Dynamics of biosolids-derived phosphorus in a Mollisol

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Dynamics of biosolids-derived phosphorus in a Mollisol

By

Yaobing Sui

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Soil Science (Soil Morphology and Genesis)

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has met the dissertation requirements of Iowa State University

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GENERAL INTRODUCTION

Biosolids (treated municipal sewage sludge) contains significant amount of organic matter as well as inorganic macro- and micronutrients necessary for healthy plant growth. Land application of biosolids has been shown to be an agronomically and environmentally acceptable means of biosolids disposal. The standards for the land application of biosolids dictate, among other things, that the amount of biosolids cannot be applied at a rate that exceeds the agronomic rate based on N. The agronomic rate of N means the amount of plant-available N needed for the crop or vegetation growth on an annual basis. Thus, in the absence of other limiting constituents in a biosolids, careful consideration must be given to calculating the agronomic rate so that the possibility of NO$_3^-$-N leaching to ground water is minimized.

The amount of P applied in biosolids, however, is generally much higher than crop needs when the biosolids is applied at a N-based agronomic rate. The mobility of P usually is very small in soils, so most of the P applied in biosolids is likely to remain in or near the surface horizon of the soil. Thus, the elevated soil P levels that result from biosolids application in the surface horizon may increase the potential for P losses to surface water bodies by runoff and erosion. Excessive P level in a water body could contaminate the water body by causing eutrophication.

The fate of biosolids-derived P in soils is determined by the characteristics of soil and biosolids, such as P adsorption and desorption capacities of soil, physical properties of soil, and P content and forms in the biosolids. Because of the variety of biosolids and environmental conditions, site-specific studies are needed to evaluate the dynamics of P.
added in biosolids. Therefore, the overall goal of this study is to investigate the fate of biosolids-derived P in a Mollisol. Specific objectives are to: (1) document the redistribution of biosolids-derived P in a Mollisol, (2) examine the influence of land application of biosolids on P in soil solutions collected by zero-tension lysimeters and in groundwater, (3) to assess the effects of land application of biosolids on P fractions in the Mollisols, and (4) to evaluate the P sorption, desorption, and buffering capacities in the biosolids-amended Mollisols.

Dissertation Organization

In addition to the Literature Review, this dissertation includes four papers. Each paper addresses the results obtained under one of the four objectives mentioned in last paragraph. The major findings and possible environmental implications are summarized in the Summary section. All references are listed at the end of this dissertation.
LITERATURE REVIEW

Biosolids: Characterization and Land Application

*Biosolids* is the portion of the wastewater solids stream which meets federal and state regulations for beneficial use by land application or other methods (Water Environment Federation, 1998).

Characterization

Inorganic nutrients

Biosolids contains both macronutrient elements such as N, P, K, Ca, Mg, and S, and micronutrient elements such as Fe, Zn, Cu, Mn, B, Mo, Na, V, and Cl. The content of each element in biosolids varies with the sources and treatment methods of biosolids. N in biosolids exists as organic and inorganic compounds. Heavy application of N-containing biosolids may result in the losses of N into surface or underground water in the form of NO$_3^-$-N or NH$_4^+$-N, which has adverse effects on environment. Thus, N is usually the limiting factor in land application of biosolids.

The amount of P in biosolids depends on P concentration in the influent and type of P removal used by wastewater treatment plants. The following reactions are usually applied to convert phosphorus from wastewater into the forms found in biosolids (Girovich, 1996).

1. $\text{Al}_2(\text{SO}_4)_3 \cdot 14.3\text{H}_2\text{O} + 2 \text{PO}_4^{3-} = 2 \text{AlPO}_4 + 3 \text{SO}_4^{2-} + 14.3 \text{H}_2\text{O}$

   $\text{FeCl}_3 + \text{PO}_4^{3-} = \text{FePO}_4 + 3\text{Cl}^-$

2. $\text{Ca}($HCO$_3$)$_2 + \text{Ca}($OH$)_2 = 2 \text{CaCO}_3 + 2 \text{H}_2\text{O}$

   $5 \text{Ca}^{2+} + 4\text{H}^+ + 3\text{HPO}_4^{2-} = \text{Ca}_5($OH$)(\text{PO}_4)_3 + 3\text{H}_2\text{O}$
K, Ca, Mg, S, and micronutrients in biosolids may serve to satisfy the needs of plant growth. But when the concentrations of the micronutrients are elevated by the heavy application of biosolids, some of them such as Cu, Zn, and Cl, can be hazardous to environment.

Organic matter

A large amount of organic matter is added to soils through the land application of biosolids. Organic matter can provide nutrients such as N and P needed for plant growth by mineralization. Organic matter itself is a nutrient source for microbial growth, too. On the other hand, applying organic matter in the forms of biosolids can have a profound impact on soil physical properties such as bulk density, porosity, pore size distribution, aggregation, water retention capacities, and water transmission properties. The detailed effects of biosolids application on soil physical properties can be found in the comprehensive review by Metzger and Yaron (1987).

Chemical pollutants

Inorganic pollutants in biosolids include heavy or trace metals, such as As, Cd, Cr, Cu, Pb, Hg, Mo, Ni, Se, Co, and Zn. The concentrations of heavy metals usually are higher in biosolids than in natural soils. According to Chaney (1994), however, most of the heavy or trace metals in biosolids cannot cause adverse effects on human, livestock or wildlife because of the high sorption capacities of heavy or trace metals by soils, which limits their levels in plants used as food or feed. Numerous man-made organic chemicals with a wide range of chemical properties can occur in biosolids. The principal group of these toxic organic compounds is the chlorobenzenes (CBs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) (Beck et al., 1995). The majority of biosolids-borne organic
chemicals occurs at low concentrations that are reduced at least 100-fold in typical (agricultural) land application scenarios, therefore concerns about the environmental fate of organic chemicals in routine land application of biosolids should be minor (O'Connor, 1994).

