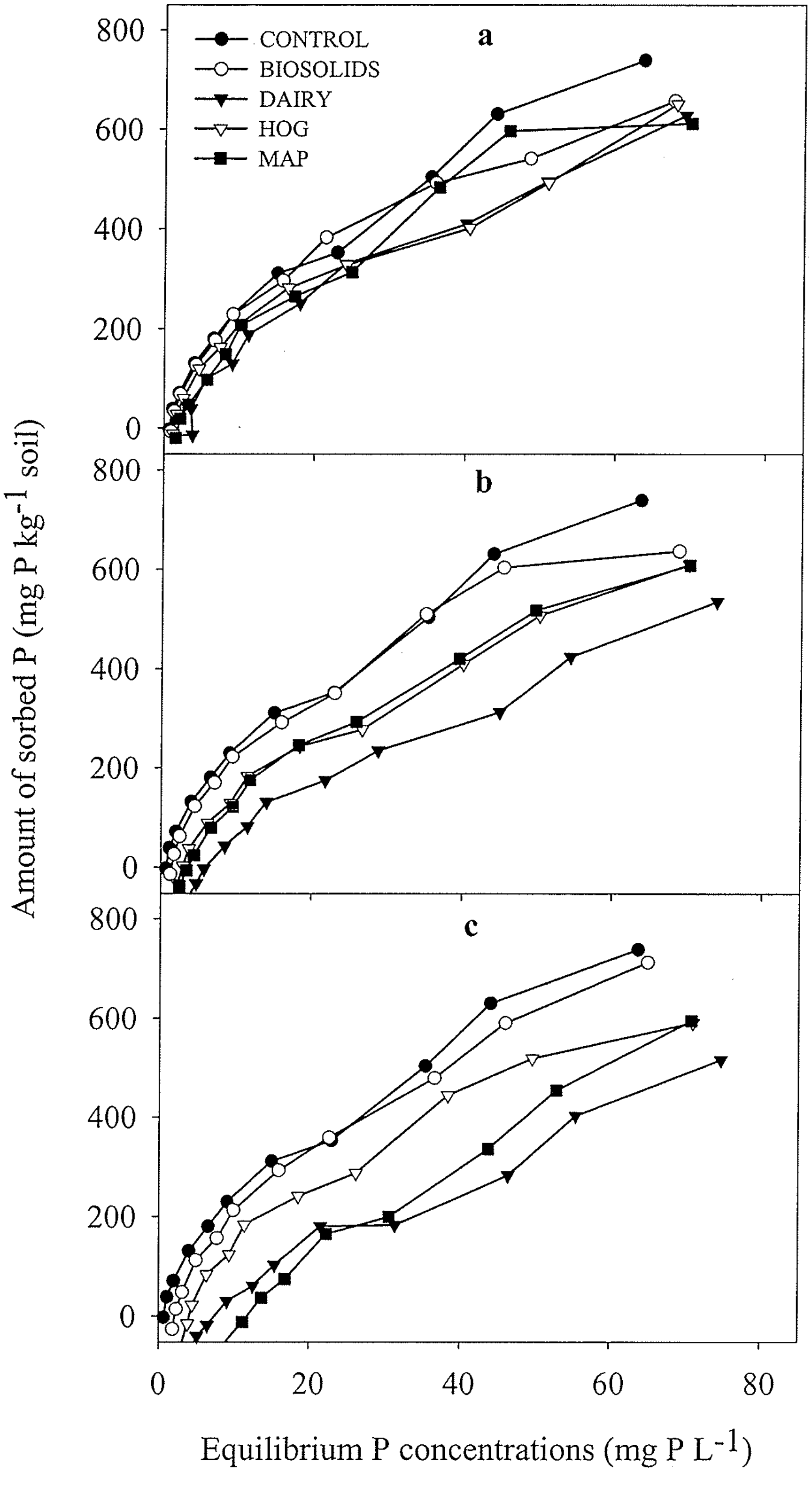


Figure 4.3. Amendment effects on P sorption in Lakeland soil at different rate (a) 248 (b) 619 (c) 1238 kg P ha^{-1}.

When the equilibrium P concentration was < 22 mg P L^{-1} (equivalent to adding 600 mg P kg^{-1} soil), P sorption was the least in MAP amended soil. That trend changed when the equilibrium P concentration was > 30 mg P L^{-1} (equivalent to adding 800 mg P kg^{-1} soil), at which point P sorption was least in the soil amended with dairy manure. Hog manure consistently reduced P sorption, whereas P sorption in biosolids amended soil was similar to the unamended soil. Overall, the greatest reduction in P sorption occurred with dairy cattle manure, as opposed to hog manure in the Osborne soil. Unlike in the Osborne soil where MAP had no effect on P sorption, MAP greatly reduced P sorption, almost to the same extent as did dairy cattle manure, in the Lakeland soil.

4.4.3.2 Rate Effects. In the biosolids amended soil, P sorption was similar to the control soil at all rates of applied P, except at the high equilibrium P concentration where it decreased at the low and medium rates (Figure 4.4a). MAP caused a decrease in P sorption with increasing rate unlike the result obtained in the Osborne soil (Figure 4.4b). The P sorption also decreased with increasing rate in the soil amended with dairy cattle manure (Figure 4.4c) and hog manure (results not shown).

Comparison of sorption isotherms in Lakeland and Osborne soils shows that P sorption was unaffected by MAP in Osborne soil but decreased with increasing rate in Lakeland. Furthermore, P sorption was least with hog manure in the Osborne whereas dairy manure reduced P sorption the most in Lakeland soil. The observed difference in P sorption isotherms confirms that P sorption may be soil specific (Beauchemin and Simard, 1999), as suggested by the differences in the physico-chemical properties of the soils (Table 4.1).

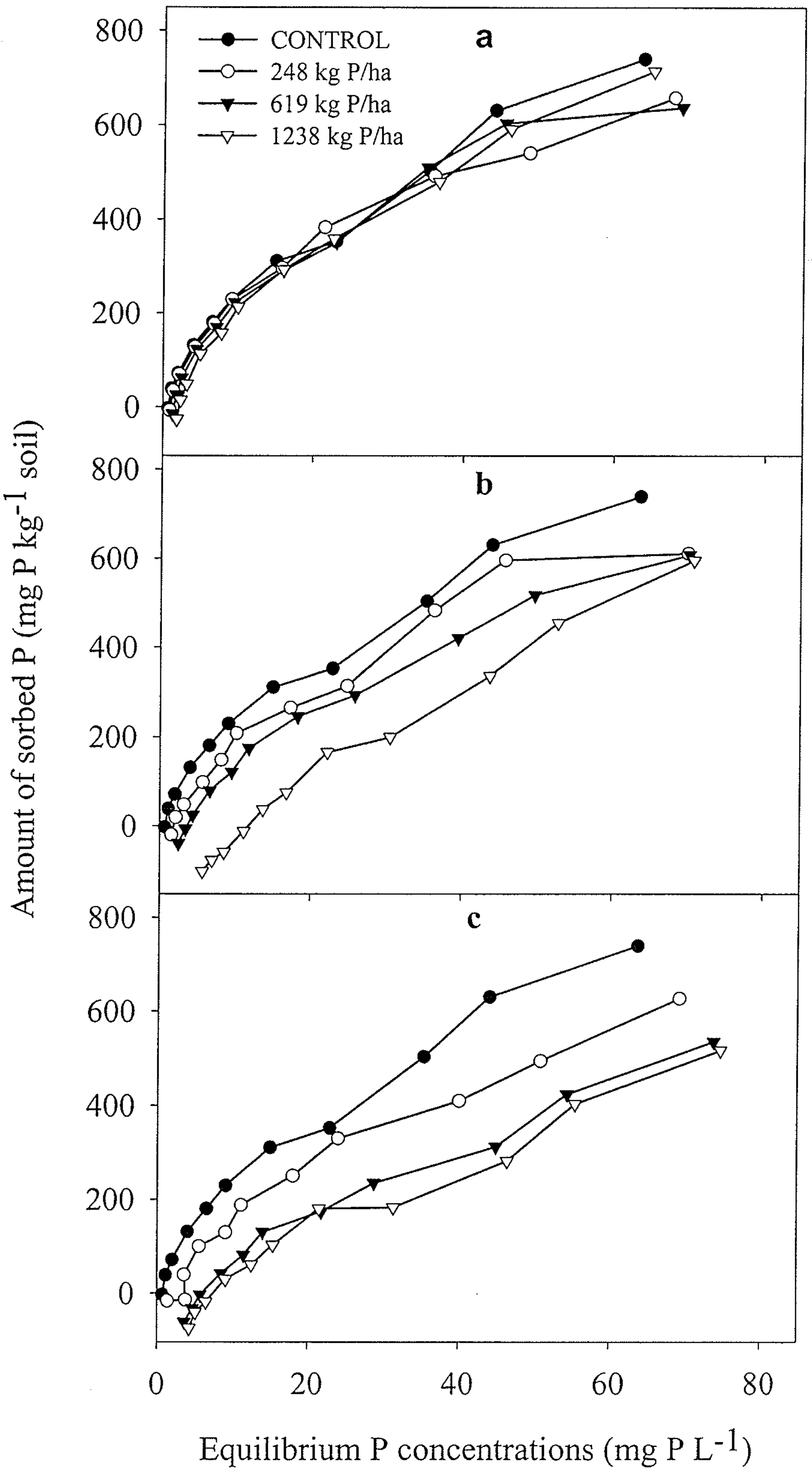


Figure 4.4. The rate effect on P sorption in Lakeland soil amended with (a) Biosolids (b) MAP fertilizer, (c) Dairy cattle manure.

The fact that MAP fertilizer did not affect P sorption in the Osborne soil but decreased it in the Lakeland soil may be due to the differences in the retention mechanism of P in the two soils. The cation exchange capacity (CEC) of these soils was not measured in this study. Nevertheless, the CEC of the two soils may differ due to the differences in their clay content. Subsequently, the level of exchangeable Ca^{2+} in the two soils (a candidate for P precipitation) may differ with a possibly lower level in the Lakeland soil. High exchangeable Ca^{2+} in Osborne soil may favor precipitation, while the low Ca^{2+} in Lakeland soil may result in a combination of precipitation and sorption as the retention mechanisms of MAP-P in the Lakeland soil.

4.4.4 P Sorption Parameters in the Amended Soils.

4.4.4.1 Osborne Soil. P sorption isotherms in the amended Osborne soil were found to fit the Langmuir and Freundlich equations. This result indicates that P sorption in the amended soil declined non-linearly with increasing equilibrium P concentrations. The coefficients of determination (R^2 in Table 4.2) ranged from 0.859 to 0.986 for Freundlich equations, and from 0.865 to 0.998 for Langmuir isotherms, excluding the high rate of dairy and hog manures. There was a significant effect of amendments on the sorption maximum (S_{max}), the affinity factor obtained from the Langmuir equation and on the Freundlich sorption constants; K and n (Appendix II). The sorption maxima (S_{max}) obtained in the soils amended with biosolids and MAP at the low and medium rates were similar to the unamended soil but Smax was reduced at the high rate (Table 4.2). The S_{max} were reduced at all rates of dairy and hog manures. However, the affinity factor (b) showed that the binding energy between sorbed P and the soil decreased with increasing rates of amendments with the exception of high rates of biosolids and MAP.

Table 4.2 P sorption isotherm parameters in the amended Osborne soils

Amendments	Rates	EPC$_o$†	PEBC†	Langmuir Parameters†			Freundlich Parameters†		
	(kg P ha^{-1})	(mg L^{-1})	(L kg^{-1})	S$_{max}$(mg kg^{-1})	b	R^2	K(mg kg^{-1})	n	R^2
Control	0	-0.02^{i}	114^{a}	655^{a}	0.060^{a}	0.954	92^{a}	0.47^{e}	0.953
Biosolids	230	0.08^{h}	77^{b}	655^{a}	0.050^{b}	0.960	78^{bcd}	0.51^{e}	0.948
	460	0.26^{g}	70^{b}	633^{ab}	0.043^{b}	0.885	80^{bc}	0.51^{e}	0.969
	920	0.56e^{f}	55^{d}	536^{d}	0.063^{a}	0.985	71^{d}	0.50^{e}	0.946
Dairy Manure	230	0.29^{g}	54d^{e}	568^{bc}	0.037^{c}	0.888	62^{e}	0.55^{cd}	0.955
	460	0.87^{d}	42^{f}	481^{e}	0.030^{d}	0.865	45^{fg}	0.60^{b}	0.959
	920	3.60^{b}	26^{g}	402^{f}	0.013^{g}	0.686	16^{h}	0.79^{a}	0.895
Hog Manure	230	0.76^{d}	44e^{f}	587^{bc}	0.033^{d}	0.915	48^{f}	0.59^{bc}	0.950
	460	1.50^{c}	43^{ef}	580^{cd}	0.023^{ef}	0.917	40^{g}	0.62^{b}	0.986
	920	4.30^{a}	22^{g}	350^{g}	0.017^{fg}	0.621	12^{h}	0.78^{a}	0.859
MAP	230	0.08^{h}	72^{b}	650^{a}	0.050^{b}	0.942	76^{cd}	0.51^{e}	0.937
	460	0.23^{g}	73^{b}	647^{a}	0.050^{b}	0.980	79^{bc}	0.51^{e}	0.966
	920	0.42^{fg}	61^{cd}	559^{cd}	0.067^{a}	0.998	85^{b}	0.47^{e}	0.969

† Within the same column, values followed by same letters are not significantly different at $p < 0.05$ according to protected Fisher's LSD test

Results from the Langmuir equation suggest that sorption capacity of this soil was significantly reduced with manures but not with biosolids and MAP. However, the quantity of P tightly bound to sorption sites was reduced in amended soils.

The sorption constant (K) from the Freundlich equation varied in all amended soils. There was a decline in K with increasing rate of manures (Table 4.2), suggesting an exponential decrease in P sorption with increasing saturation of soil surface with manure P, as depicted by this equation. Whalen and Chang (2002) also observed an exponential decrease in P sorption in calcareous soils with a 25 yr history of feedlot cattle manure. The Freundlich equation also showed that the binding energy of P to the sorption site significantly decreased in soils amended with dairy and hog manures (n in table 4.2). The decline in the P binding strength in these manures suggests that P may be easily displaced from sorption sites compared to an unamended soil.

In the Osborne soil, EPC_o increased from an initial level of 0 mg L^{-1} in the control soil to 0.56 mg L^{-1} with biosolids, 3.6 mg L^{-1} with dairy manure, 4.3 mg L^{-1} with hog manure and 0.42 mg L^{-1} with MAP at the highest rate of P addition (920 kg P ha^{-1}) (Table 4.2). The higher EPC_o in all the soils amended with dairy and hog manures is synonymous with the decrease in the amount of P bound tightly to the sorption site, as indicated by the affinity factor. The PEBC, representing the ability of the soil to buffer P concentration in the soil solution, was significantly reduced by the addition of amendments (Table 4.2). The magnitude of this reduction was least in the soil amended with biosolids and MAP compared to soils amended with dairy and hog manures. These results suggest that hog and dairy manures may contribute to P loss in runoff and by leaching more than biosolids and MAP.

4.4.4.2 Lakeland Soil. The sorption isotherms in the Lakeland soil were best described by the Freundlich equation and could not be fitted to the Langmuir equation. The coefficient of determination (R^2 in Table 4.3) ranged from 0.949 to 0.993. The Freundlich sorption coefficient (K), which is also a measure of P sorption at low P concentration equivalent to 1mg L^{-1}, was significantly reduced by the amendments except with biosolids at the low and medium rates and hog manure at the low rate (Table 4.3). The Freundlich n showed that the binding energy of P to the soil was not affected in the amended soils relative to the control, except at the medium and high rates of dairy cattle manures, and high rate of MAP. This is an indication that P may be more easily displaced in the Lakeland soil amended with dairy cattle manure.

The EPC_o in the Lakeland soil was 0.7 mg L^{-1} in the control and increased to 2.3 mg L^{-1} with biosolids, 6.7 mg L^{-1} with dairy manure, 4.1 mg L^{-1} with hog manure and 12.4 mg L^{-1} with MAP at the highest rate of P addition (1238 kg P ha^{-1}) (Table 4.3). The EPC_o values at the low rates of biosolids, hog manure, and MAP, as well as the medium rate of biosolids amendments were similar to the unamended soil (Table 4.3). The PEBC values obtained in the biosolids and hog manure amended Lakeland soils were similar to the unamended control soil, but dairy manure and MAP significantly reduced the PEBC (Table 4.3). The EPC_o values at the low rates of biosolids, hog manure, and MAP, as well as the medium rate of biosolids amendments were similar to the unamended soil (Table 4.3). The increasing EPC_o, which was only significant at the high rates of biosolids amendments, indicates that other amendments may be more effective as sources of P loss in runoff or leaching, than biosolids.

Table 4.3 P sorption parameters in the amended Lakeland soils

Amendments	Rates	EPC$_o$†	PEBC†	Freundlich Parameters†		
	(kg P ha^{-1})	(mg L^{-1})	(L kg^{-1})	K(mg kg^{-1})	n	R^2
Control	0	0.7^{f}	53^{a}	57^{a}	0.62^{def}	0.976
Biosolids	248	1.0^{f}	61^{a}	65^{a}	0.55^{f}	0.990
	619	1.5^{ef}	59^{a}	55^{a}	0.60^{ef}	0.979
	1238	2.3^{de}	58^{a}	43^{bc}	0.69^{de}	0.993
Dairy Manure	248	2.9^{cd}	10^{e}	33^{cde}	0.72^{def}	0.978
	619	5.9^{b}	27^{cd}	10^{f}	0.95^{bc}	0.979
	1238	6.7^{b}	20^{de}	6^{f}	1.12^{b}	0.963
Hog Manure	248	1.3^{ef}	50^{ab}	54^{ab}	0.57^{f}	0.950
	619	2.9^{cd}	47^{ab}	28^{de}	0.73^{def}	0.983
	1238	4.1^{c}	57^{a}	26^{e}	0.75^{de}	0.982
MAP	248	1.9^{e}	39^{b}	40^{cd}	0.67^{def}	0.962
	619	3.7^{cd}	35^{bc}	24^{e}	0.78^{cd}	0.984
	1238	12.4^{a}	15^{de}	0.9^{f}	1.61^{a}	0.949

† Within the same column, values followed by same letters are not significantly different at $p < 0.05$ according to protected Fisher's LSD test

4.4.5 P Saturation and Sorption Indices

The P sorption capacities from one-point isotherm: P_{max} and Psi, degree of P saturation (DPS), and P saturation index (PSI) are shown in Table 4.4. All of these parameters were significantly different ($p < 0.001$) among the amended soils (Appendix III).

4.4.5.1 Osborne Soil. The relative sorption capacities as measured by the single point isotherm (P_{max} and Psi) in the Osborne soil (Table 4.4) were slightly different from the S_{max} data in Table 4.2. The P_{max} at all rates of biosolids and MAP were not significantly different from the control soil as opposed to a reduced S_{max} at the high rate of biosolids. The P_{max} in the soil amended with dairy cattle and hog manures was significantly lower than the unamended control, except at the low rate. There was a significant relationship between P_{max} and S_{max} with a low coefficient of determination (r^2) of 0.39 (Figure 4.5). Gale et al. (1994) reported a strong correlation ($r^2 = 0.888$, $p<0.001$) between S_{max} and P_{max} using an initial P concentration of 100 mg P L^{-1} at a soil to solution ratio of 1:10 for sandy and mucky wetland soils. Zhou and Li (2001) also recommended the use of an initial P concentration of 400 mg P L^{-1} in estimating the single-point P sorption capacity of calcareous soil. The poor correlation obtained between S_{max} and P_{max} at 75 mg P L^{-1} in our study, suggests that the predictability of sorption maximum using a single point isotherm may depend on the choice of initial P concentration for single-point isotherm and the maximum initial concentration used to generate S_{max}, and the type of soil.

The degree of P saturation was higher in all the amended soils than in the control soil, except at the low rate of biosolids and MAP. The DPS ranged from a low of 8.56% at the low rate of dairy manure to highs of 42% and 57% at the high rates of dairy and hog manures, respectively.