**Microorganisms**

Biosolids usually contain diverse life forms. Microorganisms in biosolids can be categorized into bacteria, viruses, helminthes (parasitic worms), protozoa, and fungi. One of the major objectives of sludge treatment is pathogen elimination or reduction to acceptable levels. The U.S. Environmental Protection Agency (1993) specifies treatment technologies that are assumed to be sufficient to reduce pathogens in biosolids to levels which will protect public health and animals. Forste (1996) concluded that the land application of biosolids from a generally healthy population collected in sanitary sewage systems does not represent a significant public health risk.

**Land application**

*Land application* is the placement of biosolids in or on the soil in a manner that utilizes their fertilizing and soil conditioning properties (Girovich, 1996). It includes applications on agricultural land, non-agricultural land, and site reclamation. Prior to land application, biosolids should satisfy the following general requirements relating to human health and environmental protection: (1) pathogen reduction, (2) vector attraction reduction, (3) pollutant limits, and (4) application rates and other specific requirements (such as monitoring, record keeping, public access, etc.). If the biosolids quality meets (1), (2), and (3) mentioned above, then the biosolids application rates can not exceed the N-based agronomic rates.
N-based agronomic rates

The Part 503 regulations (U.S. Environmental Protection Agency, 1993) dictate that biosolids cannot be applied at a rate that exceeds the agronomic rate. The agronomic rate provides the amount of N needed by the crop or vegetation grown on the land and minimizes the amount of N in the biosolids that leaches below the root zone of the crop or vegetation to the ground water. The goal in N management with biosolids application is to calculate the amount of N in the biosolids that will be available to the subsequent crop (potentially available N or PAN). PAN is generally calculated assuming 100% availability of NO$_3^-$ and NH$_4^+$-N if the biosolids are injected or incorporated into the soil. For surface application, a 50 percent availability is generally calculated for NH$_4$-N to allow for volatilization losses. The difficulty is to predict the available N that will be mineralized, which is often called potentially mineralizable N (PMN). Values commonly used for first-year mineralization are: 40% for biosolids from a waste-activated or primary process, 30% for lime-stabilized, or aerobically digested, 20% for anaerobically digested, and 10% for composted biosolids. Using this information, the concentration of PAN can be estimated as follows:

\[
\text{PAN} = \text{N-NO}_3^- + \text{X-NH}_4^+ + \text{YNorg},
\]

where \( X \) is the fraction of NH$_4$-N that does not volatilize, and \( Y \) is fraction of organic-N that is expected to mineralize based on the representative values shown above.

Soil Phosphorus: Reactions, Forms, Soil Development, and Environment Pollution

P is the eleventh most abundant element in the earth’s crust. It has been stated in some literature (Smeck, 1973; Walker and Syers, 1976) that parent materials are almost the only
source of P in natural soils. Consequently, the weathering of the parent materials containing P plays an important role in controlling quantity and forms of P in natural soils. On the other hand, uptake of P by organisms converts P from inorganic form to organic forms, which initiates the biological cycling of P. Thus, geochemical, biological, and physical processes contribute to the quantity, forms, and distribution of P in natural soils. The characteristics of P in natural soils can change after the addition of P in chemical fertilizers, manure, biosolids, and others.

**Chemical reactions controlling P in soils**

**Dissolution and precipitation**

The first step of P cycling in natural soils is the dissolution of apatite, whose chemical formula is usually expressed as $\text{Ca}_{10}\text{X}_2(\text{PO}_4)_6 (\text{X} = \text{OH}^- \text{ or } \text{F})$. $\text{H}^+$ is required for apatite dissolution, and soil pH must drop below about 7.5 before significant quantities of P are dissolved (Smeck, 1973). The species of dissolved P in soils are controlled by pH. Based on the dissociation reactions (Christian, 1994):

$$
\begin{align*}
\text{H}_3\text{PO}_4 & \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}^+ & \text{pK}_a = 1.96 \\
\text{H}_2\text{PO}_4^- & \rightleftharpoons \text{HPO}_4^{2-} + \text{H}^+ & \text{pK}_a = 7.12 \\
\text{HPO}_4^{2-} & \rightleftharpoons \text{PO}_4^{3-} + \text{H} & \text{pK}_a = 12.32,
\end{align*}
$$

$\text{HPO}_4^{2-}$ and $\text{H}_2\text{PO}_4^-$ usually are the two dominant species in soil solution. The dissolved P can re-precipitate to form various Ca-, Fe-, and Al-P compounds. P precipitation can also occur after the addition of P fertilizers, and most of the P compounds formed by the reaction of P fertilizers and soil have been summarized by Sample et al. (1980).

Ion activity products, which are controlled by the species of P, divalent, and trivalent cations, and their activities in soil solutions, determine what types of P compounds will
precipitate in soils. A unified solubility diagram reflecting the solubility of various Fe, Al, and Ca phosphate minerals can be found in Lindsay (1989).

**Sorption and desorption of P**

_Sorption of P_. Sorption of P by soils is a process which removes P from soil solution. Because it is hard to distinguish the sorption and precipitation reactions that occur on soil or clay mineral surfaces, the amount of P retained by soils may include both sorbed P and precipitated P. P may be adsorbed near positively charged soil particles by anion exchange, but it is primarily absorbed on variable-charge mineral surfaces and at layer silicate particle edges by ligand exchange reactions, in which phosphate ions replace $\text{H}_2\text{O}$ or $\text{OH}^-$ or other anions associated with metal ions. Sorption of P on soil mineral and organic compounds initially proceeds by a rapid reaction, which is followed by slow reactions such as diffusion (Barrow, 1985). Barrow (1985) shows that this slow reaction is endothermic. The slow reaction may also result from the lower accessibility of surface sorption sites located within aggregates of poorly crystallized oxides such as ferrihydrite (Frossard et al., 1995).

_Factors affecting P sorption_. Sorption of P on soil components is influenced by many factors. The adsorption of P on oxides is determined by the positive charge on the oxide surface. Therefore, pH can affect adsorption of P by oxides through its effects on surface charge of oxides. P adsorption by oxides decreases with increasing pH, due to a decrease in the positive charge. pH can also influence P sorption by soils through its effects on the solubility of various phosphate compounds. Organic anions can compete with orthophosphate for sorption sites (Bingham et al., 1964; Nagarajah et al., 1970; Bowden, et al., 1980; Yuan 1980; Lopez-Hernandez et al., 1986; Sibanda and Young, 1986; Hue, 1991; Kafkafi, et al., 1988; Violante et al., 1991; Violante and Gianfreda; 1993; Geelhoed et al.,
so their presence may decrease P sorption by soils. The effect is greater when the organic compound is added before the P addition (Hue, 1991). Organic compounds can chelate metals and prevent the reaction between metals and phosphates (Earl et al., 1979), therefore decreasing P sorption by soils. However, an increase in P sorption because of addition of organic matter has also been observed (Huang and Violante, 1986; Traina et al., 1986a; Borggaard et al., 1990). Huang and Violante (1986) and Borggaard et al. (1990) found that the addition of organic compounds inhibited aluminum oxide crystallization and increased its surface area, therefore increasing P sorption. Traina et al. (1986a) identified that citrate, tartrate or formate can extract metallic ions from mineral surfaces, creating new P sorption sites. Complexes of humic compounds with Al and Fe could sorb P, too (Levesque, 1969; Borie and Zunino, 1983). The specific surface areas of soil components (Borrero et al., 1988; Holford and Mattingly, 1975b), temperature, and reaction time (Barrow, 1983) also influence the sorption of P. For the whole soils, however, there is much evidence that Al and Fe oxides are the most important components determining the P sorption capacity (Ellis and Truog, 1954; Holford and Mattingly, 1975a; Parfitt, 1978; Ryan et al., 1984; Van der Zee and Van Riemsdijk, 1991; Hamad et al., 1992). Solis and Torrent (1989) observed that the long-term sorption of P in calcareous soils is governed by calcium carbonate.

Sorption equations. Sorption isotherm techniques have been widely used for studying the sorption of P in soils. The data obtained from sorption isotherms may be properly quantified by using adsorption equations such as the standard Langmuir equation, Freundlich equation, two-surface Langmuir equation, and others.

The standard Langmuir equation has the form:

\[ Q = \frac{bKc}{1+kC}, \]
where $Q$ (mg kg$^{-1}$ or mmol kg$^{-1}$) and $C$ (mg L$^{-1}$ or mmol L$^{-1}$) represent the P sorbed by soil and P concentration in the equilibrium solution respectively; parameters $b$ (mg kg$^{-1}$ or mmol kg$^{-1}$) and $k$ (L mg$^{-1}$ or L mmol$^{-1}$) represent the sorption maximum and a constant related to energy of adsorption, respectively. The above equation can be rewritten as:

$$\frac{C}{Q} = \frac{1}{bk} + \frac{1}{b}C.$$

Then a straight line should be obtained by plotting $C/Q$ versus $C$, if the sorption isotherm data fit the standard Langmuir equation. However a curvilinear line is usually obtained unless low equilibrium concentration levels of P are used. Thus, the use of the Langmuir equation in describing P sorption has been questioned (Bowden et al., 1977; Harter and Baker, 1977; Harter and Smith, 1981; Harter, 1984).

The Freundlich equation is expressed as:

$$Q = kC^n,$$

where $Q$ (mg kg$^{-1}$ or mmol kg$^{-1}$) is the amount of P sorbed by soil, $C$ (mg L$^{-1}$ or mmol L$^{-1}$) is the equilibrium P concentration in solution, $k$ and $n$ are adjustable parameters, with $n$ constrained to lie between 0 and 1. The equation can be rearranged as following:

$$\log (Q) = \log (k) + n \log (C).$$

By plotting $\log (Q)$ versus $\log (C)$, a straight line should be obtained if the sorption isotherm data fit the Freundlich equation. The Freundlich equation often fits P sorption isotherm data better than does the Langmuir equation (Barrow, 1978; Ratkowsky, 1986), but it can not predict the sorption maximum of P.

Because the standard Langmuir equation might inaccurately describe P adsorption by soil when surfaces had more than one type of elementary space or different adsorption
energies, and the Freundlich equation cannot predict sorption maxima, even though P sorption isotherm data fit this equation well.

A "two surface" Langmuir equation (Syers et al., 1973; Holford and Mattingly, 1975a) had been used for P adsorption study. The complete derivation of the two-surface Langmuir equation can be found in Sposito (1982).

The two surface Langmuir equation is described as:

\[ Q = b_1 k_1 C / (1 + k_1 C) + b_2 k_2 C / (1 + k_2 C) \]

where \( Q \) (mg kg\(^{-1}\) or mmol kg\(^{-1}\)) and \( C \) (mg L\(^{-1}\) or mmol L\(^{-1}\)) are the amount of P sorbed and the equilibrium P concentration, respectively; \( b_1 \) (mg kg\(^{-1}\) or mmol kg\(^{-1}\)) and \( b_2 \) (mg kg\(^{-1}\) or mmol kg\(^{-1}\)) are the high- and low-affinity maxima of P sorption respectively; \( k_1 \) (L mg\(^{-1}\) or L mmol\(^{-1}\)) and \( k_2 \) (L mg\(^{-1}\) or L mmol\(^{-1}\)) are the high- and low-affinity bonding energies of sorption of P, respectively. Two straight lines can be obtained from a plot of \( Q/C \) versus \( Q \) if a sorption isotherm fits the equation well, and the parameters in the equation can be calculated based on the slopes and x-axis intercepts of the two lines (Sposito, 1982).