Table 4.4 Phosphorus sorption and saturation indices of Osborne and Lakeland soils

Treatments	Rates (kg P ha^{-1})	P_{max} (μg g^{-1} soil) †	Psi‡	DPS (%)§	PSI (%)¶
		Osborne soil			
Control	0	508^{abc}	299^{abc}	2.0^{g}	2.6^{h}
Biosolids	230	508^{abc}	300^{abc}	5.8^{fg}	7.5^{gh}
	460	517^{ab}	306^{ab}	8.6^{ef}	10.4^{fg}
	920	553^{a}	330^{a}	15.9^{cd}	15.4d^{ef}
Dairy	230	463^{bcd}	270^{bcd}	8.6^{ef}	10.5^{fg}
	460	433^{de}	251^{de}	17.3^{c}	19.3^{d}
	920	383^{ef}	219^{ef}	42.2^{b}	44.7^{b}
Hog Manure	230	455^{cd}	265^{cd}	12.4^{de}	16.4^{de}
	460	378^{ef}	216^{ef}	19.6^{c}	29.7^{c}
	920	366^{f}	209^{f}	57.0^{a}	55.2^{a}
MAP	230	501^{abc}	295^{abc}	5.8^{fg}	7.5^{gh}
	460	544^{a}	324^{a}	10.1^{ef}	11.9^{efg}
	920	550^{a}	328^{a}	16.5^{cd}	16.8^{de}
		Lakeland soil			
Control	0	630^{a}	384^{a}	-	9.6^{g}
Biosolids	248	540^{ab}	321^{bc}	-	14.0^{fg}
	619	603^{ab}	364^{a}	-	16.9^{fg}
	1238	590^{ab}	355^{ab}	-	23.9^{ef}
Dairy	248	494^{cd}	290^{cd}	-	18.7^{fg}
	619	424^{e}	244^{ef}	-	48.0^{cd}
	1238	403^{e}	232^{f}	-	69.6^{b}
Hog Manure	248	492^{cd}	288^{cde}	-	17.0^{fg}
	619	506^{cd}	298^{cd}	-	25.8^{ef}
	1238	519^{cd}	306^{cd}	-	52.4^{c}
MAP	248	596^{ab}	360^{ab}	-	25.3^{ef}
	619	517^{cd}	305^{cd}	-	37.0^{de}
	1238	454^{de}	264^{def}	-	86.7^{a}

† P_{max} = sorption capacity from one point isotherm. ‡ Psi = P sorption index = S/log C

§ Degree of P saturation = (Olsen P/S_{max})× 100. ¶ P saturation index = (Olsen P/ P_{max})× 100

For the same soil, values followed by same letters within the columns are not significantly different at $p < 0.05$ according to protected Fisher's LSD test

Overall, biosolids and MAP amended soil had the lowest DPS values (5.8 - 16%) compared to soils amended with dairy (8.6 - 42%) and hog manures (12.4 - 57%). The recalcitrant P in biosolids (Ajiboye et al. 2002) was probably not as effective as the more labile P in dairy and hog manures in saturating the P fixing sites in the soil, thereby resulting in a lower DPS with biosolids. The DPS in MAP amended soil, which was similar to the biosolids amended soil, may be indicative of P precipitation with Ca from exchange sites and carbonates due to the high P concentration around MAP granules. A very strong correlation ($r = 0.988$, $p < 0.001$) between the PSI and DPS in Osborne soil (Appendix XII) indicates that PSI is a good measure of DPS. Similarly, high correlation between PSI and DPS ($r = 0.986$, $p < 0.001$) was found by Zhou and Li (2001) for several calcareous soils.

4.4.3.2 Lakeland Soil. The P_{max} and Psi values in soils amended with dairy cattle and hog manures and MAP were significantly lower than in unamended soil. However, P_{max} and Psi were not reduced by biosolids relative to the control soil (Table 4.4). These single point estimates of the P sorption capacity again suggest that biosolids did not reduce the sorption capacity of the soil as did other amendments. The DPS was estimated only in the Osborne soil since its calculation requires S_{max}, and the P sorption data in Lakeland soil did not fit the Langmuir model. Hence, PSI was used to estimate the capacity of the soil to retain additional P in the amended soils. The PSI differed significantly among the amendment to the Lakeland soil (Appendix III). The PSI values ranged from 14-24 % with biosolids, through 20-52% and 19-70% with hog and dairy manures, respectively, to 25-88% with MAP (Table 4.4). The PSI values in soil amended at the and low and medium rates of biosolids, and low rate of dairy and hog manures, were similar to those for the control soil (Table 4.4). However, MAP had a higher PSI than the control soil at all rates. Since the PSI expresses the extent to which the soil's capacity to retain P is affected by P accumulation, a high PSI will translate to a reduced P sorption capacity.

The P sorption index (Psi, estimated from one-point isotherm) and the degree of P saturation of the two soils (DPS for Osborne soil and PSI for Lakeland soil) were significantly correlated (Figure 4.6). These relationships show that lower P sorption capacity due to amendments corresponded to higher degree of P saturation in the soils. This relationship suggests that one-point isotherm may be used as a measure of the degree of P saturation of soils. However, the coefficients of determination within each soil were modest and the relationship between PSI or DPS and Psi was much different for the two soil types. The higher single-point P sorption capacity in the Lakeland than in the Osborne may be due to the higher organic C level (difference between total C and CO_3-C in Table 4.1). Borggaard et al. (1990) reported that organic matter indirectly affects P sorption by inhibiting the formation of crystalline Al and Fe oxides, which increases the surface available for sorption. Gale et al. (1994) also observed positive correlations between the P sorption maximum and the total and water soluble organic carbon of wetland soils.

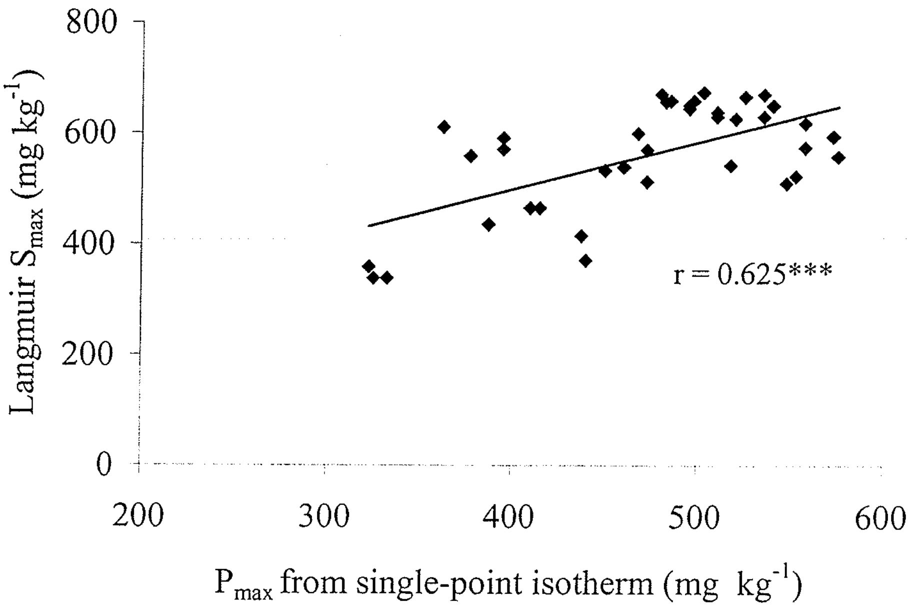


Figure 4.5 Correlation between the P sorption maximum S_{max} (from Langmuir isotherm) and sorption capacity P_{max} (from single-point isotherm) in the Osborne soil.

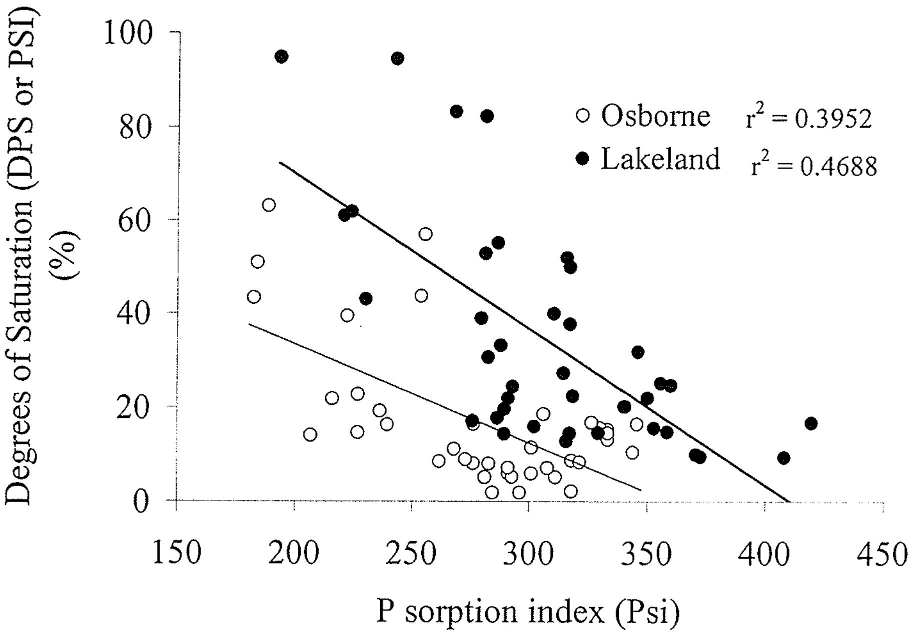


Figure 4.6 Correlations between the degree of P saturation and P sorption capacity from one-point isotherm in Osborne and Lakeland soils

4.5 Summary and Conclusions

In the Osborne soil, P sorption was not affected by biosolids and MAP fertilizer, but was reduced with dairy cattle and hog manures compared to the control. Hog manure reduced P sorption the most in Osborne soil. The magnitude of the reduction in P sorption with these manures increased with rates. In the Lakeland soil, all the amendments with the exception of biosolids decreased P sorption. Unlike in Osborne soil, MAP fertilizer reduced P sorption to the same extent as dairy cattle manure. The P sorption data obtained for Osborne soil fit the Langmuir and Freundlich sorption models whereas the data for Lakeland soil only fit the Freundlich model. In the Osborne soil, the sorption maximum was not affected by biosolids and MAP, but was significantly reduced by hog and dairy manures. The affinity of amended soil for P was significantly reduced by all the amendments compared to the control except at the high rate of biosolids and MAP. In the Lakeland soil, however, all amendments except biosolids reduced the sorption capacity (P_{max}). Similar to Osborne soil, the affinity of the amended soil for P was significantly reduced by all the amendments except at the low and medium rates of biosolids application. That MAP did not reduce P retention in Osborne soil is probably an indication that P precipitation was the dominant process for retaining P in this soil. The degree of P saturation was least with biosolids and MAP in the Osborne soil but MAP resulted in the highest degree of P saturation in the Lakeland soil. The relationship between P sorption capacities (estimated from one-point isotherm) and the degree of P saturation of the two soils showed that reduced P sorption capacity due to amendments corresponded to high degree of P saturation in the soils. The results from this study further support the conclusion from the fractionation study that biosolids may not be as vulnerable to loss compared to cattle and hog manures.

5. CONVECTIVE TRANSPORT OF PHOSPHORUS IN SOIL AMENDED WITH ORGANIC AND INORGANIC AMENDMENTS

5.1 Abstracts

The influence of different organic (biosolids, dairy and hog manures) and inorganic (monoammonium phosphates (MAP)) sources of P on the convective transport of inorganic P in Osborne clay soil amended at two rates was investigated using the miscible displacement technique. Breakthrough curves (BTC) were generated by plotting the relative concentration (C/C_o) of P in the effluent against the breakthrough time, expressed as pore volume (PV). From the BTC, retardation factor (R_1), which is a measure of the reduction in the rate of P movement, was estimated by fitting the convective-dispersion equation to the BTC data. Another measure of P retardation (R_2) was estimated as the cumulative PV when C/C_o is 0.5. The breakthrough of P occurred in the unamended soil after 5 PV. At the low rates of amendments, P breakthrough in all the amended soil was similar to the unamended soil, occurring at about 5 PV except with MAP where P had a breakthrough around 4 PV. At the high rate, breakthrough of P from biosolids amended soil was still similar to the control soil, but P breakthrough earlier, around 4 and 3 pore volumes, with dairy and hog manures, respectively. Detectable concentrations of P in the effluent prior to P breakthrough was approximately 0.7 mg P $L^{-1}$with biosolids, 2.2 mg P L^{-1} with dairy manure, 2.5 mg P L^{-1} with hog manure and 2.4 mg P L^{-1} with MAP. The amendments' main effects on R_1 were 0.64 in the control, 0.67 with biosolids, 0.61 with dairy, 0.58 for both hog manure and MAP

amended soils. The effects of amendments on R_2 value were 7.46 for the control, 7.92 with biosolids, 7.2 with dairy manure, 6.61 with hog manure, and 6.66 with MAP. The amendments' effect on P retention was in the order: MAP < Hog < Dairy ~ Control < Biosolids. The rate main effect showed that the movement of P was less retarded at the high rates of these amendments: R_1 values were 0.64 and 0.57 at the low and high rate, respectively. Similarly, R_2 values were 7.49 and 6.7 at the low and high rates respectively

5.2 Introduction

Phosphorus can be transported from agricultural soils to surface water by surface runoff, resulting from rainfall or snowmelt, and by subsurface flow (Sims et al. 1998). Subsurface movement of P in drainage water was considered as an insignificant pathway for P loss because P is confined to the soil surface through sorption onto soil components such as clays, Al and Fe oxides, carbonates and organic matter. However, the occurrence of P in the ground water, at an environmentally significant quantity in sandy and manured soils, has changed the previously held view (Heckrath et al. 1995; Sims et al. 1998; Hooda et al. 1999).

Orthophosphate can move down the soil profile through diffusion and convection-dispersion mechanisms. Diffusive transport of P occurs whenever there is a concentration gradient in the soil solution. The convective movement of P, however, refers to the transport of orthophosphate with drainage water due to the difference in either hydraulic head or matric potential of water in the soil. Convective transport of P in the soil can be measured by using miscible displacement technique and/or elution development. The degree of P sorption in the soil can also be estimated using the miscible displacement technique. In a laboratory investigation of the convective transport of labeled orthophosphates in different soils, Cho et al. (1970) found that the rate of P movement was greatly retarded by the interaction between soil and P. They also found that the retardation of P movement increased with an increase in the rate of P sorption in various soils.

A reduction in the P sorption capacity and/or increased degree of P saturation can influence P movement. For example, Hooda et al. (1999) reported that change in the slope of sorption isotherms from high affinity to relatively low affinity, with increasing P loading rates, resulted in elevated P concentrations in the subsurface drainage. Their result indicates the relevance of P sorption characteristics in assessing P movement in the soil. It is known that different organic amendments affect P sorption capacity and the degree of P saturation differently. For example Ajiboye et al. (2003) reported that P sorption capacity was unaffected by biosolids and monoammonium phosphate fertilizer, but was reduced by dairy cattle and hog manures in Osborne clay soil. The question now is whether these amendments will also affect the movement of P in the soil.

The objective of this study, therefore, was to investigate the effect of applications of biosolids, dairy and hog manures, and MAP fertilizer on the convective movement of inorganic P in the soil under a water saturated condition using repacked soil columns.

5.3 Materials and Methods

5.3.1 Soil and amendments used

Surface horizon of Osborne soil (Gleysolic Humic Vertisol) was used for the experiment.

Two kg of soil was amended with different organic and inorganic sources of P to supply 230 and 920 kg P ha^{-1}, as reported by Ajiboye et al. (2003). The amendments were biosolids from City of Winnipeg wastewater treatment plant, manures from dairy cattle and sow barns and monoammonium phosphate (MAP) fertilizer. The highest rate of P corresponded to a one-time application rate of biosolids (50 Mg ha^{-1}) by the City of Winnipeg Waste and Water Department. The amended and unamended soils were used to grow wheat in a separate greenhouse experiment (Kashem et al. 2003). At the conclusion of the greenhouse study, which took a period of about 8 weeks, the soil was air-dried after removing the plant roots, ground to pass through 2mm sieve, and stored for the transport study.

5.3.2 Miscible displacement experiment

A modification of the miscible displacement technique described by Cho et al. (1970) was used for this study. A column with an internal diameter of 5.0 cm and 15cm length (cut from acrylic tubing) was sealed at the base with a perforated circular disc of similar diameter (from the same material) to retain the soil. A plastic funnel of identical diameter was attached to the base of the column to act as a drainage port. The soil column was assembled by placing a Whatman # 50 (Hardened ashless) filter paper on the circular disc inside the column. The tip of the funnel was plugged with a rubber stopper and the column was half-filled with 0.01M KCl (a background electrolyte). Wet packing technique (Oliviera et al. 1996) was used to achieve a bulk density (ρ_b) of approximately 0.8 g cm^{-3}. This technique involved the deposition of thin layers of soil into the electrolyte while vibrating the column gently to prevent air entrapment. The ρ_b was estimated from the relationship between the mass of soil packed into the column and the volume of soil in the column (cross sectional area of column × height of soil). The tip of the funnel was thereafter unplugged to drain excess water. The surface of the packed soil, 12 cm in length, was then covered with another filter paper to distribute the influent solution and protect the soil surface from dispersion during the experiment.

A rubber stopper with a short plastic inlet at its centre was fitted to the top of the column as a mean of delivering the P solution onto the soil column. The inlet was connected by tygon tubing to a variable speed Masterflex pump that delivered 75 mg P L^{-1} solution of KH_2PO_4 (buffered against change in ionic strength by 0.01M KCl) into the column. The inflow rate of the P solution was approximately 0.8 mL min^{-1}, which is equivalent to a Darcian flux (q) of 2.4 cm hr^{-1}. Prior to introducing the P solution, approximately 0.5 pore volume (PV) of 0.01M KCl was delivered into the column at the specified rate to achieve a steady flow of solution through the column. The PV, which corresponds to the liquid capacity of the soil column under saturation, was calculated as the product of the total porosity and total volume of the soil (Equation 5.1).

$$1\,PV = V_s\left(1-\frac{\rho_b}{\rho_s}\right) \qquad [5.1]$$

where V_s is the volume of the soil in the column (cm^3) and ρ_s is the particle density (assumed to be 2.65 g cm^{-3} for mineral soils).

The effluent was collected in pre-weighed test tubes at 10 min interval using an Instrumentation Specialties model 560 fraction collector. The volume of the effluent collected in each tube was calculated as the difference in weight between the empty tube and tube plus effluent, assuming a density of 1.0 g cm^{-3} for the KH_2PO_4 solution. Each experiment was carried out in duplicate as shown in Figure 5.1.

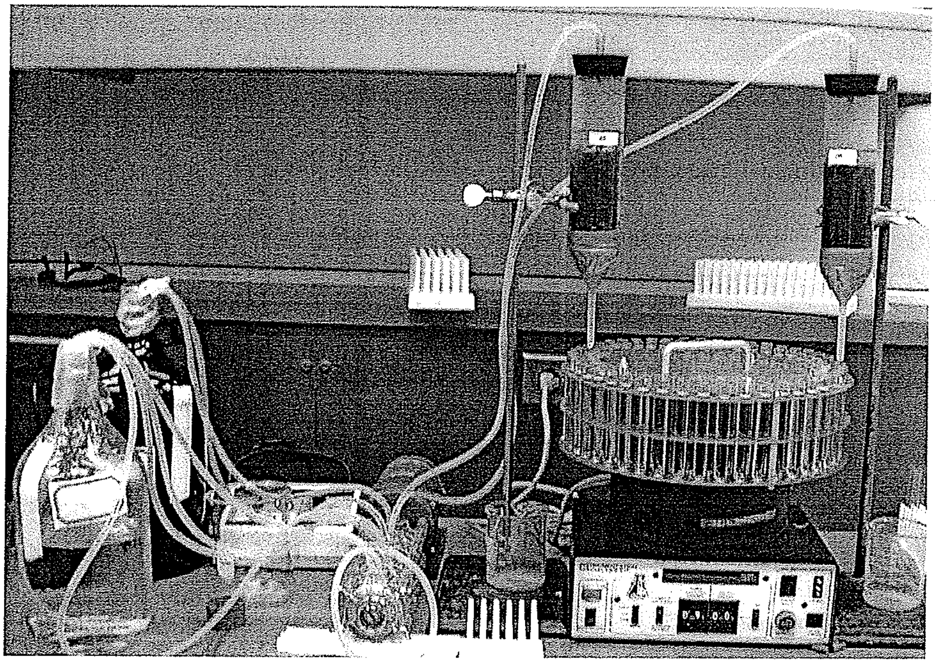


Figure 5.1 Miscible displacement experimental equipment.

The experiment was carried out until a total of 15 PV of effluent was collected. The effluent fractions collected at intervals of approximately 50 min were analyzed for P using the molybdate-blue method (Murphy and Riley, 1962). The intervals between the fractions were recalculated in units of pore volume as given by equation [5.2].

$$\text{\# of PV} = \text{Cumulative volume (mL)} / \text{1PV (mL)} \qquad [5.2]$$

During the experiment, there was some variability in flow rate of the P solution through the amended soil. Nevertheless, the breakthrough data was not corrected for this variability so as to properly account for the effect of organic amendments on P movement, which may include an improved water holding capacity due to better aggregation of the soil particles. Breakthrough curves were generated by plotting the relative concentration, given by the ratio of effluent P concentration (C) to influent P concentration (C_o), C/C_o against PV.

The amount of P retained by the amended soil during convective flow of P solution was estimated as the difference between the amount of P introduced into the column, and the total amount of P collected in the effluents up to 11 pore volumes (Equation 5.3)

$$P_{retained} = \frac{V_T\, C_o - \sum_{i}^{n}(C_i(\sum V_i - \sum_i V_{i-1})}{M_s} \qquad [5.3]$$

where $P_{retained}$ is the amount of P retained by the soil (mg/kg), V_T (in liters) is the total volume of solution collected up to 11 pore volumes, C_o is the P concentration of the influent, C_i is the P concentration in the fraction analyzed at 50 min intervals, $\sum V_i$ is the cumulative volume of the effluents up to fraction analyzed. $\sum V_{i-1}$ is the volume of effluent accumulated in the previously analyzed fraction, and M_s is the kg of soil used.

5.3.3 Estimation of Transport Parameters

Deterministic equilibrium convective-dispersive equations (CDE) algorithm in CXTFIT 2.1 (Toride et al. 1999) was used to estimate the dispersion coefficient (D) and retardation factor (R_1) of the breakthrough data. A second retardation factor (R_2) was determined simply as the cumulative PV when $C/C_o = 0.5$ (Cho et al. 1971; Dao, 2000).

5.3.4 Statistical Analyses

The P retention ($P_{retained}$) and retardation parameters (R_1 and R_2) were analyzed as a factorial experiment involving amendments at four levels (biosolids, dairy and hog manures, and MAP) and two rates of application. The eight treatments were then combined with the control (unamended) soil and analyzed as a completely randomized design (CRD). The parameters were compared using the Fisher's least significant difference (LSD) after analysis of variance showed a significant treatment effect at the 99% confidence level (SAS Institute, 2002).

5.4 Results and Discussion

5.4.1 Apparent P Movement in the Amended Soil

5.4.1.1 Amendment Effect. The observed deviation of the BTCs from the hypothetical 'piston flow' confirmed an interaction of P with the soil (Figure 5.2a). The breakthrough of P occurred in the unamended soil after five pore volumes. At the low rates of amendments, P breakthrough in all the amended soils was similar to the unamended soil, occurring at around five pore volumes except with MAP (Figure 5.2a). MAP had an earlier breakthrough and subsequent effluent P concentrations were higher than in the other amendments. This result did not agree with the sorption data earlier reported by Ajiboye et al. (2003), in which MAP did not affect P sorption. The discrepancy in the behavior of MAP in the two experiments may be due to 8 wk incubation of the soil used in the transport study compared to 16 wk incubation in the sorption study. It is possible that the precipitate formed with MAP during the 8 wk period underwent dissolution, resulting in high P concentrations in the effluents. At the high rate of amendments, the breakthrough of P from biosolids amended soil was still similar to the control soil, but occurred earlier, around 4 and 3 PV, with DAIRY and HOG, respectively (Figure 5.2b). The more rapid movement of P in the soil amended with dairy and hog manures, relative to the control and the biosolids amended soil may be due the higher degree of P saturation and lower binding strength of P to the soil with these amendments (Ajiboye et al. 2003). Lienweber et al. (1999) also reported a very strong correlation between leachate P concentrations and DPS, as well as P sorption capacity for soils with different management intensities. Similarly, Hooda et al. (1999) reported that change in the slope of sorption isotherms from high affinity to relatively low affinity, with increasing loading rate of P, corresponded to elevated P concentrations in the subsurface drainage. This was attributed to a reduced sorption capacity of the soil as the high energy sites decreased with increasing loading rates of P.

5.4.1.2 The Rate Effects. At the low rate of biosolids, the BTC was similar to the control. However, at the high rate, a detectable P concentration of ~ 0.7 mg P L^{-1} appeared prior to breakthrough (Figure 5.3a). The maximum relative concentration (C/C_o) obtained during the experiment was ~ 0.9 at the low rate and ~ 0.85 at the high rate, compared to ~ 0.95 in the control (Figure 5.3a). At the high rate of DAIRY, the breakthrough of P occurred earlier (3.5 versus 5 PV for the low rate) than the control soil. Also, a detectable P level of 2.17 mg P L^{-1} was obtained with DAIRY prior to P breakthrough (Figure 5.3b). The highest relative concentration was approximately 0.95 and 1.0 at the low and high rates, respectively (Figure 5.3b). The P breakthrough in hog manure amended soil also occurred earlier relative to control soil at the high rate. A detectable P level of 2.5 mg P L^{-1} was measured prior to breakthrough. The relative concentration was about 0.95 at the low rate and > 1.0 at the high rate (Figure 5.3c). The measured P concentrations prior to breakthrough at the high rate of

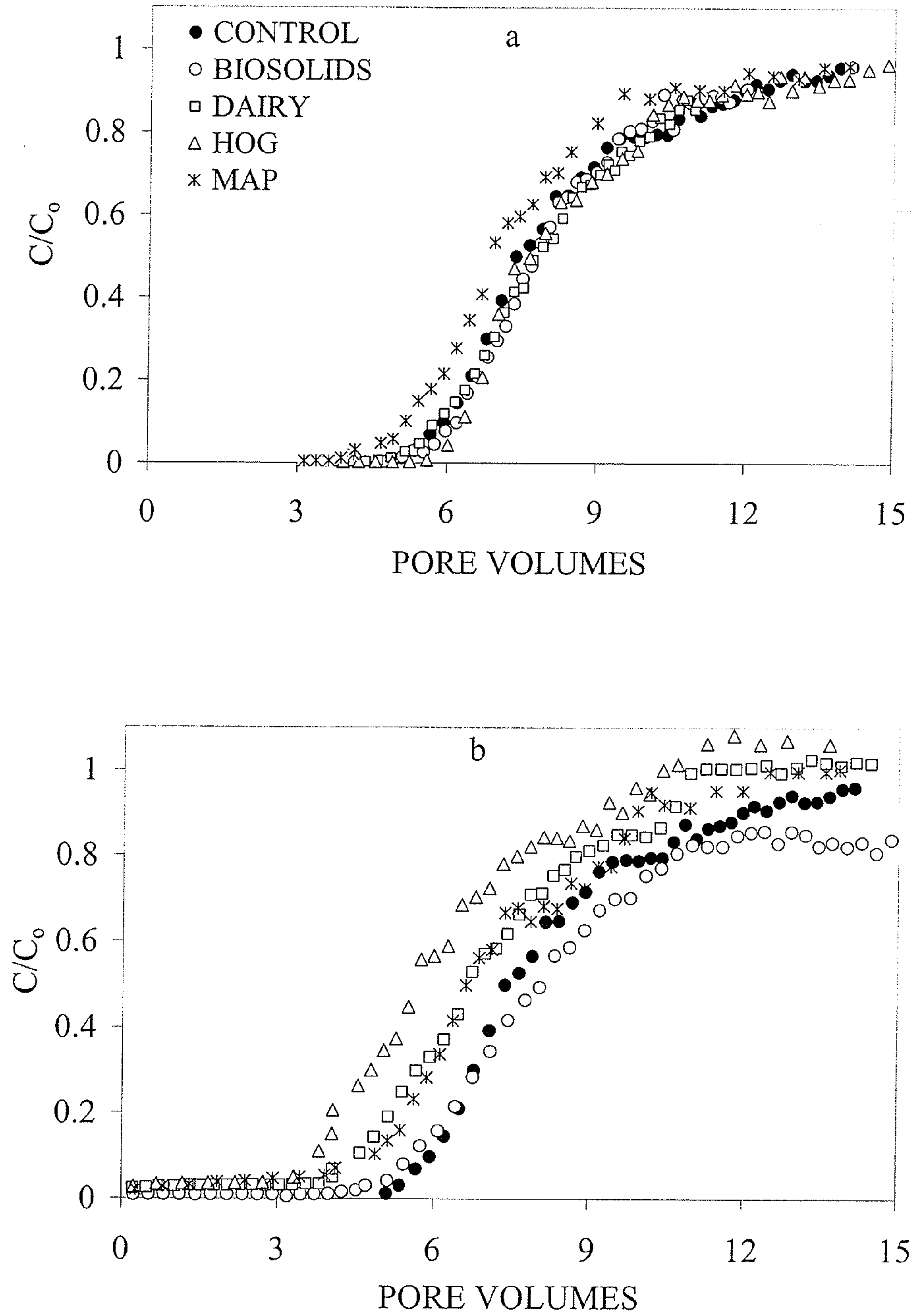


Figure 5.2. Breakthrough curves (BTCs) of P for soil amended at different rates of organic and inorganic amendments (a) 230 kg P ha^{-1}, and (b) 920 kg P ha^{-1}.

the organic amendments (biosolids and manures) are comparable to the equilibrium P concentration at zero sorption (EPC_o) of these amendments; least with biosolids and greatest with hog manure (Ajiboye et al. 2003; Table 4.3). The complete and early P breakthrough at high rates of manures (DAIRY and HOG) application is an indication of a reduced capacity of the soil to sorb applied P. This result is consistent with the higher DPS of 42.2% and 57% in the soil amended with dairy and hog manure, respectively, compared to 2% in control soil (Ajiboye et al. 2003; Table 4.4). For the MAP-amended soil, P breakthrough occurred before four pore volume with both low and high rates of applications, well earlier than the control soil (Figure 5.3d). The breakthrough of P was also complete with a relative concentration of ~ 1.0 at the end of the experiment with both levels of MAP fertilizer application.

5.4.2 Retardation of P Movement

The estimated retardations of P movement (R_1 and R_2) were statistically different among the treatments, i.e. amendments and rates (Table 5.1). There were also significant amendment by rate interactions, indicating different effects of rates of amendments on retardation factors (Table 5.2). All the amendments except biosolids decreased P retardation (R_1) relative to the control soil (Table 5.2). This reduction was greater in hog manure and MAP than in dairy cattle manure amended soils The comparison of retardation factor estimated as PV accumulated when C/C_o is 0.5 (R_2), showed that retardation of P movement was higher in biosolids amended soils than the control and other amended soils. However, hog manure and MAP amended soils had lower P retardation than dairy manure (Table 5.3).

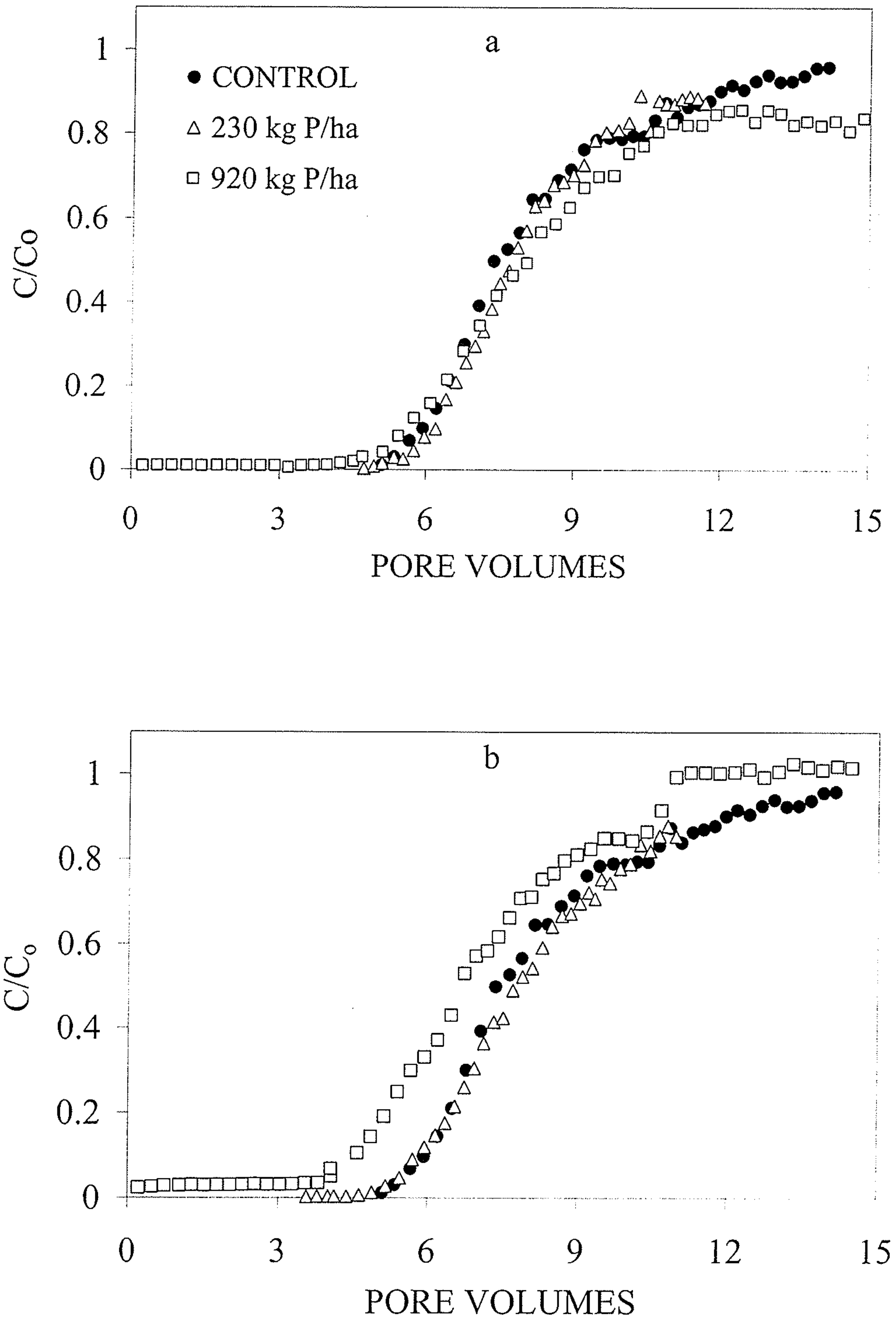
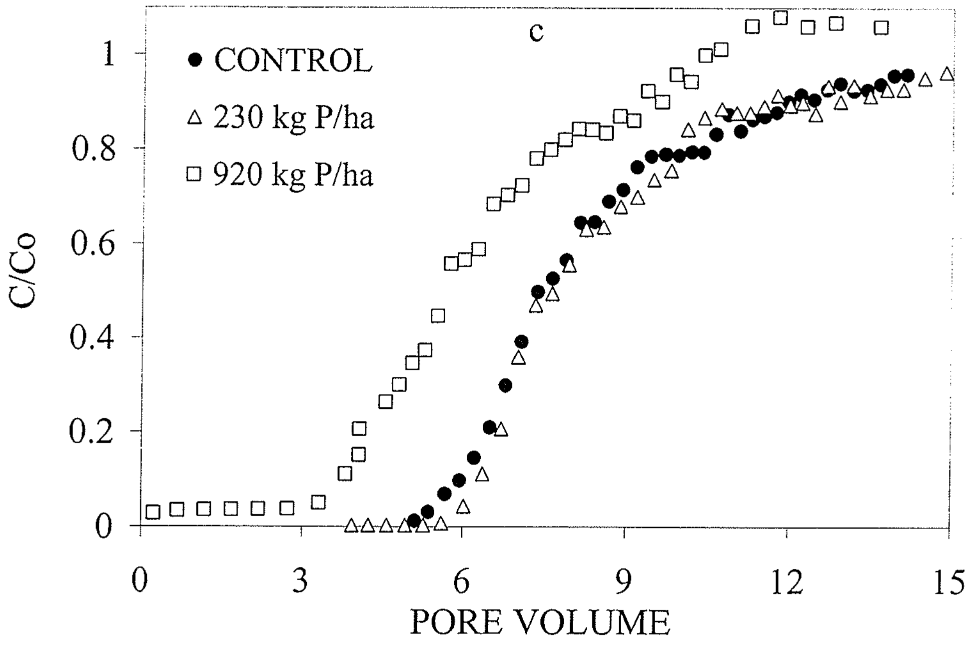


Figure 5.3 Breakthrough curves (BTCs) of P for soil amended with (a) biosolids (b) dairy manure



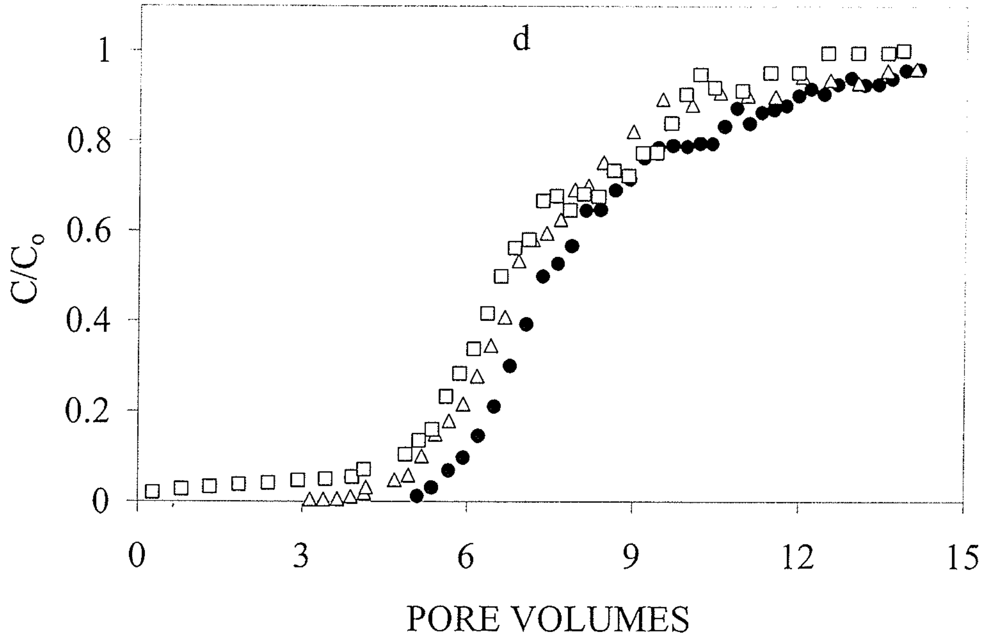


Figure 5.3 cont'd. Breakthrough curves (BTCs) of P for soil amended with (c) hog manure and (d) MAP fertilizer

Table 5.1 Mean squares of ANOVA of P retardations and retention parameters

Source	df	------------ Mean Squares ----------	
		R_1	R_2
Amendments	3	0.0083***	1.4885***
Rates	1	0.0197***	2.5043***
Amendment × Rate	3	0.0089***	1.1501***

*** significant at 0.1% level

Table 5.2 Amendments and rates main effects on P retardation R_1 estimated using CXTFIT algorithm (Toride et al. 1999).