*Desorption of P.* P desorption is the transfer of P from solid phase to the liquid phase. Frossard et al. (1995) summarized the approaches which are currently used to estimate the quantity of P desorption from soils. They are: (1) directly desorbing P from soils with free or dilute electrolyte or using a chemical extractant, (2) introducing a P sink such as an anionic resin or iron-oxide-coated filter paper into a soil suspension so that more P can be desorbed, and (3) using isotopic exchange of \(^{32}\)P to assess the amount of P able to be desorbed.

Barrow (1979, 1983) showed that P desorption from soils was influenced by incubation, desorption time, and liquid/solids ratio. The amount of P desorbed increases with increasing desorption time and liquid/solid ratio but decreases with increasing incubation.
Various kinetic models expressing the effects of desorption time and liquid/solids ratio on P desorption from soils have been developed (Barrow, 1979, 1983; Sharpley et al., 1981; Pavlatou and Polyzopoulos, 1988). The empirical model developed by Sharpley et al. (1981) to describe the desorption of soil P at different water/soil ratios during a short period of time is:

\[ P_d = KP_o^{\alpha}W^\beta \]

where \( P_d \) (mg kg\(^{-1}\)) is the amount of P desorbed in time \( t \) (hr), at a water/soil ratio, \( W \), with \( P_o \) (mg kg\(^{-1}\)) being the initial amount of desorbable P present in the soil, and \( K, \alpha, \) and \( \beta \) being constants for a given soil. The desorption of P from soils is also influenced by organic compounds (Fox et al., 1990; Fox and Comerford, 1992) and by reducing conditions (Ponnamperuma, 1972; Sah et al., 1989).

**Forms and fractionation of P in soils**

Definitions of the forms of P in soils have largely come from chemical fractionation schemes, which are intended to extract discrete groups of P components using selective chemical reagents. The fractionation procedure developed by Chang and Jackson (1957) has been widely used for investigating the forms of native inorganic P. Their fractionation scheme is as follows: (1) Al-P is extracted with 0.1 N NH\(_4\)F, (2) Fe-P is extracted with 0.1 N NaOH, (3) Ca-P is extracted with 0.5 N H\(_2\)SO\(_4\), (4) occluded Fe-P is extracted with dithionate-citrate, (5) occluded Al-P is extracted with 0.5 N NH\(_4\)F after dithionate-citrate extraction. Limitations of chemical fractionation schemes for characterizing inorganic P in soils has been discussed by Stevenson (1986). Partly because organic P was not separated in the procedure of Chang and Jackson, a fractionation procedure has been developed by Hedley et al. (1982) in an attempt to separate inorganic and organic forms of P. This
Sequential fractionation scheme is as follows: (1) resin Pi, inorganic P extracted with water and removed with an anion exchange resin; (2) bicarbonate-Pi and -Po, inorganic and organic P extracted with 0.5 M NaHCO₃; (3) NaOH-Pi and -Po, inorganic and organic P extracted with 0.1 M NaOH, including Fe- and Al-P and the P adsorbed on the sesquioxides; (4) sonic NaOH Pi and Po, inorganic and organic P extracted with NaOH following ultrasonification, including the P held on internal surfaces of soil aggregates; (5) HCl Pi, inorganic P extracted with 1 M HCl, including the forms of Ca-P and the P occluded with sesquioxides; and (6) residual P, digested with H₂SO₄ and H₂O₂, including occluded inorganic and organic P.

P and soil development

Transformation of P

Transformation of P following soil weathering has ultimately converted primary P minerals to occluded P. The complete transformation from primary to occluded P may require hundreds to thousands of years (Smeck, 1985). Soluble P taken up by plants and utilized by microorganisms produces organic P. Thus, the end-point of P transformations in soil is occluded P and stable organic P. A relationship between taxonomic classification of soils and the distribution of soil P among the various forms has been reported (Tiessen et al., 1984; Smeck, 1985; Cross and Schlesinger, 1995). Smeck (1985) observed that total P as well as primary, secondary, and organic P all decreased as the degree of weathering increased. Tiessen et al. (1984) fractionated P in 168 benchmark soils representing eight orders and concluded that P forms are related to the orders of Soil Taxonomy (Soil Survey Staff, 1998). Cross and Schlesinger (1995) reviewed 17 studies using the P sequential fractionation scheme developed by Hedley et al. (1982), including 88 samples of natural soils belonging to nine soil orders from the United States, Spain, Canada, and several locations in
South America. They found: (1) total P decreased with increasing the degree of soil development; (2) the NaOH- and sonicated-NaOH-P was most prominent in acidic, highly weathered soils, and HCl-P was dominant in the less weathered soils; (3) the residual P consistently made up about 40% of the total P across all the orders; (4) the percentage of total organic P (biological P) in total P increased from 5% in Entisols to 35% in Oxisols; and (5) the percentage of total inorganic P (geochemical P) in total P decreased along the weathering gradient, from about 95% in the Entisols to 65% in the Oxisols.