Amendments	Rates (kg P ha^{-1})		Amendments main effects (LSD = 0.03)
	230	920	
Control	-	-	0.65a
Biosolids	0.66	0.68	0.67a
Dairy	0.66	0.56	0.61b
Hog	0.66	0.47	0.58c
MAP	0.59	0.57	0.58c
Rates main effect (LSD = 0.01)	0.64a	0.57b	

Values followed within same row or column followed by same letters are not statistically different at $p < 0.05$ according to Fisher's LSD test

5.4.3 P Retention during the Convective Flow of P through the Amended Soils

The amount of P retained in amended soils was in the order: MAP < Hog < Dairy ~ Control < Biosolids (Table 5.4). Although, Ajiboye et al. (2003) suggested that precipitation of MAP with the exchangeable Ca resulted in MAP not affecting P sorption, but reduced P sorption with MAP in this study as opposed to that in sorption study, may be due to a shorter incubation period in the latter (8 wks for transport versus 16 wks for sorption). We hypothesized that a relatively soluble DCPD (dicalcium phosphate dihydrate) was formed during the shorter incubation period, whereas the longer incubation period resulted in the formation of insoluble OCP (octacalcium phosphate). Several studies have identified DCPD as the dominant initial product formed when water-soluble P fertilizers such as MAP are added to alkaline and calcareous soils (Racz and Soper, 1967; Olsen and Flowerday, 1971). The dissolution of DCPD may explain the higher effluent concentration of P and lower P sorption in MAP amended soil compared to the control.

Table 5.3 Amendments and rates main effects on P retardation estimated from the breakthrough curves (R_2) as pore volume accumulated when $C/C_o = 0.5$

	Rates (kg P ha^{-1})		Amendments
Amendments	230	920	main effects (LSD = 0.26)
Control			7.46b
Biosolids	7.80	8.04	7.92a
Dairy	7.82	6.59	7.20b
Hog	7.66	5.57	6.61c
MAP	6.70	6.62	6.66c
Rates main effect (LSD = 0.18)	7.49a	6.70b	

Values followed within same row or column followed by same letters are not statistically different at $p < 0.05$ according to Fisher's LSD test

Table 5.4 Amendments and rates main effects on P sorption ($P_{retained}$) during the miscible displacement experiment

Amendments	Rates (kg P ha^{-1})		Amendments main effects (LSD = 18.78)
	230	920	
Control			529b
Biosolids	575	533	554a
Dairy	587	462	524b
Hog	505	407	456d
MAP	512	482	497c
Rates main effect (LSD = 13.28)	545a	471b	

Values followed within same row or column followed by same letters are not statistically different at $p < 0.05$ according to Fisher's LSD test

In general, the retardation factors indicate that P movement was more rapid in soils amended with MAP and manures than in the control and biosolids amended soils. The reduced movement of P in the soil with biosolids compared to other amendments may be due to higher sorption capacities and reduced degree of saturation in biosolids amended soil. Previous results from fractionation of biosolids and manure (Ajiboye et al. 2002) showed that about 23% of the biosolids P was in the labile form compared to 63-70% in dairy and hog manures. The lower labile P contents in biosolids relative to manures were suggested to be responsible for the lower degree of P saturation in soil amended with biosolids compared to manure amended soils (Ajiboye et al. 2003). So the lower degree of P saturation in biosolids amended soil might have resulted in the retention of solution P causing a reduced P movement relative to the manure amended soil. This is also consistent with the higher amount of P retained in the soil amended with biosolids than the control soil (Table 5.4). However, the higher or similar retardation of P movement and/or retention of P between the control and biosolids amended soils may also have been due to improved water holding capacity of the biosolids amended soil which reduced the flow rate of P solution and increased the interaction between solution P and the amended soil. The most rapid P movement in MAP amended soil observed may be due to dissolution of P compounds formed earlier with MAP, by the continuous dilution of the soil in this study.

5.5 Summary and Conclusions

The convective movement of P in soils amended with biosolids dairy and hog manures, and MAP was investigated in this study. P movement was not affected by biosolids relative to the control, but was more rapid in soils amended with dairy cattle and hog manures. The amount of P retained during the convective flow was higher in the biosolids amended soil than in the control and soils amended with dairy and hog manures. The reduced P movement obtained in biosolids-amended soil may be an indication of a lower saturation of P fixing sites with biosolids P than with P fertilizer and manures (hog and dairy). The more rapid movement of P with dairy and hog manure may be due to high amount of labile P they contain which resulted in a higher degree of P saturation of soil receiving these amendments, relative to the control soil. However, the most rapid P movement in MAP amended soil may be due to dissolution of precipitate of MAP with dilution during the convective flow. Overall, the results from this study indicate that P movement in biosolids-amended soil may be less of a concern than in soil receiving manures (hog and dairy) and P fertilizers.

6. GENERAL DISCUSSION

The results obtained in the fractionation study provided a very important insight into forms of P in biosolids and manures. For example, the labile P fraction, representing the readily available forms of P for biological uptake and run-off loss, and long-term bioavailable P represented a small proportion (about 23%) of total P in biosolids but higher proportions (63 - 70%) in the manures. On the other hand, the recalcitrant P was predominant in biosolids compared to manures. The recalcitrant nature of biosolids P, which was partly attributed to the Fe, Al and Ca contents of biosolids, confirmed the importance of chemical removal of P in organic amendments. Maguire et al. (2001) reported that Fe-treated biosolids produced a lower water-soluble P and FeO-P (i.e. P that easily desorbs from soils onto Fe oxide strip during 24-h equilibration) than those without Fe additions. Penn and Sims (2002) also reported higher Mehlich-3 extractable P (29 - 68%) and water soluble P (10 - 45%) in biosolids that were not treated with Fe than in Fe or Al treated biosolids, which contained 0.4 - 13% Mehlich-3 P and 0.4 - 5% water soluble P. A higher proportion of recalcitrant P in biosolids indicates that biosolids P may be less vulnerable to run-off loss compared to manures when applied to agricultural lands at same loading rates. Since the labile P in biosolids can be reduced with chemical additions, the same P removal method can be applied to manures to reduce the risk of P loss in run-off and leaching. Chemicals such as alum ($Al_2(SO_4)_3.2H_2O$) and Fe salts ($FeSO_4$) can be added to manures to reduce the labile P content. For example, Dao (1999) reported that addition of alum increased the ratio of N to water extractable P in manures. While this might be a favorable situation in minimizing P loss to run-off, it also means that P is 'tied up' in a relatively unavailable form for plant uptake. A good way to assess the feasibility of P 'tie-up' for agri-environmental sustainability will be to monitor the release of P in chemically treated manure so as to improve on the timing of manure applications, whether manures can be applied in the fall or spring. Phosphorus based nutrient management plan aimed at protecting water quality and ensuring optimum crop production should therefore consider factors, such as, labile P contents in organic amendments, and the release and uptake of P by crops.

The effect of organic amendments on P sorption in the two soils used for the sorption study confirmed the importance of the fractionation study. The greater reduction in P sorption in manure amended soils than in soil that received biosolids indicated that the highly labile P in manures occupied the sorption sites and caused a decline in P sorption capacity of the soil. The reduced sorption capacity was evident by the lower S_{max} and P_{max} in the manured soil than in biosolids amended soils. The lower degree of P saturation in the soil with biosolids than with manures, which corresponded with lower equilibrium P concentration in the solution at zero sorption, also suggested that the recalcitrant P in biosolids (Ajiboye et al. 2002) was probably not effective in reducing the soils' P sorption capacity. The fact that MAP fertilizer did not affect P sorption in the Osborne soil, but decreased it significantly in the Lakeland soil may be due to differences in retention mechanism of P in the two soils. The level of exchangeable Ca^{2+} in the two soils may differ with lower levels in the Lakeland soil due to its lower clay contents than Osborne soil. High exchangeable Ca^{2+} in Osborne soil may favor P precipitation (Akinremi and Cho, 1991a, b), while the low exchangeable Ca^{2+} in Lakeland soil may result in a combination of precipitation and sorption. Precipitation of inorganic P in the soil may be a favorable process in preventing P loss if the precipitates formed become relatively insoluble. The poor correlation obtained between S_{max} and P_{max} suggests that the predictability of sorption capacity using a single point isotherm may depend on the choice of initial P concentration of the equilibrating solution, the maximum P concentration used in generating the S_{max} and the type of soil.

The effect of organic amendments and fertilizer on P retention was further buttressed by the data generated from the convective movement of inorganic P in the soil. The more rapid movement of P in the soil amended with manures, relative to biosolids amended soils, confirmed the higher degree of P saturation and lower binding strength of P to the soil with manures. The more rapid movement of P at higher loading of manure P also indicated a decrease in P sorption with increasing rate of P additions. Hooda et al. (1999) attributed the elevated P concentration in the subsurface drainage to a reduced sorption capacity of the soil as the high energy sites decreased with increasing loading rates of P. The earlier P breakthrough in the MAP amended soil which did not match the result from the sorption study; where MAP did not affect P sorption, may be due to the dissolution of relatively soluble DCPD formed during incubation. The result from the convective transport study further indicated that recalcitrant P in biosolids which resulted in the lower soils' DPS with biosolids than with manures, also increased the retardation of P movement. Hence, P movement in biosolids-amended soil may be less of a concern than in soil receiving dairy and hog manures. It should be noted that these experiments were short-term studies and as such, may not reflect the behavior of these amendments in the long-term.

7. SUMMARY AND CONCLUSIONS

Results from fractionation study showed that most of the P in biosolids was recalcitrant. However, P in hog and cattle manures was mainly in labile forms that are soluble in water and $NaHCO_3$. Inorganic P predominated in biosolids, hog and dairy cattle manures but not in beef cattle. The solubility of a higher proportion of biosolids P in strong extractants like NaOH and HCl indicate that biosolids P may be less vulnerable to run-off loss compared to other amendments when applied to agricultural lands. Although oven dry manures are easier to handle compared to fresh forms, results from this study indicate that caution should be exercised in using pre-treatments, such as oven drying, for manure P studies.

In the Osborne soil, P sorption was not affected by biosolids and MAP fertilizer, but was reduced with dairy cattle and hog manures. The magnitude of the reduction in P sorption with these manures increased with rates. Hog manure was the most efficient in reducing P sorption in the Osborne soil. In the Lakeland soil, all amendments with the exception of biosolids decreased P sorption. Unlike in Osborne soil, MAP fertilizer reduced sorption the most. The P sorption data obtained for Osborne soil fit the Langmuir and Freundlich sorption models whereas the data for Lakeland soil only fit the Freundlich model. In the Osborne soil, the sorption maximum was not affected by biosolids and MAP but significantly reduced by hog and dairy manures. The affinity of amended soil for P was significantly reduced by all the amendments relative to the control except at the high rate of biosolids and MAP. In the Lakeland soil, however, all amendments except biosolids reduced the sorption maximum. Similar to the Osborne soil, the affinity of the amended soil for P was significantly reduced by all the amendments except at the low and medium rates of biosolids application in the Lakeland soil. That MAP did not reduce P retention in Osborne soil is an indication of P precipitation in the soil. The degree of P saturation was least with biosolids and MAP in the Osborne soil but MAP resulted in the highest degree of P saturation in the Lakeland soil. These results suggest that P in biosolids may not be labile enough to saturate the P sorption sites as did hog and dairy manure P.

The convective movement of P was not affected by biosolids relative to the control, but was more rapid in soils amended with dairy cattle and hog manures. The amount of P retained during the convective flow was higher in the biosolids amended soil than the control and soils amended with dairy and hog manures. The reduced movement of P obtained in biosolids-amended soil may be an indication of lower degree of P saturation in biosolids amended soil than with P fertilizer and manures (hog and dairy). The more rapid movement of P in dairy and hog manure amended soils than in the control soil may be due to the competition of organic anions in these manures with P for sorption sites. However, the most rapid P movement in MAP amended soil may be due to dissolution of precipitate earlier formed with MAP which contributed to P concentrations in the effluents. From an environmental point of view, results presented here suggest a lower risk of P loss in run-off and by leaching with biosolids application than with hog and cattle manure at equal rates of P applications.

8. CONTRIBUTION TO KNOWLEDGE

Results from the fractionation of organic amendments showed that forms of P in biosolids are mainly recalcitrant in nature as opposed to the relatively labile P in dairy and hog manure. The relative distribution of labile Pin the organic amendments was responsible for the least reduction in P sorption capacity and saturation of Osborne clay loam (Gleysolic Humic Vertisol) and Lakeland silty clay loam (Rego Black Chernozerm) soils with biosolids compared to dairy and hog manures. In the same way, movement of inorganic P was more rapid in the soil amended with manures (dairy and hog) and MAP fertilizer than biosolids. The overall results indicate that application of biosolids may be less of a concern to P pollution of surface water than manures and P fertilizer.

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10. APPENDICES

Appendix Ia. P extracted (% of total P) by various extractant in the fresh amendments.

FRESH	H_2O Pi	H_2O Po	Bicarb Pi	Bicarb Po	NaOH Pi	NaOH Po	HCl P	Residual
BIO 1	7.84	2.60	9.80	4.99	24.80	11.36	28.57	10.04
	7.96	2.88	10.41	3.42	22.61	14.09	28.84	9.78
	7.57	2.99	10.06	3.57	23.55	11.95	29.82	10.49
BIO 2	6.37	1.32	12.81	3.07	26.05	10.46	29.49	10.43
	6.49	0.63	12.36	4.70	27.68	8.24	29.49	10.42
	6.80	0.93	12.05	3.76	30.19	5.58	29.97	10.72
DAIRY	11.37	8.05	43.88	8.65	6.09	10.49	3.33	8.14
	11.81	7.50	42.96	7.13	5.29	10.86	5.80	8.64
	11.54	8.61	43.19	5.95	5.25	10.84	5.38	9.25
BEEF	21.88	11.92	17.85	6.10	2.69	19.48	8.22	11.86
	21.83	12.75	17.40	7.02	2.64	18.11	7.80	12.46
	21.61	10.30	18.38	9.65	2.29	18.20	8.37	11.21
HOG-OLD	22.87	13.19	8.76	10.10	7.63	1.67	30.72	5.06
	21.90	14.01	8.95	8.83	8.05	1.43	31.85	4.99
	22.02	15.34	8.61	9.47	8.60	1.25	29.47	5.24
HOG-SOW	13.39	28.46	9.63	11.45	5.02	0.90	26.36	4.78
	13.08	28.95	9.60	11.00	4.78	0.82	27.15	4.62
	14.30	29.02	10.37	9.66	5.12	1.19	25.43	4.91
HOG-NUR	21.10	19.47	11.10	14.20	6.61	1.26	19.49	6.78
	22.78	17.47	11.28	11.61	6.66	2.19	21.03	6.97
	23.29	16.75	11.24	12.33	7.40	1.61	20.25	7.14

Appendix Ib. P extracted (% of total P) by various extractant in the oven dry amendments.

DRY	H_2O Pi	H_2O Po	Bicarb Pi	Bicarb Po	NaOH Pi	NaOH Po	HCl P	Residual
BIO 1	6.78	4.04	12.53	3.96	21.79	6.09	36.41	8.40
	6.79	5.04	12.54	4.35	20.64	8.13	35.26	7.25
	6.35	3.44	13.45	2.41	22.02	6.46	36.78	9.09
BIO 2	4.16	4.78	14.83	1.96	27.77	5.23	35.33	5.94
	4.32	2.92	15.08	1.74	30.46	3.29	34.30	7.89
	3.81	3.07	14.82	2.59	28.22	4.25	35.31	7.92
DAIRY	37.54	6.27	29.58	-2.29	4.70	9.45	8.60	6.14
	36.53	6.05	29.56	0.25	3.88	7.79	9.11	6.82
	30.40	12.54	24.83	2.61	4.31	9.63	9.76	5.92
BEEF	11.44	21.45	13.54	14.35	1.72	8.30	19.85	9.36
	14.90	19.08	14.43	9.08	1.77	6.38	26.07	8.30
	15.01	18.50	12.57	10.47	1.65	7.54	25.02	9.23
HOG-OLD	40.87	-3.41	8.81	7.26	11.76	1.50	28.25	4.96
	34.13	-0.99	11.07	5.69	12.71	1.26	31.73	4.40
	39.40	-3.03	8.51	9.24	12.01	1.00	28.23	4.65
HOG-SOW	32.55	8.21	6.86	8.74	6.00	1.24	28.39	8.02
	35.60	4.51	8.56	11.00	5.71	1.79	24.81	8.03
	36.46	4.24	9.08	7.07	5.33	5.12	24.70	8.00
HOG-NUR	39.87	1.62	11.32	5.66	10.40	3.17	23.44	4.53
	40.36	0.55	12.27	7.30	10.13	2.48	22.34	4.57
	34.08	7.79	10.12	8.14	12.23	2.09	21.40	4.15

Appendix II. Mean squares of analysis of variance for P sorption parameters and saturation indices

Soils	Source	df	Mean squares						
			S_{max}	P_{max}	b	n	K	DPS	PSI
Lakeland	Treat	12	-	14789***	-	0.25***	1289***	-	1661***
Osborne	Treat	12	12527*	13281***	0.001***	0.03***	1952***	733 ***	709 ***

significant at 5% level , ** significant at 1% level , *** significant at 0.1% level, and ^{ns} not significant

Appendix IIIa. P sorption data for the unamended (control) Osborne soil.

			0 Mg ha^{-1}			
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	0.04	2.15	-3.32	0.76	0.02
	2	0.03	2.22	-3.43	0.80	0.01
	3	0.04	2.17	-3.35	0.77	0.02
2.5	1	0.27	47.42	-1.30	3.86	0.01
	2	0.27	47.52	-1.32	3.86	0.01
	3	0.27	47.42	-1.30	3.86	0.01
5	1	0.78	87.37	-0.25	4.47	0.01
	2	0.76	87.62	-0.27	4.47	0.01
	3	0.73	88.32	-0.32	4.48	0.01
10	1	3.29	137.07	1.19	4.92	0.02
	2	3.52	132.47	1.26	4.89	0.03
	3	3.55	131.87	1.27	4.88	0.03
15	1	4.52	212.47	1.51	5.36	0.02
	2	4.60	210.87	1.53	5.35	0.02
	3	4.70	208.87	1.55	5.34	0.02
20	1	7.08	261.37	1.96	5.57	0.03
	2	6.93	264.37	1.94	5.58	0.03
	3	6.73	268.37	1.91	5.59	0.03
30	1	13.24	338.07	2.58	5.82	0.04
	2	13.84	326.07	2.63	5.79	0.04
	3	13.88	325.27	2.63	5.78	0.04
40	1	20.55	391.87	3.02	5.97	0.05
	2	20.75	387.87	3.03	5.96	0.05
	3	20.95	383.87	3.04	5.95	0.05
60	1	36.31	476.62	3.59	6.17	0.08
	2	37.75	447.87	3.63	6.10	0.08
	3	38.06	441.62	3.64	6.09	0.09
75	1	50.00	602.87	3.91	6.40	0.08
	2	47.50	652.87	3.86	6.48	0.07
	3	49.38	615.37	3.90	6.42	0.08
100	1	68.60	630.87	4.23	6.45	0.11
	2	67.20	658.87	4.21	6.49	0.10
	3	66.40	674.87	4.20	6.51	0.10

Appendix IIIb. P sorption for Osborne soil amended with biosolids at 12.5 Mg ha^{-1}.

		12.5 Mg ha^{-1}				
Conc (mg P L^{-1})	Reps	C (mg P L^{-1})	S (mg P kg^{-1})	lnC	lnS	C/S
0	1	0.13	0.25	-2.03	-1.41	0.54
	2	0.12	0.40	-2.09	-0.93	0.31
	3	0.13	0.35	-2.07	-1.06	0.37
3	1	0.50	42.87	-0.69	3.76	0.01
	2	0.54	42.02	-0.61	3.74	0.01
	3	0.53	42.27	-0.63	3.74	0.01
5	1	1.12	80.52	0.11	4.39	0.01
	2	1.04	82.12	0.04	4.41	0.01
	3	1.31	76.62	0.27	4.34	0.02
10	1	3.95	123.87	1.37	4.82	0.03
	2	3.97	123.47	1.38	4.82	0.03
	3	4.09	121.07	1.41	4.80	0.03
15	1	5.20	198.87	1.65	5.29	0.03
	2	5.06	201.67	1.62	5.31	0.03
	3	5.46	193.67	1.70	5.27	0.03
20	1	7.58	251.37	2.02	5.53	0.03
	2	7.05	261.87	1.95	5.57	0.03
	3	7.78	247.37	2.05	5.51	0.03
30	1	14.28	317.27	2.66	5.76	0.05
	2	13.92	324.47	2.63	5.78	0.04
	3	14.04	322.07	2.64	5.77	0.04
40	1	21.35	375.87	3.06	5.93	0.06
	2	20.65	389.87	3.03	5.97	0.05
	3	21.70	368.87	3.08	5.91	0.06
60	1	37.25	457.87	3.62	6.13	0.08
	2	37.50	452.87	3.62	6.12	0.08
	3	38.38	435.37	3.65	6.08	0.09
75	1	51.25	577.87	3.94	6.36	0.09
	2	52.25	557.87	3.96	6.32	0.09
	3	52.75	547.87	3.97	6.31	0.10
100	1	66.80	666.87	4.20	6.50	0.10
	2	66.60	670.87	4.20	6.51	0.10
	3	68.80	626.87	4.23	6.44	0.11

Appendix IIIc. P sorption for Osborne soil amended with biosolids at 25 Mg ha^{-1}.

			25 Mg ha^{-1}			
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	0.28	-2.65	-1.29	-	-0.10
	2	0.20	-1.17	-1.60	-	-0.17
	3	0.22	-1.45	-1.53	-	-0.15
3	1	0.92	34.42	-0.08	3.54	0.03
	2	0.71	38.72	-0.35	3.66	0.02
	3	0.75	37.97	-0.29	3.64	0.02
5	1	1.43	74.37	0.35	4.31	0.02
	2	1.34	76.07	0.29	4.33	0.02
	3	1.25	77.97	0.22	4.36	0.02
10	1	3.60	130.87	1.28	4.87	0.03
	2	3.39	135.07	1.22	4.91	0.03
	3	3.10	140.87	1.13	4.95	0.02
15	1	5.62	190.47	1.73	5.25	0.03
	2	5.20	198.87	1.65	5.29	0.03
	3	5.28	197.27	1.66	5.28	0.03
20	1	8.18	239.37	2.10	5.48	0.03
	2	7.15	259.87	1.97	5.56	0.03
	3	7.65	249.87	2.03	5.52	0.03
30	1	14.44	314.07	2.67	5.75	0.05
	2	13.08	341.27	2.57	5.83	0.04
	3	13.84	326.07	2.63	5.79	0.04
40	1	22.05	361.87	3.09	5.89	0.06
	2	21.45	373.87	3.07	5.92	0.06
	3	21.90	364.87	3.09	5.90	0.06
60	1	38.88	425.37	3.66	6.05	0.09
	2	37.56	451.62	3.63	6.11	0.08
	3	39.13	420.37	3.67	6.04	0.09
75	1	50.38	595.37	3.92	6.39	0.08
	2	47.25	657.87	3.86	6.49	0.07
	3	47.88	645.37	3.87	6.47	0.07
100	1	65.00	702.87	4.17	6.56	0.09
	2	61.40	774.87	4.12	6.65	0.08
	3	67.00	662.87	4.20	6.50	0.10

Appendix IIId. P sorption for Osborne soil amended with biosolids at 50 Mg ha^{-1}.

				50 Mg ha^{-1}		
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	0.52	-7.53	-0.65	-	-0.07
	2	0.47	-6.53	-0.76	-	-0.07
	3	0.46	-6.38	-0.77	-	-0.07
3	1	1.09	31.12	0.08	3.44	0.03
	2	1.03	32.32	0.03	3.48	0.03
	3	1.01	32.77	0.00	3.49	0.03
5	1	1.89	65.17	0.63	4.18	0.03
	2	1.74	68.07	0.55	4.22	0.03
	3	1.79	67.17	0.58	4.21	0.03
10	1	3.90	124.87	1.36	4.83	0.03
	2	3.75	127.87	1.32	4.85	0.03
	3	3.91	124.62	1.36	4.83	0.03
15	1	6.88	165.27	1.93	5.11	0.04
	2	6.90	164.87	1.93	5.11	0.04
	3	6.76	167.67	1.91	5.12	0.04
20	1	8.20	238.87	2.10	5.48	0.03
	2	8.30	236.87	2.12	5.47	0.04
	3	8.70	228.87	2.16	5.43	0.04
30	1	15.28	297.27	2.73	5.69	0.05
	2	15.08	301.27	2.71	5.71	0.05
	3	14.76	307.67	2.69	5.73	0.05
40	1	21.90	364.87	3.09	5.90	0.06
	2	21.05	381.87	3.05	5.95	0.06
	3	21.80	366.87	3.08	5.91	0.06
60	1	37.70	448.87	3.63	6.11	0.08
	2	33.60	530.87	3.51	6.27	0.06
	3	37.80	446.87	3.63	6.10	0.08
75	1	51.38	575.37	3.94	6.36	0.09
	2	54.00	522.87	3.99	6.26	0.10
	3	54.63	510.37	4.00	6.24	0.11
100	1	74.00	522.87	4.30	6.26	0.14
	2	75.20	498.87	4.32	6.21	0.15
	3	74.60	510.87	4.31	6.24	0.15

Appendix IVa. P sorption for Osborne soil amended with dairy cattle manure at biosolids P equivalent rate of 12.5 Mg ha^{-1}

				12.5 Mg ha^{-1}		
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	0.35	-4.08	-1.06	-	-0.09
	2	0.30	-3.08	-1.21	-	-0.10
	3	0.28	-2.78	-1.26	-	-0.10
3	1	0.69	39.17	-0.38	3.67	0.02
	2	0.75	37.87	-0.29	3.63	0.02
	3	0.80	36.87	-0.22	3.61	0.02
5	1	1.56	71.72	0.44	4.27	0.02
	2	1.75	67.97	0.56	4.22	0.03
	3	1.53	72.37	0.42	4.28	0.02
10	1	4.25	117.87	1.45	4.77	0.04
	2	4.43	114.27	1.49	4.74	0.04
	3	4.33	116.27	1.47	4.76	0.04
15	1	6.12	180.47	1.81	5.20	0.03
	2	6.00	182.87	1.79	5.21	0.03
	3	6.02	182.47	1.80	5.21	0.03
20	1	8.60	230.87	2.15	5.44	0.04
	2	8.55	231.87	2.15	5.45	0.04
	3	8.45	233.87	2.13	5.45	0.04
30	1	15.32	296.47	2.73	5.69	0.05
	2	15.16	299.67	2.72	5.70	0.05
	3	14.96	303.67	2.71	5.72	0.05
40	1	23.10	340.87	3.14	5.83	0.07
	2	22.70	348.87	3.12	5.85	0.07
	3	22.95	343.87	3.13	5.84	0.07
60	1	40.38	395.37	3.70	5.98	0.10
	2	40.63	390.37	3.70	5.97	0.10
	3	40.13	400.37	3.69	5.99	0.10
75	1	53.50	532.87	3.98	6.28	0.10
	2	51.63	570.37	3.94	6.35	0.09
	3	50.13	600.37	3.91	6.40	0.08
100	1	68.00	642.87	4.22	6.47	0.11
	2	64.80	706.87	4.17	6.56	0.09
	3	69.00	622.87	4.23	6.43	0.11

Appendix IVb. P sorption for Osborne soil amended with dairy cattle manure at biosolids P equivalent rate of 25 Mg ha^{-1}.

				25 Mg ha^{-1}		
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	0.63	-9.65	-0.47	-	-0.06
	2	0.65	-10.21	-0.42	-	-0.06
	3	0.64	-10.01	-0.44	-	-0.06
3	1	1.48	23.22	0.39	3.15	0.06
	2	1.43	24.32	0.36	3.19	0.06
	3	1.41	24.77	0.34	3.21	0.06
5	1	2.52	52.47	0.92	3.96	0.05
	2	2.15	59.97	0.76	4.09	0.04
	3	2.17	59.47	0.77	4.09	0.04
10	1	5.03	102.27	1.62	4.63	0.05
	2	5.13	100.27	1.64	4.61	0.05
	3	5.24	98.07	1.66	4.59	0.05
15	1	7.54	152.07	2.02	5.02	0.05
	2	7.06	161.67	1.95	5.09	0.04
	3	7.02	162.47	1.95	5.09	0.04
20	1	10.50	192.87	2.35	5.26	0.05
	2	10.33	196.37	2.33	5.28	0.05
	3	9.88	205.37	2.29	5.32	0.05
30	1	16.40	274.87	2.80	5.62	0.06
	2	16.24	278.07	2.79	5.63	0.06
	3	16.64	270.07	2.81	5.60	0.06
40	1	25.30	296.87	3.23	5.69	0.09
	2	24.60	310.87	3.20	5.74	0.08
	3	24.85	305.87	3.21	5.72	0.08
60	1	42.69	349.12	3.75	5.86	0.12
	2	42.00	362.87	3.74	5.89	0.12
	3	42.06	361.62	3.74	5.89	0.12
75	1	56.88	465.37	4.04	6.14	0.12
	2	54.50	512.87	4.00	6.24	0.11
	3	56.88	465.37	4.04	6.14	0.12
100	1	67.60	650.87	4.21	6.48	0.10
	2	69.60	610.87	4.24	6.41	0.11
	3	70.40	594.87	4.25	6.39	0.12

Appendix IVc. P sorption for Osborne soil amended with dairy cattle manure at biosolids P equivalent rate of 50 Mg ha^{-1}.

			50 Mg ha^{-1}			
Conc (mg P L^{-1})	Reps	C (mg P L^{-1})	S (mg P kg^{-1})	lnC	lnS	C/S
0	1	2.36	-44.23	0.86	-	-0.05
	2	1.93	-35.73	0.66	-	-0.05
	3	2.09	-38.83	0.73	-	-0.05
3	1	3.24	-11.93	1.18	-	-0.27
	2	3.13	-9.73	1.14	-	-0.32
	3	3.14	-9.93	1.14	-	-0.32
5	1	4.54	12.07	1.51	2.49	0.38
	2	3.96	23.67	1.38	3.16	0.17
	3	4.32	16.47	1.46	2.80	0.26
10	1	7.55	51.87	2.02	3.95	0.15
	2	7.18	59.37	1.97	4.08	0.12
	3	7.35	55.87	1.99	4.02	0.13
15	1	10.75	87.87	2.37	4.48	0.12
	2	10.50	92.87	2.35	4.53	0.11
	3	10.55	91.87	2.36	4.52	0.11
20	1	12.98	143.37	2.56	4.97	0.09
	2	12.80	146.87	2.55	4.99	0.09
	3	12.80	146.87	2.55	4.99	0.09
30	1	18.44	234.07	2.91	5.46	0.08
	2	19.52	212.47	2.97	5.36	0.09
	3	19.92	204.47	2.99	5.32	0.10
40	1	26.30	276.87	3.27	5.62	0.09
	2	26.05	281.87	3.26	5.64	0.09
	3	26.10	280.87	3.26	5.64	0.09
60	1	42.80	346.87	3.76	5.85	0.12
	2	43.50	332.87	3.77	5.81	0.13
	3	44.70	308.87	3.80	5.73	0.14
75	1	61.50	372.87	4.12	5.92	0.16
	2	61.50	372.87	4.12	5.92	0.16
	3	60.00	402.87	4.09	6.00	0.15
100	1	79.40	414.87	4.37	6.03	0.19
	2	82.20	358.87	4.41	5.88	0.23
	3	78.40	434.87	4.36	6.08	0.18

Appendix Va. P sorption for Osborne soil amended with hog manure at biosolids P equivalent rate of 12.5 Mg ha^{-1}.

			12.5 Mg ha^{-1}			
Conc ($mg\ P\ L^{-1}$)	**Reps**	**C ($mg\ P\ L^{-1}$)**	**S ($mg\ P\ kg^{-1}$)**	**lnC**	**lnS**	**C/S**
0	1	0.66	-10.23	-0.42	-	-0.06
	2	0.52	-7.48	-0.66	-	-0.07
	3	0.54	-7.88	-0.62	-	-0.07
3	1	1.36	25.67	0.31	3.25	0.05
	2	1.37	25.57	0.31	3.24	0.05
	3	1.28	27.37	0.24	3.31	0.05
5	1	2.31	56.77	0.84	4.04	0.04
	2	2.00	62.87	0.69	4.14	0.03
	3	2.08	61.37	0.73	4.12	0.03
10	1	5.16	99.67	1.64	4.60	0.05
	2	5.15	99.87	1.64	4.60	0.05
	3	5.12	100.47	1.63	4.61	0.05
15	1	7.26	157.67	1.98	5.06	0.05
	2	6.94	164.07	1.94	5.10	0.04
	3	6.72	168.47	1.91	5.13	0.04
20	1	9.90	204.87	2.29	5.32	0.05
	2	9.40	214.87	2.24	5.37	0.04
	3	8.95	223.87	2.19	5.41	0.04
30	1	16.92	264.47	2.83	5.58	0.06
	2	16.40	274.87	2.80	5.62	0.06
	3	16.04	282.07	2.78	5.64	0.06
40	1	25.10	300.87	3.22	5.71	0.08
	2	23.85	325.87	3.17	5.79	0.07
	3	23.25	337.87	3.15	5.82	0.07
60	1	43.44	334.12	3.77	5.81	0.13
	2	40.13	400.37	3.69	5.99	0.10
	3	40.56	391.62	3.70	5.97	0.10
75	1	54.13	520.37	3.99	6.25	0.10
	2	53.63	530.37	3.98	6.27	0.10
	3	53.38	535.37	3.98	6.28	0.10
100	1	70.60	590.87	4.26	6.38	0.12
	2	68.60	630.87	4.23	6.45	0.11
	3	73.20	538.87	4.29	6.29	0.14

Appendix Vb. P sorption for Osborne soil amended with hog manure at biosolids P equivalent rate of 25 Mg ha^{-1}.

				25 Mg ha^{-1}		
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	1.01	-17.23	0.00	-	-0.06
	2	1.18	-20.73	0.17	-	-0.06
	3	1.11	-19.23	0.10	-	-0.06
3	1	1.69	19.17	0.52	2.95	0.09
	2	1.91	14.77	0.64	2.69	0.13
	3	1.71	18.67	0.54	2.93	0.09
5	1	2.44	54.07	0.89	3.99	0.05
	2	2.99	43.07	1.10	3.76	0.07
	3	2.65	49.87	0.97	3.91	0.05
10	1	5.08	101.27	1.63	4.62	0.05
	2	5.18	99.27	1.64	4.60	0.05
	3	5.23	98.27	1.65	4.59	0.05
15	1	7.50	152.87	2.01	5.03	0.05
	2	7.56	151.67	2.02	5.02	0.05
	3	7.90	144.87	2.07	4.98	0.05
20	1	10.63	190.37	2.36	5.25	0.06
	2	11.78	167.37	2.47	5.12	0.07
	3	11.00	182.87	2.40	5.21	0.06
30	1	16.76	267.67	2.82	5.59	0.06
	2	18.12	240.47	2.90	5.48	0.08
	3	17.28	257.27	2.85	5.55	0.07
40	1	25.25	297.87	3.23	5.70	0.08
	2	27.05	261.87	3.30	5.57	0.10
	3	26.35	275.87	3.27	5.62	0.10
60	1	40.13	400.37	3.69	5.99	0.10
	2	42.13	360.37	3.74	5.89	0.12
	3	41.94	364.12	3.74	5.90	0.12
75	1	57.13	460.37	4.05	6.13	0.12
	2	55.38	495.37	4.01	6.21	0.11
	3	57.13	460.37	4.05	6.13	0.12
100	1	69.60	610.87	4.24	6.41	0.11
	2	72.20	558.87	4.28	6.33	0.13
	3	71.60	570.87	4.27	6.35	0.13

Appendix Vc. P sorption for Osborne soil amended with hog manure at biosolids P equivalent rate of 50 Mg ha^{-1}.

				50 Mg ha^{-1}		
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	2.39	-44.83	0.87	-	-0.05
	2	2.60	-49.13	0.96	-	-0.05
	3	2.29	-42.93	0.83	-	-0.05
3	1	3.52	-17.53	1.26	-	-0.20
	2	3.42	-15.53	1.23	-	-0.22
	3	3.30	-13.13	1.19	-	-0.25
5	1	4.70	8.87	1.55	2.18	0.53
	2	4.94	4.07	1.60	1.40	1.21
	3	4.66	9.67	1.54	2.27	0.48
10	1	7.90	44.87	2.07	3.80	0.18
	2	7.73	48.37	2.04	3.88	0.16
	3	7.48	53.37	2.01	3.98	0.14
15	1	10.85	85.87	2.38	4.45	0.13
	2	10.75	87.87	2.37	4.48	0.12
	3	10.55	91.87	2.36	4.52	0.11
20	1	12.00	162.87	2.48	5.09	0.07
	2	12.83	146.37	2.55	4.99	0.09
	3	12.93	144.37	2.56	4.97	0.09
30	1	20.44	194.07	3.02	5.27	0.11
	2	19.84	206.07	2.99	5.33	0.10
	3	20.44	194.07	3.02	5.27	0.11
40	1	28.20	238.87	3.34	5.48	0.12
	2	26.95	263.87	3.29	5.58	0.10
	3	26.80	266.87	3.29	5.59	0.10
60	1	44.80	306.87	3.80	5.73	0.15
	2	43.60	330.87	3.78	5.80	0.13
	3	43.70	328.87	3.78	5.80	0.13
75	1	61.38	375.37	4.12	5.93	0.16
	2	59.25	417.87	4.08	6.04	0.14
	3	63.13	340.37	4.15	5.83	0.19
100	1	81.60	370.87	4.40	5.92	0.22
	2	83.20	338.87	4.42	5.83	0.25
	3	83.20	338.87	4.42	5.83	0.25

Appendix VIa. P sorption for Osborne soil amended with MAP at biosolids P equivalent rate of 12.5 Mg ha^{-1}.

Conc (mg P L^{-1})	Reps	C (mg P L^{-1})	12.5 Mg ha^{-1} S (mg P kg^{-1})	lnC	lnS	C/S
0	1	0.14	0.11	-1.98	-2.20	1.25
	2	0.19	-0.97	-1.65	-	-0.20
	3	0.12	0.47	-2.12	-0.75	0.26
3	1	0.51	42.72	-0.68	3.75	0.01
	2	0.50	42.92	-0.70	3.76	0.01
	3	0.46	43.62	-0.77	3.78	0.01
5	1	1.12	80.47	0.11	4.39	0.01
	2	1.26	77.67	0.23	4.35	0.02
	3	1.20	78.97	0.18	4.37	0.02
10	1	4.28	117.27	1.45	4.76	0.04
	2	4.32	116.47	1.46	4.76	0.04
	3	3.83	126.27	1.34	4.84	0.03
15	1	5.14	200.07	1.64	5.30	0.03
	2	5.28	197.27	1.66	5.28	0.03
	3	5.02	202.47	1.61	5.31	0.02
20	1	7.70	248.87	2.04	5.52	0.03
	2	7.68	249.37	2.04	5.52	0.03
	3	7.73	248.37	2.04	5.51	0.03
30	1	14.00	322.87	2.64	5.78	0.04
	2	14.12	320.47	2.65	5.77	0.04
	3	14.12	320.47	2.65	5.77	0.04
40	1	21.40	374.87	3.06	5.93	0.06
	2	22.25	357.87	3.10	5.88	0.06
	3	21.80	366.87	3.08	5.91	0.06
60	1	38.44	434.12	3.65	6.07	0.09
	2	39.00	422.87	3.66	6.05	0.09
	3	38.31	436.62	3.65	6.08	0.09
75	1	50.25	597.87	3.92	6.39	0.08
	2	52.00	562.87	3.95	6.33	0.09
	3	52.13	560.37	3.95	6.33	0.09
100	1	68.20	638.87	4.22	6.46	0.11
	2	67.60	650.87	4.21	6.48	0.10
	3	67.20	658.87	4.21	6.49	0.10

Appendix VIb. P sorption for Osborne soil amended with MAP at biosolids P equivalent rate of 25 Mg ha^{-1}.