**Distribution of P**

Distributions of P in soils, including two-dimensional (soil profile) and three-dimensional (landscape) distribution, are closely related to soil genetic processes. Two-dimensional distribution of P in soils shows an eluvial-illuvial distribution pattern with depth in the soil profile. Both total and available P are higher near the surface, decrease to minimum quantities in lower A or upper B horizon, attain maximum quantities in lower B or upper C horizons, and then decrease to levels characteristic of the parent material. The relative magnitude of P redistribution within the profile is a function of the degree of profile development and parent material. In addition, it has been observed that vegetation had an effect on the distribution of P in soil (Fenton et al., 1967; Frossard et al., 1989). After studying 24 loess- and 13 till-derived soil profiles comprising 12 different biosequences, Fenton et al. (1967) reported that the zone of minimum total P content occurred at relatively greater depths in prairie-influenced soils, at intermediate depths for transitional soils, and at relatively shallow depths in forest-influenced soils. Walker and Syers (1976) stated that the landscape may influence the distribution of P in soil because of variations in aspect, slope, or height of water table. Smeck (1985) carried out a study on P distribution in four
toposequences in Illinois and Iowa. In each toposequence, the parent material and vegetation were within the same macroclimate, and the only difference among members was topographic position. The results showed that in each toposequence, total P content was the highest in soils on the low end of the hydrological gradient, and organic P contents tended to parallel total P.

**P and environmental pollution**

**The role of P in eutrophication**

P has been associated with environmental pollution through the eutrophication of lakes, bays, and non-flowing water bodies. Eutrophication is the response of a water body (lake, reservoir, slow-flowing river, and certain coastal waters) to overenrichment by nutrients. The principal impacts of eutrophication relate to four phenomena (Sharpley et al., 1994): (1) algal blooms and heavy growth of certain aquatic plants, (2) oxygen depletion, (3) pH variability, and (4) plant species quality and food-chain effects. Eutrophication has limited the use of surface waters for aesthetics, fisheries, recreation, industry, and the drinking. Although N and C are required for algal growth, much of the concern with eutrophication has focused on P. Mackenthun (1973) indicates that high phosphorus concentrations are associated with accelerated eutrophication of water when other growth-promoting factors are present.

**Loss of P from agricultural land**

Because of the easier identification compared with non-point sources of P, point source of P pollution has been greatly reduced. The potential for P loss from agricultural land increases with the continual application of fertilizer and/or manure, so non-point sources of P now contribute a greater portion of P inputs to freshwater (Sharpley et al., 1994). The loss of P in erosion and runoff occurs in dissolved (DP) and particulate P (PP) forms. DP is
immediately available for algal uptake, and PP can be a variable but long-term source of P to aquatic biota (Sharpley, 1993).

Protection of surface water from eutrophication

Phosphorus loss from agricultural land can be minimized by controlling erosion and runoff and by appropriately managing P sources. The ways to minimize P loss by erosion and runoff include buffer strips, riparian zones, terracing, contour tillage, and cover crops (Sharpley et al., 1994). Appropriate management of P sources involves fertilizer placement and following soil test P recommendations. Subsurface placement of P is one of the measures which can reduce the potential for P loss by runoff. The standard procedures for the determination of environmental soil test P have not been developed, but many of the issues related to environmental soil P test have been summarized by Sims (1993). Overall, the amount of soil P to be desorbed and subsequently to be available to aquatic organisms must be evaluated if the environmental issue is the priority consideration. The U.S. National Resource Conservation Service (Lemunyon and Gilbert, 1993) proposed a more comprehensive P index to rank the potential of a site to deliver excessive P to surface water within a given watershed. Soil P availability, fertilizer and organic manure and waste management, and erosion and runoff are those factors considered in that index. Once a water body has been identified as being sensitive to P inputs, soils vulnerable to P loss in runoff and erosion must be carefully managed.
REDISTRIBUTION OF BIOSOLIDS- Derived Phosphorus Applied to a Mollisol

A paper submitted to the Journal of Environmental Quality

Yaobing Sui, Michael L. Thompson, Carl A. Mize

ABSTRACT

The amount of P applied to land with biosolids is generally more than plants need when the application rate is based on the potentially available N. The subsequent accumulation of P is of environmental rather than agronomic concern, because it could lead to eutrophication of water bodies if P is carried off-site in surface runoff, subsurface drainage water, or eroded soil. A large-scale field study with three biosolids application rates (approximately 0, 7.4, and 13.0 Mg dry matter ha^{-1}) was conducted to investigate the redistribution of P derived from surface-applied biosolids in soil under poplars and switchgrass. Soil samples were collected from two depths (0–5 cm and 5–25 cm), and total P was determined by colorimetry after strong acid digestion. Total P in mobile soil water samples collected by zero-tension lysimeters was determined by inductively coupled plasma spectrometry. After 6 years of continuous biosolids application to poplar tree plots, total P in soil increased significantly (at 0.05 significant level) at both the 0–5- and 5–25-cm depths under poplars. Also at both depths, a linear relationship between total P in soil and the amount of P applied with biosolids (at 0.05 significant level) was found. Under switchgrass, total P increased significantly (at 0.05 significant level) at only the 0–5-cm depth. A linear relationship between total P in soil and the amount of P applied with biosolids (at 0.05 significant level) was found at the 0–5-cm depth under switchgrass but not at the 5–25-cm depth. The amount of P taken up annually by switchgrass was estimated to be 5 times more
than that taken up by poplars. The amount of P leached in mobile soil solution of switchgrass plots was estimated to be twice that leached in soil solution of poplar tree plots. Phosphorus that accumulated in the upper 5 cm of the soil accounted for $\geq 45\%$ or more of the total P applied with biosolids, except for the low biosolids application rate to switchgrass plots where the value was 28%.

**INTRODUCTION**

Biosolids is a product of wastewater treatment that can be beneficially used (Girovich, 1996). Land application of biosolids can improve the physical (Epstein et al., 1976; Metzger and Yaron, 1987) and biological (Katterman and Day, 1989) properties of soils and provide plant nutrients that are necessary for plant growth (Pierzynski, 1994). Land application is carefully regulated, however, because of the potential presence of unwanted constituents in the biosolids such as heavy metals or toxic organics. The potential for high loading of N and P in the soil also raises environmental and health issues.