			25 Mg ha^{-1}			
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	0.22	-1.53	-1.51	-	-0.14
	2	0.26	-2.28	-1.36	-	-0.11
	3	0.26	-2.28	-1.36	-	-0.11
3	1	0.70	38.87	-0.36	3.66	0.02
	2	0.87	35.57	-0.15	3.57	0.02
	3	0.70	38.97	-0.36	3.66	0.02
5	1	1.29	77.17	0.25	4.35	0.02
	2	1.63	70.27	0.49	4.25	0.02
	3	1.54	72.17	0.43	4.28	0.02
10	1	3.79	127.07	1.33	4.84	0.03
	2	3.94	124.07	1.37	4.82	0.03
	3	3.67	129.47	1.30	4.86	0.03
15	1	5.28	197.27	1.66	5.28	0.03
	2	5.30	196.87	1.67	5.28	0.03
	3	5.24	198.07	1.66	5.29	0.03
20	1	7.65	249.87	2.03	5.52	0.03
	2	8.05	241.87	2.09	5.49	0.03
	3	7.38	255.37	2.00	5.54	0.03
30	1	13.60	330.87	2.61	5.80	0.04
	2	13.80	326.87	2.62	5.79	0.04
	3	13.88	325.27	2.63	5.78	0.04
40	1	21.05	381.87	3.05	5.95	0.06
	2	21.45	373.87	3.07	5.92	0.06
	3	21.65	369.87	3.08	5.91	0.06
60	1	36.06	481.62	3.59	6.18	0.07
	2	35.94	484.12	3.58	6.18	0.07
	3	37.25	457.87	3.62	6.13	0.08
75	1	52.38	555.37	3.96	6.32	0.09
	2	50.50	592.87	3.92	6.38	0.09
	3	51.75	567.87	3.95	6.34	0.09
100	1	66.60	670.87	4.20	6.51	0.10
	2	69.20	618.87	4.24	6.43	0.11
	3	67.60	650.87	4.21	6.48	0.10

Appendix VIc. P sorption for Osborne soil amended with MAP at biosolids P equivalent rate of 50 Mg ha^{-1}.

				50 Mg ha^{-1}		
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	0.41	-5.28	-0.90	-	-0.08
	2	0.44	-5.83	-0.83	-	-0.07
	3	0.34	-3.93	-1.08	-	-0.09
3	1	0.86	35.62	-0.15	3.57	0.02
	2	0.88	35.22	-0.12	3.56	0.03
	3	0.68	39.32	-0.39	3.67	0.02
5	1	1.54	72.07	0.43	4.28	0.02
	2	1.36	75.77	0.30	4.33	0.02
	3	1.41	74.77	0.34	4.31	0.02
10	1	3.19	139.12	1.16	4.94	0.02
	2	3.65	129.87	1.29	4.87	0.03
	3	3.13	140.37	1.14	4.94	0.02
15	1	6.28	177.27	1.84	5.18	0.04
	2	6.20	178.87	1.82	5.19	0.03
	3	5.40	194.87	1.69	5.27	0.03
20	1	8.60	230.87	2.15	5.44	0.04
	2	7.80	246.87	2.05	5.51	0.03
	3	7.88	245.37	2.06	5.50	0.03
30	1	14.12	320.47	2.65	5.77	0.04
	2	14.32	316.47	2.66	5.76	0.05
	3	13.32	336.47	2.59	5.82	0.04
40	1	21.20	378.87	3.05	5.94	0.06
	2	21.05	381.87	3.05	5.95	0.06
	3	19.90	404.87	2.99	6.00	0.05
60	1	34.80	506.87	3.55	6.23	0.07
	2	36.00	482.87	3.58	6.18	0.07
	3	35.50	492.87	3.57	6.20	0.07
75	1	54.13	520.37	3.99	6.25	0.10
	2	52.38	555.37	3.96	6.32	0.09
	3	52.13	560.37	3.95	6.33	0.09
100	1	73.00	542.87	4.29	6.30	0.13
	2	72.20	558.87	4.28	6.33	0.13
	3	71.40	574.87	4.27	6.35	0.12

Appendix VII. P sorption for the unamended (control) Lakeland soil.

				0 Mg ha^{-1}		
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	0.65	-1.96	-0.43	-	-0.33
	2	0.69	-2.76	-0.37	-	-0.25
	3	0.73	-3.56	-0.31	-	-0.21
2.5	1	1.08	39.54	0.07	3.68	0.03
	2	1.20	37.14	0.18	3.61	0.03
	3	1.13	38.54	0.12	3.65	0.03
5	1	1.99	71.24	0.69	4.27	0.03
	2	2.08	69.54	0.73	4.24	0.03
	3	1.98	71.44	0.68	4.27	0.03
10	1	3.97	131.64	1.38	4.88	0.03
	2	4.08	129.44	1.41	4.86	0.03
	3	3.95	132.04	1.37	4.88	0.03
15	1	5.89	193.29	1.77	5.26	0.03
	2	6.71	176.79	1.90	5.17	0.04
	3	7.00	171.04	1.95	5.14	0.04
20	1	8.92	232.64	2.19	5.45	0.04
	2	9.64	218.24	2.27	5.39	0.04
	3	8.68	237.44	2.16	5.47	0.04
30	1	14.53	320.54	2.68	5.77	0.05
	2	15.53	300.54	2.74	5.71	0.05
	3	14.98	311.54	2.71	5.74	0.05
40	1	23.40	343.04	3.15	5.84	0.07
	2	22.76	355.84	3.13	5.87	0.06
	3	22.64	358.24	3.12	5.88	0.06
60	1	35.00	511.04	3.56	6.24	0.07
	2	35.15	508.04	3.56	6.23	0.07
	3	36.00	491.04	3.58	6.20	0.07
75	1	44.81	614.79	3.80	6.42	0.07
	2	42.38	663.54	3.75	6.50	0.06
	3	44.94	612.29	3.81	6.42	0.07
100	1	62.38	763.54	4.13	6.64	0.08
	2	64.00	731.04	4.16	6.59	0.09
	3	64.50	721.04	4.17	6.58	0.09

Appendix VIIIa. P sorption for Osborne soil amended with biosolids at 12.5 Mg ha^{-1}.

				12.5 Mg ha^{-1}		
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	0.84	-5.76	-0.17	-	-0.15
	2	1.10	-10.96	0.10	-	-0.10
	3	0.86	-6.06	-0.16	-	-0.14
2.5	1	1.27	35.64	0.24	3.57	0.04
	2	1.56	29.94	0.44	3.40	0.05
	3	1.30	35.04	0.26	3.56	0.04
5	1	2.09	69.24	0.74	4.24	0.03
	2	2.24	66.24	0.81	4.19	0.03
	3	2.11	68.84	0.75	4.23	0.03
10	1	4.34	124.29	1.47	4.82	0.03
	2	4.30	125.04	1.46	4.83	0.03
	3	3.99	131.29	1.38	4.88	0.03
15	1	6.48	181.44	1.87	5.20	0.04
	2	7.12	168.64	1.96	5.13	0.04
	3	6.60	179.04	1.89	5.19	0.04
20	1	8.75	236.04	2.17	5.46	0.04
	2	9.35	224.04	2.24	5.41	0.04
	3	9.20	227.04	2.22	5.43	0.04
30	1	15.52	300.64	2.74	5.71	0.05
	2	16.44	282.24	2.80	5.64	0.06
	3	15.28	305.44	2.73	5.72	0.05
40	1	20.85	394.04	3.04	5.98	0.05
	2	21.10	389.04	3.05	5.96	0.05
	3	22.30	365.04	3.10	5.90	0.06
60	1	34.63	518.54	3.54	6.25	0.07
	2	36.63	478.54	3.60	6.17	0.08
	3	36.69	477.29	3.60	6.17	0.08
75	1	48.90	533.04	3.89	6.28	0.09
	2	48.80	535.04	3.89	6.28	0.09
	3	47.90	553.04	3.87	6.32	0.09
100	1	67.38	663.54	4.21	6.50	0.10
	2	68.63	638.54	4.23	6.46	0.11
	3	67.13	668.54	4.21	6.51	0.10

Appendix VIIIb. P sorption for Osborne soil amended with biosolids at 25 Mg ha^{-1}.

		25 Mg ha^{-1}				
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	1.22	-13.26	0.19	-	-0.09
	2	1.60	-20.86	0.47	-	-0.08
	3	1.02	-9.26	0.01	-	-0.11
2.5	1	1.70	27.14	0.53	3.30	0.06
	2	1.86	23.84	0.62	3.17	0.08
	3	1.76	25.84	0.57	3.25	0.07
5	1	2.52	60.64	0.92	4.10	0.04
	2	2.74	56.24	1.01	4.03	0.05
	3	2.20	67.04	0.79	4.21	0.03
10	1	4.63	118.54	1.53	4.78	0.04
	2	4.56	119.79	1.52	4.79	0.04
	3	4.18	127.54	1.43	4.85	0.03
15	1	6.94	172.24	1.94	5.15	0.04
	2	7.60	159.04	2.03	5.07	0.05
	3	6.68	177.44	1.90	5.18	0.04
20	1	9.85	214.04	2.29	5.37	0.05
	2	9.70	217.04	2.27	5.38	0.04
	3	8.80	235.04	2.17	5.46	0.04
30	1	15.40	303.04	2.73	5.71	0.05
	2	16.16	287.84	2.78	5.66	0.06
	3	16.40	283.04	2.80	5.65	0.06
40	1	22.65	358.04	3.12	5.88	0.06
	2	23.90	333.04	3.17	5.81	0.07
	3	22.50	361.04	3.11	5.89	0.06
60	1	33.88	533.54	3.52	6.28	0.06
	2	37.25	466.04	3.62	6.14	0.08
	3	34.06	529.79	3.53	6.27	0.06
75	1	42.90	653.04	3.76	6.48	0.07
	2	47.10	569.04	3.85	6.34	0.08
	3	46.20	587.04	3.83	6.38	0.08
100	1	69.25	626.04	4.24	6.44	0.11
	2	67.50	661.04	4.21	6.49	0.10
	3	69.50	621.04	4.24	6.43	0.11

Appendix VIIIc. P sorption for Osborne soil amended with biosolids at 50 Mg ha^{-1}.

		50 Mg ha^{-1}				
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	1.90	-26.86	0.64	-	-0.07
	2	1.68	-22.56	0.52	-	-0.07
	3	2.04	-29.76	0.71	-	-0.07
2.5	1	2.45	12.14	0.89	2.50	0.20
	2	2.16	17.84	0.77	2.88	0.12
	3	2.47	11.74	0.90	2.46	0.21
5	1	3.14	48.24	1.14	3.88	0.07
	2	3.14	48.24	1.14	3.88	0.07
	3	3.17	47.64	1.15	3.86	0.07
10	1	5.14	108.29	1.64	4.68	0.05
	2	4.69	117.29	1.54	4.76	0.04
	3	5.00	111.04	1.61	4.71	0.05
15	1	8.06	149.84	2.09	5.01	0.05
	2	7.34	164.24	1.99	5.10	0.04
	3	7.74	156.24	2.05	5.05	0.05
20	1	10.55	200.04	2.36	5.30	0.05
	2	9.20	227.04	2.22	5.43	0.04
	3	10.00	211.04	2.30	5.35	0.05
30	1	16.44	282.24	2.80	5.64	0.06
	2	14.84	314.24	2.70	5.75	0.05
	3	16.52	280.64	2.80	5.64	0.06
40	1	24.20	327.04	3.19	5.79	0.07
	2	21.50	381.04	3.07	5.94	0.06
	3	22.20	367.04	3.10	5.91	0.06
60	1	37.38	463.54	3.62	6.14	0.08
	2	35.25	506.04	3.56	6.23	0.07
	3	37.13	468.54	3.61	6.15	0.08
75	1	46.40	583.04	3.84	6.37	0.08
	2	46.00	591.04	3.83	6.38	0.08
	3	45.70	597.04	3.82	6.39	0.08
100	1	63.13	748.54	4.15	6.62	0.08
	2	65.88	693.54	4.19	6.54	0.09
	3	65.75	696.04	4.19	6.55	0.09

Appendix IXa. P sorption for Osborne soil amended with dairy manure at biosolids P equivalent rate of 12.5 Mg ha^{-1}.

		12.5 Mg ha^{-1}				
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	1.11	-11.16	0.10	-	-0.10
	2	1.53	-19.46	0.42	-	-0.08
	3	1.49	-18.76	0.40	-	-0.08
2.5	1	3.66	-12.16	1.30	-	-0.30
	2	3.74	-13.76	1.32	-	-0.27
	3	3.87	-16.36	1.35	-	-0.24
5	1	2.99	51.29	1.09	3.94	0.06
	2	4.15	28.04	1.42	3.33	0.15
	3	3.61	38.79	1.28	3.66	0.09
10	1	5.30	105.04	1.67	4.65	0.05
	2	6.24	86.29	1.83	4.46	0.07
	3	5.14	108.29	1.64	4.68	0.05
15	1	8.35	144.04	2.12	4.97	0.06
	2	10.78	95.54	2.38	4.56	0.11
	3	8.05	150.04	2.09	5.01	0.05
20	1	10.64	198.24	2.36	5.29	0.05
	2	11.48	181.44	2.44	5.20	0.06
	3	11.32	184.64	2.43	5.22	0.06
30	1	17.76	255.84	2.88	5.54	0.07
	2	18.28	245.44	2.91	5.50	0.07
	3	18.00	251.04	2.89	5.53	0.07
40	1	22.06	369.79	3.09	5.91	0.06
	2	26.19	287.29	3.27	5.66	0.09
	3	23.88	333.54	3.17	5.81	0.07
60	1	38.70	437.04	3.66	6.08	0.09
	2	40.90	393.04	3.71	5.97	0.10
	3	40.60	399.04	3.70	5.99	0.10
75	1	50.88	493.54	3.93	6.20	0.10
	2	50.75	496.04	3.93	6.21	0.10
	3	50.88	493.54	3.93	6.20	0.10
100	1	70.20	607.04	4.25	6.41	0.12
	2	67.20	667.04	4.21	6.50	0.10
	3	70.20	607.04	4.25	6.41	0.12

Appendix IXb. P sorption for Osborne soil amended with dairy manure at biosolids P equivalent rate of 25 Mg ha^{-1}.

				25 Mg ha^{-1}		
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	3.33	-55.56	1.20	-	-0.06
	2	3.51	-59.06	1.25	-	-0.06
	3	3.95	-67.86	1.37	-	-0.06
2.5	1	4.91	-37.21	1.59	-	-0.13
	2	4.64	-31.71	1.53	-	-0.15
	3	4.50	-28.96	1.50	-	-0.16
5	1	5.93	-7.46	1.78	-	-0.79
	2	5.53	0.54	1.71	-0.62	10.23
	3	5.73	-3.46	1.74	-	-1.65
10	1	8.43	42.54	2.13	3.75	0.20
	2	8.30	45.04	2.12	3.81	0.18
	3	8.65	38.04	2.16	3.64	0.23
15	1	11.96	71.84	2.48	4.27	0.17
	2	10.28	105.44	2.33	4.66	0.10
	3	12.24	66.24	2.50	4.19	0.18
20	1	14.40	123.04	2.67	4.81	0.12
	2	14.28	125.44	2.66	4.83	0.11
	3	13.40	143.04	2.60	4.96	0.09
30	1	21.90	173.04	3.09	5.15	0.13
	2	21.40	183.04	3.06	5.21	0.12
	3	22.20	167.04	3.10	5.12	0.13
40	1	30.13	208.54	3.41	5.34	0.14
	2	27.25	266.04	3.31	5.58	0.10
	3	29.06	229.79	3.37	5.44	0.13
60	1	45.60	299.04	3.82	5.70	0.15
	2	44.80	315.04	3.80	5.75	0.14
	3	44.40	323.04	3.79	5.78	0.14
75	1	51.63	478.54	3.94	6.17	0.11
	2	55.50	401.04	4.02	5.99	0.14
	3	56.00	391.04	4.03	5.97	0.14
100	1	73.00	551.04	4.29	6.31	0.13
	2	73.80	535.04	4.30	6.28	0.14
	3	74.60	519.04	4.31	6.25	0.14

Appendix IXc. P sorption for Osborne soil amended with dairy manure at biosolids P equivalent rate of 50 Mg ha^{-1}.

			50 Mg ha^{-1}			
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	5.42	-97.36	1.69	-	-0.06
	2	3.28	-54.56	1.19	-	-0.06
	3	4.03	-69.56	1.39	-	-0.06
2.5	1	5.69	-52.71	1.74	-	-0.11
	2	4.89	-36.71	1.59	-	-0.13
	3	4.65	-31.96	1.54	-	-0.15
5	1	7.93	-47.46	2.07	-	-0.17
	2	5.13	8.54	1.63	2.14	0.60
	3	6.35	-15.96	1.85	-	-0.40
10	1	10.75	-3.96	2.37	-	-2.71
	2	7.93	52.54	2.07	3.96	0.15
	3	8.53	40.54	2.14	3.70	0.21
15	1	13.88	33.44	2.63	3.51	0.42
	2	11.00	91.04	2.40	4.51	0.12
	3	12.68	57.44	2.54	4.05	0.22
20	1	17.32	64.64	2.85	4.17	0.27
	2	13.96	131.84	2.64	4.88	0.11
	3	14.96	111.84	2.71	4.72	0.13
30	1	22.90	153.04	3.13	5.03	0.15
	2	19.90	213.04	2.99	5.36	0.09
	3	21.80	175.04	3.08	5.17	0.12
40	1	34.75	116.04	3.55	4.75	0.30
	2	30.00	211.04	3.40	5.35	0.14
	3	29.44	222.29	3.38	5.40	0.13
60	1	48.10	249.04	3.87	5.52	0.19
	2	46.90	273.04	3.85	5.61	0.17
	3	44.30	325.04	3.79	5.78	0.14
75	1	58.50	341.04	4.07	5.83	0.17
	2	51.50	481.04	3.94	6.18	0.11
	3	56.25	386.04	4.03	5.96	0.15
100	1	77.80	455.04	4.35	6.12	0.17
	2	72.20	567.04	4.28	6.34	0.13
	3	74.20	527.04	4.31	6.27	0.14

Appendix Xa. P sorption for Osborne soil amended with hog manure at biosolids P equivalent rate of 12.5 Mg ha^{-1}.

				12.5 Mg ha^{-1}		
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	1.23	-13.56	0.21	-	-0.09
	2	1.13	-11.46	0.12	-	-0.10
	3	1.17	-12.36	0.16	-	-0.09
2.5	1	1.61	28.94	0.47	3.37	0.06
	2	1.68	27.44	0.52	3.31	0.06
	3	1.71	26.94	0.53	3.29	0.06
5	1	2.60	59.04	0.96	4.08	0.04
	2	2.53	60.44	0.93	4.10	0.04
	3	2.56	59.84	0.94	4.09	0.04
10	1	4.59	119.29	1.52	4.78	0.04
	2	4.45	122.04	1.49	4.80	0.04
	3	4.70	117.04	1.55	4.76	0.04
15	1	7.84	154.24	2.06	5.04	0.05
	2	7.24	166.24	1.98	5.11	0.04
	3	7.16	167.84	1.97	5.12	0.04
20	1	10.48	201.54	2.35	5.31	0.05
	2	9.63	218.54	2.26	5.39	0.04
	3	10.05	210.04	2.31	5.35	0.05
30	1	16.04	290.24	2.78	5.67	0.06
	2	16.12	288.64	2.78	5.67	0.06
	3	17.20	267.04	2.84	5.59	0.06
40	1	24.60	319.04	3.20	5.77	0.08
	2	24.10	329.04	3.18	5.80	0.07
	3	23.80	335.04	3.17	5.81	0.07
60	1	40.38	403.54	3.70	6.00	0.10
	2	40.44	402.29	3.70	6.00	0.10
	3	40.63	398.54	3.70	5.99	0.10
75	1	51.90	473.04	3.95	6.16	0.11
	2	51.10	489.04	3.93	6.19	0.10
	3	49.90	513.04	3.91	6.24	0.10
100	1	68.13	648.54	4.22	6.47	0.11
	2	67.38	663.54	4.21	6.50	0.10
	3	68.63	638.54	4.23	6.46	0.11

Appendix Xb. P sorption for Osborne soil amended with hog manure at biosolids P equivalent rate of 25 Mg ha^{-1}.