In order to minimize the amount of biosolids-derived N that could potentially leach below the root zone to groundwater, U.S. Environmental Protection Agency regulations (1993) require that biosolids be applied at rates no greater than agronomic rates. In practice, the amount of N needed by the crop or vegetation grown on the land is calculated and compared with the potentially available N in the biosolids. But when a biosolids application rate is based on potentially available N, the total P application rates are generally much greater than crop needs. This imbalance between N and P in biosolids increases the potential for off-site movement of P (Pierzynski, 1994).

The continued addition of P in excess of crop requirements leads to an accumulation in the soil surface horizons. Furrer (1981) found that total P in 0–15-cm depth of a clay soil
increased by a factor of two after 4 years of biosolids application. After 18 years of biosolids application, P was found to accumulate mainly at the 0–30-cm depth of a sandy loam soil (Johnston, 1981). A study by Webber (1981) showed that there had been little downward movement of P beyond 5 cm in a loam soil after 4 years of biosolids treatment. On the other hand, added P was distributed through the upper 50 cm of soil following 45 years of intermittent flooding of raw sewage water of domestic and industrial origin on a sandy soil (Beek et al., 1977).

Phosphorus accumulation in surface horizons of soils is of environmental rather than agronomic concern because it could be a source of surface water and ground water pollution. Erosion and runoff account for a large share of surface water quality problems (Iseimann, 1993; Sharpley et al., 1994; Sharpley et al., 1995). Eroded soils with high P levels are non-point sources of P, especially in agricultural watersheds (Abrams and Jarrell, 1995). Because of the high P fixation capacity of most soils, vertical movement of P through the soil profile is generally considered of little importance. Both Webber (1981) and Furrer (1981) found that total P concentrations in leachates collected from laboratory lysimeter experiments were not affected by biosolids application. On the other hand, increases in soluble P in soil drainage waters have also been reported in response to soil P accumulation in soil surface horizons (Heckrath et al., 1995; Smith et al., 1995; Eghball et al., 1996). An increase in the concentration of extractable inorganic P in subsoil as deep as 210 cm was observed by James et al. (1996) after heavy manuring.

The fixation and redistribution of P in biosolids-amended soils are influenced by both soil and biosolids properties, such as the P adsorption and desorption capacity of the soil, physical properties of soil, and P content and forms in the biosolids. They are also influenced
by the rates and methods of biosolids application, soil management, rainfall, and topography. In addition, different types of vegetation may have variable effects on the fate of P applied with biosolids. Because of the variety of biosolids and environmental conditions, case-specific studies are required to evaluate the redistribution of P added with biosolids amendments. In this large-scale field experiment, our objectives were: (1) to document the mobility in the soil of P derived from surface-applied biosolids and (2) to compare the effects of hybrid poplar-cottonwood trees (Populus × euramericana – clone NC–5326) and switchgrass (Panicum virgatum L.) on the fate of biosolids-applied P.

The investigation was not originally undertaken with the primary goal to calculate a rigorous mass balance of P. Plot scale, biosolids application method, and changes in site management over time introduced uncertainties that made short-term P dynamics difficult to interpret. Still, we believe it is valuable to document the trends in P dynamics at the site and to highlight those aspects of P redistribution in soil that invite further study.

**MATERIALS AND METHODS**

**Research Site**

The research site (Fig. 1), located at the Ames (IA) Water Pollution Control Facility, covers about 16 ha of land and consists of 360-m-long, alternating strips of poplar trees and alleys of perennial switchgrass. The soil in the study area, which is on the Skunk River floodplain (about 2 km from the river), is classified as a fine, smectitic, mesic Cumulic Vertic Endoaquoll. Slope at the site is 0%, and groundwater depth is normally about 3.5 m. Selected properties of a representative pedon before biosolids application began are shown in Table 1.
Fig. 1. Ames Agroforestry Project with the Water Pollution Control Facility in the foreground and research plots in the background.
Table 1. Selected chemical and physical characteristics of a representative pedon before biosolids was applied at the Water Pollution Control Facility research site

<table>
<thead>
<tr>
<th>Depth</th>
<th>pH</th>
<th>Total P</th>
<th>Sand</th>
<th>Silt</th>
<th>Clay</th>
<th>Organic C</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm</td>
<td></td>
<td>mg kg⁻¹</td>
<td>g kg⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–14</td>
<td>6.2</td>
<td>694</td>
<td>250</td>
<td>350</td>
<td>400</td>
<td>25.9</td>
</tr>
<tr>
<td>14–28</td>
<td>6.0</td>
<td>645</td>
<td>270</td>
<td>350</td>
<td>380</td>
<td>24.5</td>
</tr>
<tr>
<td>28–54</td>
<td>6.0</td>
<td>468</td>
<td>310</td>
<td>320</td>
<td>370</td>
<td>16.3</td>
</tr>
<tr>
<td>54–142</td>
<td>6.2</td>
<td>302</td>
<td>420</td>
<td>280</td>
<td>300</td>
<td>6.4</td>
</tr>
<tr>
<td>142–148</td>
<td>5.2</td>
<td>306</td>
<td>640</td>
<td>190</td>
<td>170</td>
<td>3.1</td>
</tr>
</tbody>
</table>
Experimental Design

A completely randomized block experiment with four blocks and three biosolids treatments was designed for this study (Fig. 2). Each block was divided into three plots, and each plot (experimental unit) was 60 m long and 15 m wide. Two vegetation treatments, poplar trees and switchgrass, were paired adjacent to each other in the south-north direction. Both poplars and switchgrass were planted in blocks 1 and 2 in 1990 and in blocks 3 and 4 in 1991. The tree strips consisted of 6 rows of poplars planted in three sets of two closely spaced rows. Spacing between rows was 2.4 m; between double-row sets the spacing was 4.6 m to allow access for the biosolids application truck. Spacing between trees within rows was 1.2 m. The understory was dominated by volunteer grasses. The switchgrass strips between the tree alleys were 16.5 m wide.

The three biosolids treatments were control (no biosolids applied), a low biosolids application rate (averaging 6.4 Mg dry matter ha⁻¹ yr⁻¹ to poplar tree plots and 8.4 Mg dry matter ha⁻¹ yr⁻¹ to switchgrass plots), and a high biosolids application rate (averaging 13.1 Mg dry matter ha⁻¹ yr⁻¹ to poplar tree plots and 14.6 Mg dry matter ha⁻¹ yr⁻¹ to switchgrass plots) (Table 2). The biosolids application rates varied from year to year in response to weather conditions and availability of biosolids.

Biosolids was surface-applied (Fig. 3) to the poplar and switchgrass plots in both spring and fall. Biosolids was first applied on blocks 1 and 2 in 1991. Application began on blocks 3 and 4 in 1992. Biosolids application to switchgrass was stopped after 1993 because the switchgrass had limited tolerance to the high biosolids application rate and the heavy wheel traffic that occurred during biosolids application. Dry matter in biosolids ranged from 3.2 to 5.5% and pH ranged from 7.2 to 7.6. The range of total P in dry matter was 1.7 to
Fig. 2. A diagram of the research design: 0X = 0 rate of biosolids, 1X = low rate of biosolids, and 2X = high rate of biosolids.
Table 2. Annual amounts of biosolids and P applied to poplar and switchgrass plots

<table>
<thead>
<tr>
<th>Year</th>
<th>Poplar Low</th>
<th>Poplar High</th>
<th>Switchgrass Low</th>
<th>Switchgrass High</th>
<th>Poplar Low</th>
<th>Poplar High</th>
<th>Switchgrass Low</th>
<th>Switchgrass High</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mg ha⁻¹</td>
<td>Mg ha⁻¹</td>
<td>Mg ha⁻¹</td>
<td>Mg ha⁻¹</td>
<td>kg ha⁻¹</td>
<td>kg ha⁻¹</td>
<td>kg ha⁻¹</td>
<td>kg ha⁻¹</td>
</tr>
<tr>
<td>1991</td>
<td>8.3</td>
<td>17.2</td>
<td>7.5</td>
<td>7.5</td>
<td>158</td>
<td>327</td>
<td>143</td>
<td>143</td>
</tr>
<tr>
<td>1992</td>
<td>4.1</td>
<td>8.8</td>
<td>9.9</td>
<td>20.5</td>
<td>103</td>
<td>220</td>
<td>248</td>
<td>513</td>
</tr>
<tr>
<td>1993</td>
<td>11.1</td>
<td>19.9</td>
<td>7.8</td>
<td>15.7</td>
<td>278</td>
<td>498</td>
<td>195</td>
<td>393</td>
</tr>
<tr>
<td>1994</td>
<td>2.8</td>
<td>2.8</td>
<td>NA</td>
<td>NA</td>
<td>64</td>
<td>64</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>1995</td>
<td>3.9</td>
<td>7.8</td>
<td>NA</td>
<td>NA</td>
<td>113</td>
<td>214</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>1996</td>
<td>8.3</td>
<td>12.4</td>
<td>NA</td>
<td>NA</td>
<td>205</td>
<td>303</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Mean</td>
<td>6.4</td>
<td>11.5</td>
<td>8.4</td>
<td>14.6</td>
<td>154</td>
<td>271</td>
<td>195</td>
<td>350</td>
</tr>
</tbody>
</table>

¹ NA = no application
Fig. 3. Biosolids was sprayed on the soil surface by using large application trucks.
Biosolids was applied by City of Ames personnel using large application trucks that sprayed biosolids on the soil surface.

**Soil and Woody Biomass Sampling**

Before biosolids application began at the site, eight pedons were sampled by genetic horizons in 1990. Subsequently, the research plots were sampled each fall at depths of 0–5 and 5–25 cm. Soil samples were collected only from blocks 1 and 2 in 1991–1994, but they were collected from all four blocks in 1996. In order to decrease the sampling errors within each plot, four subsamples were collected on a grid basis and mixed to form a composite soil sample. Soil samples were air-dried and ground to pass a 100-mesh sieve before total P analysis. In the fall of 1996, soil bulk density was determined in the research plots by the method of Doran and Mielke (1984).

All trees were measured for height and diameter at the end of the 1995 growing season. Two trees from each biosolids treatment in blocks 1 and 2 were cut and subsampled for tissue analysis of P. Above-ground tree biomass in that year was calculated using equations developed from trees harvested in 1993.

**Collection of Soil Solution**

Soil solution was collected with zero tension lysimeters (ZTLs) that were installed about 50 cm below the soil surface in the fall of 1991 and spring of 1992. The ZTL consisted of a polycarbonate cylinder, 8 cm high and 8.2 cm internal diameter, sealed to a polycarbonate base at one end. Details of the design, function, and installation of these ZTLs were described by Thompson and Scharf (1994). Soil solution in ZTLs was sampled normally within 24 hours after each significant rainfall (≥~13 mm). Water samples were frozen to preserve the samples for total P analysis. The advantages of this type of lysimeter
are (1) they are inexpensive, (2) they can be installed with a minimum of disturbance to the soil, and (3) multiple lysimeters can be installed cheaply to assess spatial variability at a research site. In this study, one lysimeter was installed in each of the four replicate plots for each treatment.