			25 Mg ha^{-1}			
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	2.28	-34.46	0.82	-	-0.07
	2	2.10	-30.96	0.74	-	-0.07
	3	2.24	-33.76	0.81	-	-0.07
2.5	1	2.94	2.34	1.08	0.85	1.25
	2	2.86	3.84	1.05	1.35	0.74
	3	3.00	1.04	1.10	0.04	2.88
5	1	3.58	39.44	1.28	3.67	0.09
	2	3.59	39.24	1.28	3.67	0.09
	3	3.94	32.24	1.37	3.47	0.12
10	1	6.13	88.54	1.81	4.48	0.07
	2	6.08	89.54	1.80	4.49	0.07
	3	6.23	86.54	1.83	4.46	0.07
15	1	9.12	128.64	2.21	4.86	0.07
	2	9.10	129.04	2.21	4.86	0.07
	3	9.28	125.44	2.23	4.83	0.07
20	1	11.03	190.54	2.40	5.25	0.06
	2	11.35	184.04	2.43	5.22	0.06
	3	11.90	173.04	2.48	5.15	0.07
30	1	18.44	242.24	2.91	5.49	0.08
	2	18.04	250.24	2.89	5.52	0.07
	3	18.64	238.24	2.93	5.47	0.08
40	1	27.40	263.04	3.31	5.57	0.10
	2	26.00	291.04	3.26	5.67	0.09
	3	26.65	278.04	3.28	5.63	0.10
60	1	41.19	387.29	3.72	5.96	0.11
	2	39.13	428.54	3.67	6.06	0.09
	3	39.94	412.29	3.69	6.02	0.10
75	1	50.60	499.04	3.92	6.21	0.10
	2	48.70	537.04	3.89	6.29	0.09
	3	51.40	483.04	3.94	6.18	0.11
100	1	74.00	531.04	4.30	6.27	0.14
	2	69.50	621.04	4.24	6.43	0.11
	3	66.75	676.04	4.20	6.52	0.10

Appendix Xc. P sorption for Osborne soil amended with hog manure at biosolids P equivalent rate of 50 Mg ha^{-1}.

				50 Mg ha^{-1}		
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	3.32	-55.36	1.20	-	-0.06
	2	2.86	-46.16	1.05	-	-0.06
	3	3.23	-53.56	1.17	-	-0.06
2.5	1	3.96	-18.16	1.38	-	-0.22
	2	3.67	-12.36	1.30	-	-0.30
	3	3.88	-16.56	1.36	-	-0.23
5	1	4.56	19.79	1.52	2.99	0.23
	2	4.33	24.54	1.46	3.20	0.18
	3	4.46	21.79	1.50	3.08	0.20
10	1	6.62	78.64	1.89	4.36	0.08
	2	6.22	86.64	1.83	4.46	0.07
	3	6.28	85.44	1.84	4.45	0.07
15	1	9.50	121.04	2.25	4.80	0.08
	2	9.20	127.04	2.22	4.84	0.07
	3	9.38	123.54	2.24	4.82	0.08
20	1	11.00	191.04	2.40	5.25	0.06
	2	11.53	180.54	2.44	5.20	0.06
	3	11.58	179.54	2.45	5.19	0.06
30	1	17.84	254.24	2.88	5.54	0.07
	2	18.56	239.84	2.92	5.48	0.08
	3	19.16	227.84	2.95	5.43	0.08
40	1	25.95	292.04	3.26	5.68	0.09
	2	26.30	285.04	3.27	5.65	0.09
	3	26.35	284.04	3.27	5.65	0.09
60	1	38.69	437.29	3.66	6.08	0.09
	2	36.94	472.29	3.61	6.16	0.08
	3	39.38	423.54	3.67	6.05	0.09
75	1	51.10	489.04	3.93	6.19	0.10
	2	48.80	535.04	3.89	6.28	0.09
	3	48.90	533.04	3.89	6.28	0.09
100	1	71.00	591.04	4.26	6.38	0.12
	2	69.88	613.54	4.25	6.42	0.11
	3	72.13	568.54	4.28	6.34	0.13

Appendix XIa. P sorption for Osborne soil amended with MAP at biosolids P equivalent rate of 12.5 Mg ha^{-1}.

				12.5 Mg ha^{-1}		
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1.40	-16.96	0.34	-	-0.08	1.40
	1.92	-27.26	0.65	-	-0.07	1.92
	1.38	-16.46	0.32	-	-0.08	1.38
2.5	2.19	17.34	0.78	2.85	0.13	2.19
	2.14	18.24	0.76	2.90	0.12	2.14
	2.05	20.14	0.72	3.00	0.10	2.05
5	3.00	51.04	1.10	3.93	0.06	3.00
	3.68	37.54	1.30	3.63	0.10	3.68
	2.90	53.04	1.06	3.97	0.05	2.90
10	5.08	109.44	1.63	4.70	0.05	5.08
	6.20	87.04	1.82	4.47	0.07	6.20
	5.74	96.24	1.75	4.57	0.06	5.74
15	7.63	158.54	2.03	5.07	0.05	7.63
	8.13	148.54	2.09	5.00	0.05	8.13
	8.65	138.04	2.16	4.93	0.06	8.65
20	10.45	202.04	2.35	5.31	0.05	10.45
	10.50	201.04	2.35	5.30	0.05	10.50
	9.53	220.54	2.25	5.40	0.04	9.53
30	16.48	281.44	2.80	5.64	0.06	16.48
	18.08	249.44	2.89	5.52	0.07	18.08
	17.36	263.84	2.85	5.58	0.07	17.36
40	25.35	304.04	3.23	5.72	0.08	25.35
	25.10	309.04	3.22	5.73	0.08	25.10
	24.15	328.04	3.18	5.79	0.07	24.15
60	37.44	462.29	3.62	6.14	0.08	37.44
	36.63	478.54	3.60	6.17	0.08	36.63
	35.19	507.29	3.56	6.23	0.07	35.19
75	41.60	679.04	3.73	6.52	0.06	41.60
	49.00	531.04	3.89	6.27	0.09	49.00
	46.70	577.04	3.84	6.36	0.08	46.70
100	70.00	611.04	4.25	6.42	0.11	70.00
	70.63	598.54	4.26	6.39	0.12	70.63
	69.38	623.54	4.24	6.44	0.11	69.38

Appendix XIb. P sorption for Osborne soil amended with MAP at biosolids P equivalent rate of 25 Mg ha^{-1}.

			25 Mg ha^{-1}			
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	2.22	-33.26	0.80	-	-0.07
	2	2.73	-43.46	1.00	-	-0.06
	3	2.56	-40.06	0.94	-	-0.06
2.5	1	3.44	-7.76	1.24	-	-0.44
	2	3.35	-5.96	1.21	-	-0.56
	3	3.40	-6.96	1.22	-	-0.49
5	1	3.90	33.04	1.36	3.50	0.12
	2	4.10	29.04	1.41	3.37	0.14
	3	5.09	9.29	1.63	2.23	0.55
10	1	6.22	86.64	1.83	4.46	0.07
	2	6.48	81.44	1.87	4.40	0.08
	3	7.12	68.64	1.96	4.23	0.10
15	1	8.93	132.54	2.19	4.89	0.07
	2	9.28	125.54	2.23	4.83	0.07
	3	10.35	104.04	2.34	4.64	0.10
20	1	11.43	182.54	2.44	5.21	0.06
	2	11.40	183.04	2.43	5.21	0.06
	3	12.63	158.54	2.54	5.07	0.08
30	1	17.92	252.64	2.89	5.53	0.07
	2	18.00	251.04	2.89	5.53	0.07
	3	18.88	233.44	2.94	5.45	0.08
40	1	26.15	288.04	3.26	5.66	0.09
	2	24.90	313.04	3.21	5.75	0.08
	3	26.70	277.04	3.28	5.62	0.10
60	1	38.44	442.29	3.65	6.09	0.09
	2	38.94	432.29	3.66	6.07	0.09
	3	41.31	384.79	3.72	5.95	0.11
75	1	51.00	491.04	3.93	6.20	0.10
	2	49.30	525.04	3.90	6.26	0.09
	3	48.80	535.04	3.89	6.28	0.09
100	1	71.25	586.04	4.27	6.37	0.12
	2	68.00	651.04	4.22	6.48	0.10
	3	71.25	586.04	4.27	6.37	0.12

Appendix XIc. P sorption for Osborne soil amended with MAP at biosolids P equivalent rate of 50 Mg ha^{-1}.

			50 Mg ha^{-1}			
Conc (mg P L^{-1})	**Reps**	**C (mg P L^{-1})**	**S (mg P kg^{-1})**	**lnC**	**lnS**	**C/S**
0	1	6.06	-110.16	1.80	-	-0.06
	2	5.61	-101.16	1.72	-	-0.06
	3	5.33	-95.56	1.67	-	-0.06
2.5	1	6.63	-71.46	1.89	-	-0.09
	2	7.28	-84.46	1.98	-	-0.09
	3	6.83	-75.46	1.92	-	-0.09
5	1	8.55	-59.96	2.15	-	-0.14
	2	8.98	-68.46	2.19	-	-0.13
	3	7.98	-48.46	2.08	-	-0.16
10	1	11.18	-12.46	2.41	-	-0.90
	2	11.33	-15.46	2.43	-	-0.73
	3	11.00	-8.96	2.40	-	-1.23
15	1	13.56	39.84	2.61	3.68	0.34
	2	14.24	26.24	2.66	3.27	0.54
	3	13.36	43.84	2.59	3.78	0.30
20	1	16.95	72.04	2.83	4.28	0.24
	2	16.75	76.04	2.82	4.33	0.22
	3	16.75	76.04	2.82	4.33	0.22
30	1	22.45	162.04	3.11	5.09	0.14
	2	22.55	160.04	3.12	5.08	0.14
	3	21.85	174.04	3.08	5.16	0.13
40	1	30.88	193.54	3.43	5.27	0.16
	2	30.81	194.79	3.43	5.27	0.16
	3	30.06	209.79	3.40	5.35	0.14
60	1	44.30	325.04	3.79	5.78	0.14
	2	43.50	341.04	3.77	5.83	0.13
	3	43.50	341.04	3.77	5.83	0.13
75	1	52.50	461.04	3.96	6.13	0.11
	2	51.50	481.04	3.94	6.18	0.11
	3	54.50	421.04	4.00	6.04	0.13
100	1	71.00	591.04	4.26	6.38	0.12
	2	69.40	623.04	4.24	6.43	0.11
	3	72.00	571.04	4.28	6.35	0.13

Appendix XII. Pearson Correlation Coefficients (r) matrix for sorption parameters in the amended Osborne soil.

	S_{max} (mg P kg^{-1})	**DPS(%)**	**PSI(%)**
S_{max}	1.000	-0.948***	-0.942 ***
DPS		1.000	0.988***
PSI			1.000

Appendix XIII. P breakthrough data for unamended (control) Osborne soil.

Rep1		**Rep2**		**Mean**	
Pore Volume	**C/Co**	**Pore Volume**	**C/Co**	**Pore Volume**	**C/Co**
5.0009	0.0117	5.2040	0.0120	5.1024	0.0119
5.2470	0.0305	5.4664	0.0308	5.3567	0.0307
5.5508	0.0687	5.7927	0.0688	5.6718	0.0688
5.8134	0.0975	6.0646	0.0977	5.9390	0.0976
6.0846	0.1460	6.3365	0.1443	6.2106	0.1452
6.3558	0.2107	6.6372	0.2093	6.4965	0.2100
6.6270	0.3000	6.9379	0.2987	6.7825	0.2993
6.9098	0.3907	7.2386	0.3933	7.0742	0.3920
7.1926	0.5000	7.5393	0.4967	7.3659	0.4983
7.4638	0.5250	7.8210	0.5283	7.6424	0.5267
7.7177	0.5667	8.0742	0.5650	7.8959	0.5658
7.9716	0.6433	8.3274	0.6467	8.1495	0.6450
8.2255	0.6500	8.5806	0.6433	8.4031	0.6467
8.4794	0.6917	8.8482	0.6883	8.6638	0.6900
8.7333	0.7167	9.1141	0.7133	8.9237	0.7150
8.9872	0.7667	9.3788	0.7583	9.1830	0.7625
9.2412	0.7867	9.6435	0.7833	9.4423	0.7850
9.4951	0.7917	9.9082	0.7883	9.7016	0.7900
9.7334	0.7850	10.1660	0.7900	9.9497	0.7875
9.9567	0.7950	10.4094	0.7950	10.1831	0.7950
10.1731	0.8000	10.6382	0.7883	10.4057	0.7942
10.3895	0.8350	10.8670	0.8300	10.6282	0.8325
10.6059	0.8683	11.0957	0.8783	10.8508	0.8733
10.8223	0.8467	11.3245	0.8317	11.0734	0.8392
11.0387	0.8617	11.5532	0.8650	11.2960	0.8633
11.2551	0.8717	11.7820	0.8683	11.5185	0.8700
11.4715	0.8833	12.0107	0.8733	11.7411	0.8783
11.6879	0.9017	12.2395	0.9000	11.9637	0.9008
11.9043	0.9250	12.4682	0.9067	12.1863	0.9158
12.1207	0.9100	12.7329	0.9000	12.4268	0.9050
12.3458	0.9333	12.9976	0.9183	12.6717	0.9258
12.5708	0.9300	13.2624	0.9500	12.9166	0.9400
12.7959	0.9533	13.5271	0.8950	13.1615	0.9242
13.0209	0.9517	13.7918	0.9000	13.4064	0.9258
13.2460	0.9567	14.0565	0.9200	13.6513	0.9383
13.4711	0.9550	14.3212	0.9583	13.8961	0.9567
13.6961	0.9617	14.5859	0.9567	14.1410	0.9592

Appendix XIVa. P breakthrough data for Osborne soil amended at low rate of biosolids.

Rep1		Rep2		Mean	
Pore Volume	C/Co	Pore Volume	C/Co	Pore Volume	C/Co
4.7438	0.0032			4.7438	0.0032
4.9354	0.0080			4.9354	0.0080
5.1187	0.0150			5.1187	0.0150
5.3517	0.0293			5.3517	0.0293
5.5499	0.0490	5.5394	0.0019	5.5446	0.0255
5.7615	0.0783	5.7443	0.0112	5.7529	0.0448
5.9855	0.1107	5.9599	0.0435	5.9727	0.0771
6.1954	0.1423	6.1968	0.0517	6.1961	0.0970
6.3974	0.1753	6.4151	0.1603	6.4063	0.1678
6.5953	0.2133	6.6255	0.2037	6.6104	0.2085
6.7890	0.2480	6.8383	0.2629	6.8136	0.2555
6.9604	0.2885	7.0381	0.3019	6.9993	0.2952
7.1220	0.3195	7.2165	0.3408	7.1692	0.3301
7.2856	0.3793	7.3841	0.3893	7.3348	0.3843
7.4526	0.4113	7.5477	0.4792	7.5002	0.4453
7.6322	0.4667	7.7183	0.4850	7.6752	0.4758
7.8109	0.5133	7.9049	0.5483	7.8579	0.5308
7.9803	0.5767	8.0900	0.5650	8.0351	0.5708
8.1463	0.6417	8.2595	0.6167	8.2029	0.6292
8.3303	0.6617	8.4306	0.6217	8.3805	0.6417
8.5204	0.6717	8.6202	0.6867	8.5703	0.6792
8.7235	0.6767	8.8158	0.6950	8.7696	0.6858
8.9285	0.7200	9.0237	0.6840	8.9761	0.7020
9.1371	0.7217	9.2376	0.7320	9.1873	0.7268
9.3571	0.7683	9.4616	0.8000	9.4093	0.7842
9.5812	0.8000	9.6938	0.8060	9.6375	0.8030
9.8036	0.7867	9.9328	0.8300	9.8682	0.8083
10.0225	0.8083	10.1691	0.8460	10.0958	0.8272
10.2385	0.8500	10.4152	0.9320	10.3268	0.8910
10.4215	0.6933	10.6370	0.9200	10.5292	0.8067
10.5674	0.8133	10.8413	0.9440	10.7043	0.8787
10.7120	0.8500	11.0064	0.8920	10.8592	0.8710
10.8580	0.8133	11.1692	0.9280	11.0136	0.8707
11.0050	0.8500	11.3267	0.9160	11.1658	0.8830
11.1518	0.8533	11.4942	0.9240	11.3230	0.8887
11.3021	0.8533	11.6673	0.9160	11.4847	0.8847
11.4504	0.8500	11.8394	0.8960	11.6449	0.8730
		12.0089	0.9040	12.0089	0.9040

Appendix XIVb. P breakthrough data for Osborne soil amended at high rate of biosolids.

Rep1		**Rep2**		**Mean**	
Pore Volume	**C/Co**	**Pore Volume**	**C/Co**	**Pore Volume**	**C/Co**
0.2419	0.0091	0.2277	0.0094	0.2348	0.0093
0.5442	0.0098	0.5123	0.0104	0.5283	0.0101
0.8466	0.0091	0.7992	0.0103	0.8229	0.0097
1.1489	0.0091	1.1042	0.0101	1.1266	0.0096
1.4513	0.0089	1.4115	0.0098	1.4314	0.0094
1.7537	0.0093	1.7187	0.0104	1.7362	0.0098
2.0560	0.0095	2.0260	0.0097	2.0410	0.0096
2.3584	0.0096	2.3152	0.0106	2.3368	0.0101
2.6607	0.0095	2.5998	0.0102	2.6303	0.0099
2.9504	0.0091	2.8844	0.0100	2.9174	0.0096
3.2317	0.0000	3.1457	0.0100	3.1887	0.0050
3.5118	0.0092	3.4013	0.0107	3.4565	0.0100
3.7893	0.0095	3.6542	0.0117	3.7217	0.0106
4.0662	0.0107	3.9065	0.0129	3.9863	0.0118
4.3431	0.0134	4.1587	0.0181	4.2509	0.0158
4.6276	0.0170	4.4162	0.0222	4.5219	0.0196
4.9714	0.0269	4.4421	0.0345	4.7067	0.0307
5.2578	0.0418	4.9854	0.0420	5.1216	0.0419
5.5856	0.0827	5.2895	0.0775	5.4375	0.0801
5.9134	0.1410	5.5935	0.1057	5.7535	0.1233
6.2603	0.1703	5.9169	0.1460	6.0886	0.1582
6.6073	0.2163	6.2404	0.2140	6.4238	0.2152
6.9542	0.2867	6.5638	0.2800	6.7590	0.2833
7.3011	0.3460	6.8873	0.3427	7.0942	0.3443
7.6480	0.4207	7.2107	0.4120	7.4293	0.4163
7.9949	0.4683	7.5231	0.4600	7.7590	0.4642
8.2852	0.4950	7.8032	0.4933	8.0442	0.4942
8.5780	0.5850	8.0846	0.5500	8.3313	0.5675
8.8708	0.6033	8.3660	0.5700	8.6184	0.5867
9.1636	0.6300	8.6474	0.6217	8.9055	0.6258
9.4583	0.6850	8.9320	0.6600	9.1952	0.6725
9.7607	0.7033	9.2296	0.6933	9.4951	0.6983
10.0630	0.7133	9.5271	0.6883	9.7951	0.7008
10.3654	0.7600	9.8247	0.7467	10.0950	0.7533
10.6677	0.7817	10.1223	0.7600	10.3950	0.7708
10.9701	0.8117	10.4198	0.7983	10.6950	0.8050
11.2661	0.8300	10.7141	0.8200	10.9901	0.8250
11.5621	0.8283	11.0085	0.8133	11.2853	0.8208
11.8581	0.8150	11.3028	0.8267	11.5804	0.8208
12.1445	0.8350	11.5874	0.8567	11.8660	0.8458
12.4055	0.8383	11.8462	0.8700	12.1258	0.8542
12.6744	0.8283	12.1049	0.8850	12.3897	0.8567
12.9433	0.8300	12.3637	0.8267	12.6535	0.8283
13.2123	0.8517	12.6224	0.8600	12.9174	0.8558
13.4812	0.8533	12.8812	0.8433	13.1812	0.8483
13.7502	0.8333	13.1399	0.8100	13.4450	0.8217
14.0191	0.8283	13.3987	0.8317	13.7089	0.8300
14.3160	0.8150	13.6791	0.8250	13.9976	0.8200
14.6130	0.8333	13.9605	0.8283	14.2867	0.8308
14.9099	0.7967	14.2419	0.8167	14.5759	0.8067
15.2069	0.8467	14.5233	0.8283	14.8651	0.8375
15.5038	0.8750	14.8046	0.8750	15.1542	0.8750

Appendix XVa. P breakthrough data for Osborne soil amended at low rate of cattle manure.

Rep1		**Rep2**		**Mean**	
Pore Volume	**C/Co**	**Pore Volume**	**C/Co**	**Pore Volume**	**C/Co**
3.5753	0.0026			3.5753	0.0026
3.7927	0.0028			3.7927	0.0028
4.0102	0.0028	4.0221	0.0028	4.0102	0.0028
4.2502	0.0030	4.2714	0.0029	4.1361	0.0029
4.4959	0.0040	4.5241	0.0033	4.3836	0.0035
4.7439	0.0093	4.7863	0.0053	4.6340	0.0063
4.9924	0.0200	5.0531	0.0124	4.8894	0.0127
5.2906	0.0417	5.3731	0.0168	5.1718	0.0271
5.5402	0.0767	5.6343	0.0713	5.4567	0.0467
5.7888	0.1100	5.8870	0.1033	5.7115	0.0907
6.0158	0.1347	6.1161	0.1260	5.9514	0.1190
6.2107	0.1687	6.3098	0.1503	6.1634	0.1473
6.4055	0.2020	6.5035	0.1770	6.3577	0.1762
6.6004	0.2533	6.6973	0.2480	6.5520	0.2152
6.7953	0.2727	6.8910	0.2747	6.7463	0.2603
6.9901	0.3340	7.0847	0.3407	6.9406	0.3043
7.1850	0.3867	7.2785	0.4000	7.1349	0.3637
7.3798	0.4283	7.4722	0.4350	7.3292	0.4142
7.5634	0.4117	7.6659	0.4767	7.5178	0.4233
7.7470	0.5033	7.8790	0.5150	7.7065	0.4900
7.9305	0.5300	8.0921	0.5333	7.9048	0.5225
8.1141	0.5517	8.2946	0.5717	8.1031	0.5425
8.2977	0.6117	8.4970	0.6183	8.2961	0.5917
8.4835	0.6650	8.6771	0.6817	8.4903	0.6417
8.6783	0.6533	8.8421	0.6750	8.6777	0.6675
8.8738	0.6700	9.0183	0.6850	8.8580	0.6725
9.0714	0.7083	9.2148	0.7100	9.0448	0.6967
9.2127	0.7350	9.3552	0.7500	9.2137	0.7225
9.3397	0.6650	9.4815	0.7533	9.3475	0.7075
9.4764	0.7533	9.6283	0.7633	9.4790	0.7533
9.6515	0.7250	9.8569	0.7650	9.6399	0.7442
9.8266	0.7917	10.0854	0.7850	9.8417	0.7783
10.0017	0.7933	10.3140	0.8267	10.0436	0.7892
10.1768	0.8417	10.5425	0.8500	10.2454	0.8342
10.3428	0.7900	10.7579	0.8700	10.4427	0.8200
10.5089	0.8400	10.9208	0.8783	10.6334	0.8550
10.6750	0.8783	11.0836	0.8767	10.7979	0.8783
10.8410	0.8317	11.2465	0.8750	10.9623	0.8542

Appendix XVb. P breakthrough data for Osborne soil amended at high rate of cattle manure.

Rep1		**Rep2**		**Mean**	
Pore Volume	**C/Co**	**Pore Volume**	**C/Co**	**Pore Volume**	**C/Co**
0.2197	0.0235	0.2080	0.0232	0.2139	0.0234
0.4944	0.0261	0.4681	0.0250	0.4812	0.0256
0.7548	0.0283	0.7147	0.0280	0.7347	0.0281
1.0630	0.0291	1.0067	0.0280	1.0348	0.0286
1.3198	0.0305	1.2500	0.0299	1.2849	0.0302
1.5767	0.0297	1.4933	0.0300	1.5350	0.0298
1.8352	0.0303	1.7400	0.0302	1.7876	0.0303
2.0956	0.0308	1.9913	0.0306	2.0435	0.0307
2.3487	0.0314	2.2296	0.0312	2.2891	0.0313
2.6018	0.0319	2.4678	0.0317	2.5348	0.0318
2.8549	0.0308	2.7203	0.0309	2.7876	0.0308
3.1080	0.0309	2.9727	0.0319	3.0404	0.0314
3.3612	0.0321	3.2252	0.0322	3.2932	0.0321
3.6205	0.0345	3.4855	0.0339	3.5530	0.0342
3.8798	0.0351	3.7459	0.0343	3.8129	0.0347
4.1392	0.0508	4.0062	0.0500	4.0727	0.0504
4.1223	0.0690	4.0034	0.0685	4.0629	0.0688
4.6623	0.1053	4.5295	0.1067	4.5959	0.1060
4.9294	0.1433	4.7977	0.1443	4.8636	0.1438
5.1966	0.1927	5.0660	0.1900	5.1313	0.1913
5.4637	0.2527	5.3342	0.2453	5.3989	0.2490
5.7309	0.2973	5.6024	0.3000	5.6666	0.2987
5.9980	0.3287	5.8707	0.3333	5.9343	0.3310
6.2652	0.3793	6.1389	0.3633	6.2020	0.3713
6.5323	0.4473	6.4072	0.4133	6.4697	0.4303
6.7995	0.5317	6.6754	0.5283	6.7374	0.5300
7.0334	0.5800	6.9027	0.5633	6.9681	0.5717
7.2590	0.5917	7.1199	0.5767	7.1894	0.5842
7.4847	0.6217	7.3370	0.6133	7.4108	0.6175
7.7103	0.6717	7.5541	0.6533	7.6322	0.6625
7.9360	0.7300	7.7712	0.6867	7.8536	0.7083
8.1538	0.7100	7.9883	0.7133	8.0711	0.7117
8.3716	0.7600	8.2054	0.7467	8.2885	0.7533
8.5895	0.7683	8.4226	0.7667	8.5060	0.7675
8.8073	0.8033	8.6397	0.7917	8.7235	0.7975
9.0592	0.8100	8.8931	0.8117	8.9762	0.8108
9.3339	0.8283	9.1709	0.8200	9.2524	0.8242
9.6085	0.8517	9.4486	0.8467	9.5285	0.8492
9.8832	0.8450	9.7263	0.8517	9.8047	0.8483
10.1578	0.8300	10.0040	0.8583	10.0809	0.8442
10.4487	0.8633	10.2918	0.8667	10.3702	0.8650
10.7420	0.9317	10.5821	0.8983	10.6621	0.9150
11.0354	1.0000	10.8724	0.9867	10.9539	0.9933
11.3288	1.0080	11.1628	1.0000	11.2458	1.0040
11.6221	0.9947	11.4531	1.0133	11.5376	1.0040
11.9155	1.0213	11.7434	0.9840	11.8295	1.0027
12.2089	1.0107	12.0338	1.0000	12.1213	1.0053
12.5022	1.0133	12.3241	1.0107	12.4132	1.0120
12.7956	0.9707	12.6144	1.0160	12.7050	0.9933
13.0889	1.0080	12.9048	1.0053	12.9969	1.0067
13.3823	1.0373	13.1951	1.0133	13.2887	1.0253
13.6757	1.0160	13.4854	1.0187	13.5805	1.0173
13.9690	0.9973	13.7758	1.0240	13.8724	1.0107
14.2624	1.0267	14.0661	1.0107	14.1642	1.0187
14.5558	1.0107	14.3564	1.0213	14.4561	1.0160

Appendix XVIa. P breakthrough data for Osborne soil amended at low rate of hog manure.

Rep1		**Rep2**		**Mean**	
Pore Volume	**C/Co**	**Pore Volume**	**C/Co**	**Pore Volume**	**C/Co**
3.9767	0.0030	3.8784	0.0034	3.9275	0.0032
4.2933	0.0032	4.1853	0.0032	4.2393	0.0032
4.6360	0.0032	4.5184	0.0032	4.5772	0.0032
4.9848	0.0028	4.8547	0.0034	4.9197	0.0031
5.3335	0.0034	5.1909	0.0033	5.2622	0.0034
5.6823	0.0077	5.5301	0.0067	5.6062	0.0072
6.1008	0.0430	5.9378	0.0433	6.0193	0.0432
6.4496	0.1107	6.2777	0.1133	6.3636	0.1120
6.7984	0.2007	6.6175	0.2133	6.7079	0.2070
7.1121	0.3587	6.9233	0.3600	7.0177	0.3593
7.4258	0.4760	7.2292	0.4653	7.3275	0.4707
7.7395	0.4883	7.5350	0.5017	7.6373	0.4950
8.0533	0.5533	7.8408	0.5583	7.9471	0.5558
8.3670	0.6283	8.1467	0.6333	8.2568	0.6308
8.6807	0.6417	8.4525	0.6300	8.5666	0.6358
8.9944	0.7017	8.7584	0.6583	8.8764	0.6800
9.3081	0.7150	9.0642	0.6850	9.1862	0.7000
9.6215	0.7600	9.3655	0.7133	9.4935	0.7367
9.9348	0.7750	9.6667	0.7367	9.8008	0.7558
10.2482	0.8567	9.9679	0.8300	10.1081	0.8433
10.5616	0.8733	10.2692	0.8617	10.4154	0.8675
10.8749	0.8933	10.5704	0.8800	10.7227	0.8867
11.1535	0.8700	10.8396	0.8850	10.9965	0.8775
11.4088	0.8717	11.0874	0.8833	11.2481	0.8775
11.6640	0.8850	11.3352	0.8967	11.4996	0.8908
11.9193	0.9200	11.5829	0.9100	11.7511	0.9150
12.1579	0.8817	11.8166	0.9050	11.9872	0.8933
12.3923	0.9000	12.0467	0.8967	12.2195	0.8983
12.6267	0.8400	12.2767	0.9100	12.4517	0.8750
12.8611	0.9573	12.5068	0.9120	12.6840	0.9347
13.0955	0.8800	12.7369	0.9227	12.9162	0.9013
13.3381	0.9413	12.9727	0.9307	13.1554	0.9360
13.6451	0.8880	13.2736	0.9387	13.4593	0.9133
13.9521	0.9120	13.5744	0.9413	13.7633	0.9267
14.2591	0.9280	13.8753	0.9280	14.0672	0.9280
14.6677	0.9520	14.2690	0.9520	14.4683	0.9520
15.0763	0.9653	14.6626	0.9627	14.8695	0.9640
15.4850	0.9600	15.0562	0.9787	15.2706	0.9693

Appendix XVIb. P breakthrough data for Osborne soil amended at low high low rate of hog manure.

Rep1		**Rep2**		**Mean**	
Pore Volume	**C/Co**	**Pore Volume**	**C/Co**	**Pore Volume**	**C/Co**
0.2358	0.0273	0.2402	0.0274	0.2380	0.0274
0.6695	0.0329	0.6889	0.0339	0.6792	0.0334
1.1722	0.0356	1.1840	0.0353	1.1781	0.0354
1.6868	0.0360	1.6809	0.0362	1.6838	0.0361
2.2014	0.0368	2.1777	0.0372	2.1896	0.0370
2.7604	0.0370	2.6995	0.0374	2.7300	0.0372
3.3639	0.0500	3.2590	0.0497	3.3114	0.0498
3.8706	0.1090	3.7423	0.1133	3.8064	0.1112
4.1239	0.1530	3.9839	0.1493	4.0539	0.1512
4.1414	0.2057	3.9853	0.2067	4.0634	0.2062
4.6306	0.2567	4.4672	0.2707	4.5489	0.2637
4.8840	0.2993	4.7088	0.3020	4.7964	0.3007
5.1314	0.3487	4.9477	0.3440	5.0396	0.3463
5.3701	0.3720	5.1826	0.3753	5.2763	0.3737
5.6087	0.4480	5.4174	0.4473	5.5131	0.4477
5.8474	0.5500	5.6523	0.5667	5.7498	0.5583
6.0969	0.5700	5.8982	0.5633	5.9975	0.5667
6.3627	0.5850	6.1607	0.5933	6.2617	0.5892
6.6285	0.6883	6.4232	0.6817	6.5259	0.6850
6.8942	0.6983	6.6858	0.7083	6.7900	0.7033
7.1600	0.7217	6.9483	0.7267	7.0542	0.7242
7.4258	0.7783	7.2108	0.7833	7.3183	0.7808
7.6916	0.7967	7.4733	0.8017	7.5825	0.7992
7.9574	0.8250	7.7358	0.8167	7.8466	0.8208
8.2108	0.8367	7.9820	0.8500	8.0964	0.8433
8.4641	0.8233	8.2281	0.8600	8.3461	0.8417
8.7185	0.8183	8.4759	0.8517	8.5972	0.8350
8.9773	0.8683	8.7299	0.8717	8.8536	0.8700
9.2360	0.8517	8.9840	0.8700	9.1100	0.8608
9.4947	0.9383	9.2380	0.9100	9.3664	0.9242
9.7534	0.8833	9.4921	0.9183	9.6228	0.9008
10.0151	0.9800	9.7506	0.9383	9.8829	0.9592
10.2812	0.9417	10.0160	0.9467	10.1486	0.9442
10.5472	0.9973	10.2813	1.0027	10.4143	1.0000
10.8314	1.0133	10.5642	1.0133	10.6978	1.0133
11.3998	1.0507	11.1298	1.0747	11.2648	1.0627
11.9188	1.0720	11.6486	1.0907	11.7837	1.0813
12.4221	1.0613	12.1555	1.0613	12.2888	1.0613
12.9542	1.0427	12.6772	1.0960	12.8157	1.0693
13.5175	1.1067	13.2135	1.1013	13.3655	1.1040
13.7991	1.0293	13.4817	1.0933	13.6404	1.0613

Appendix XVIIa. P breakthrough data for Osborne soil amended at low rate of MAP fertilizer.

Rep1		**Rep2**		**Mean**	
Pore Volume	**C/Co**	**Pore Volume**	**C/Co**	**Pore Volume**	**C/Co**
3.1629	0.0051	3.1086	0.0045	3.1357	0.0048
3.4171	0.0052	3.3585	0.0049	3.3878	0.0051
3.6680	0.0063	3.6049	0.0050	3.6365	0.0057
3.9188	0.0112	3.8514	0.0113	3.8851	0.0113
4.1697	0.0191	4.0979	0.0190	4.1338	0.0191
4.1999	0.0319	4.1274	0.0321	4.1636	0.0320
4.7215	0.0473	4.6402	0.0493	4.6808	0.0483
4.9724	0.0580	4.8867	0.0583	4.9295	0.0582
5.2232	0.1010	5.1332	0.1017	5.1782	0.1013
5.4740	0.1453	5.3789	0.1537	5.4264	0.1495
5.7306	0.1773	5.6282	0.1793	5.6794	0.1783
5.9871	0.2133	5.8775	0.2180	5.9323	0.2157
6.2408	0.2753	6.1245	0.2800	6.1827	0.2777
6.4945	0.3447	6.3716	0.3460	6.4330	0.3453
6.7482	0.4000	6.6187	0.4167	6.6834	0.4083
7.0019	0.5500	6.8657	0.5167	6.9338	0.5333
7.2556	0.5833	7.1128	0.5783	7.1842	0.5808
7.5093	0.5900	7.3598	0.6017	7.4345	0.5958
7.7630	0.5883	7.6069	0.6633	7.6849	0.6258
8.0166	0.6983	7.8553	0.6850	7.9360	0.6917
8.2703	0.7067	8.1046	0.6967	8.1875	0.7017
8.5383	0.7500	8.3653	0.7550	8.4518	0.7525
9.0742	0.8250	8.8866	0.8183	8.9804	0.8217
9.6101	0.8833	9.4079	0.9033	9.5090	0.8933
10.1459	0.8683	9.9292	0.8933	10.0376	0.8808
10.6579	0.9133	10.4335	0.9017	10.5457	0.9075
11.1596	0.8950	10.9208	0.9083	11.0402	0.9017
11.6613	0.8933	11.4081	0.9050	11.5347	0.8992
12.1629	0.9600	11.8954	0.9267	12.0292	0.9433
12.6703	0.9383	12.3884	0.9350	12.5293	0.9367
13.1948	0.9283	12.8983	0.9300	13.0466	0.9292
13.7193	0.9617	13.4083	0.9517	13.5638	0.9567
14.2438	0.9633	13.9183	0.9583	14.0810	0.9608

Appendix XVIIb. P breakthrough data for Osborne soil amended at high rate of MAP fertilizer.

Rep1		**Rep2**		**Mean**	
Pore Volume	**C/Co**	**Pore Volume**	**C/Co**	**Pore Volume**	**C/Co**
0.2719	0.0207	0.2705	0.0194	0.2712	0.0200
0.8015	0.0277	0.7972	0.0272	0.7993	0.0274
1.3167	0.0319	1.3096	0.0323	1.3132	0.0321
1.8525	0.0374	1.8426	0.0383	1.8476	0.0379
2.3907	0.0407	2.3779	0.0411	2.3843	0.0409
2.9288	0.0460	2.9131	0.0467	2.9209	0.0464
3.4343	0.0503	3.4159	0.0500	3.4251	0.0502
3.9209	0.0550	3.8999	0.0545	3.9104	0.0548
4.1356	0.0710	4.1134	0.0708	4.1245	0.0709
4.8941	0.1040	4.8679	0.1042	4.8810	0.1041
5.1374	0.1360	5.1099	0.1343	5.1236	0.1352
5.3807	0.1587	5.3519	0.1607	5.3663	0.1597
5.6326	0.2333	5.6024	0.2320	5.6175	0.2327
5.8845	0.2827	5.8530	0.2833	5.8687	0.2830
6.1335	0.3367	6.1007	0.3380	6.1171	0.3373
6.3825	0.4153	6.3484	0.4167	6.3654	0.4160
6.6316	0.4967	6.5961	0.5000	6.6138	0.4983
6.8806	0.5667	6.8438	0.5567	6.8622	0.5617
7.1296	0.5817	7.0914	0.5800	7.1105	0.5808
7.3786	0.6683	7.3391	0.6650	7.3589	0.6667
7.6277	0.6767	7.5868	0.6783	7.6072	0.6775
7.8767	0.6483	7.8345	0.6433	7.8556	0.6458
8.1257	0.6850	8.0822	0.6783	8.1040	0.6817
8.3885	0.6867	8.3436	0.6650	8.3660	0.6758
8.6547	0.7267	8.6084	0.7433	8.6315	0.7350
8.9209	0.7317	8.8731	0.7133	8.8970	0.7225
9.1785	0.7650	9.1294	0.7817	9.1539	0.7733
9.4361	0.7750	9.3856	0.7733	9.4109	0.7742
9.6937	0.8373	9.6418	0.8427	9.6678	0.8400
9.9513	0.9067	9.8981	0.9013	9.9247	0.9040
10.2090	0.9467	10.1543	0.9493	10.1816	0.9480
10.4666	0.9307	10.4105	0.9067	10.4386	0.9187
10.9675	0.9360	10.9088	0.8880	10.9381	0.9120
11.4770	0.9627	11.4156	0.9413	11.4463	0.9520
11.9922	0.9600	11.9280	0.9440	11.9601	0.9520
12.5232	0.9893	12.4576	1.0027	12.4904	0.9960
13.0642	0.9973	12.9985	0.9947	13.0313	0.9960
13.6052	0.9947	13.5395	0.9973	13.5723	0.9960
13.8757	1.0000	13.8099	1.0027	13.8428	1.0013