**Analytical Methods**

Total P in soils was extracted with H$_2$SO$_4$-H$_2$O$_2$-HF (Bowman, 1988) and determined by the method of Murphy and Riley (1962). Total P in soil solution collected by ZTLs was determined directly by inductively coupled plasma (ICP) spectrometry. Tissue samples collected from the poplar trees were dried at 60°C, ground to pass a 2-mm sieve, and digested in sulfuric acid before total P was determined colorimetrically.

**Calculation of Each Pool of P**

The amounts of P applied were calculated from analyses of the biosolids at the Water Pollution Control Facility laboratory and records of the volume of biosolids applied to each pool. The amount of P accumulated in each depth of soil amended with biosolids was calculated following the equation:

$$M = (C\cdot D - C_0\cdot D_0)\cdot H\cdot A\cdot 10^{-3},$$

where $M$ (kg ha$^{-1}$) is the difference in the amount of total soil P between control and biosolids treatments in 1996; $C_0$ and $C$ are the P concentrations (mg kg$^{-1}$) of soil samples from control and biosolids treatment plots in 1996, respectively; $D_0$ and $D$ are soil bulk densities (Mg m$^{-3}$) in control and biosolids treatments in 1996, respectively; and $H$ (m) and $A$ (m$^2$) are the thickness of the soil zone sampled and the area of one hectare of soil, respectively.
The P content of switchgrass grown at the research site was not determined in the early years of the project, so we calculated the amount of P uptake by switchgrass from the estimated yield of switchgrass and literature values of P concentration in switchgrass. The dry biomass of harvested switchgrass (removed from the site) was estimated to be 10,000 kg ha\(^{-1}\) yr\(^{-1}\) in all three treatments by I. C. Anderson (personal communication), and the typical P concentration in dry matter of switchgrass is about 0.25% (Pierzynski and Logan, 1993). So the P removed by switchgrass was estimated to be 25 kg ha\(^{-1}\) yr\(^{-1}\) in both low and high biosolids treatments, with the total P removed during the 6-year period being 150 kg ha\(^{-1}\).

The amount of P in the above-ground biomass of poplar trees was determined in 1995 to be 14 kg ha\(^{-1}\) in the low-rate treatment and 25 kg ha\(^{-1}\) in the high-rate treatment. By assuming that the amount of P taken up by poplars in 1996 was equal to the average annual uptake by poplars during the first 5-year period, we estimated the amount of P in above-ground biomass of the poplars in 1996 as 17 kg ha\(^{-1}\) in the low-rate treatment and 30 kg ha\(^{-1}\) in the high-rate treatment.

The amount of P leached in soil solution for each replication was calculated based on the following equation:

\[
Q = \frac{(A/S)}{\sum (V_i \times C_i)} \times 10^{-3},
\]

where Q is the amount of P in the soil solution (kg ha\(^{-1}\)); \(V_i\) and \(C_i\) are the volume (m\(^3\)) and concentration (g m\(^{-3}\)) of each soil solution sample collected by ZTL in that replication; S is the surface area of the ZTL (m\(^2\)); and A (m\(^2\)) is the area of one hectare of soil. For each treatment, the amount of P leached to 50 cm in soil solution for each treatment was calculated by averaging the values from four replications. Because the amounts of P leached in soil solution in 1991, 1992, 1995, and 1996 were not available, the amount of P leached in
soil solution from 1991 to 1996 was estimated by multiplying the mean annual value of
amounts of P leached in 1993 and 1994 by six years. All data were analyzed using the

RESULTS AND DISCUSSION

Total P at Two Depths under Poplars

In the fall of 1996, after 6 years of biosolids application to the poplar plots, the mean
values of total P concentrations at the 0–5-cm depth of soil in the four blocks were 1810 and
2833 mg kg\(^{-1}\) in the low and high treatments, respectively (Table 3, last column to the right).
This was an increase of 118% and 241% over the 832 mg kg\(^{-1}\) in the control treatment.
Biosolids application had a significant effect on total P at the 0–5-cm depth (P<0.01); further,
the total P at the 0–5-cm depth was significantly different between any two of the three
treatments. Calculated on a mass-to-area basis, the amount of total P in the 0–5-cm depth of
the soil increased 418 and 814 kg ha\(^{-1}\) in the low and high biosolids treatments, respectively,
accounting for 45% and 50% of the total P added with biosolids (Table 4).

At the 5–25-cm depth of the poplar plots, the mean values of total P concentrations in
the four blocks in 1996 were 689 and 750 mg kg\(^{-1}\) in low and high treatments, respectively,
increasing 31% and 42% compared with 527 mg kg\(^{-1}\) in the control treatment (Table 3). At
the 5–25-cm depth biosolids application had a significant effect on total P content, but the
concentrations were significantly different only between the control and either of the two
biosolids treatments rather than between the two biosolids treatments. Calculated on a mass-
to-area basis, the amount of P at the 5–25-cm depths increased 344 kg ha\(^{-1}\) in the low-rate
and 411 kg ha\(^{-1}\) in the high-rate treatments, i.e., 37% and 25% of the P added (Table 4).
Table 3. Total P in soil from 1992 to 1996, calculated with the data of blocks 1 and 2 from 1992 to 1995 and with the data of all 4 blocks in 1996.

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm</td>
<td>(2 blocks)</td>
<td>(4 blocks)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T0</td>
<td>0–5</td>
<td>694</td>
<td>880</td>
<td>870</td>
<td>879</td>
<td>873</td>
<td>832a</td>
</tr>
<tr>
<td>T1</td>
<td>0–5</td>
<td>976</td>
<td>1446</td>
<td>1199</td>
<td>1506</td>
<td>1840</td>
<td>1810b</td>
</tr>
<tr>
<td>T2</td>
<td>0–5</td>
<td>1248</td>
<td>2177</td>
<td>1284</td>
<td>2667</td>
<td>3265</td>
<td>2833c</td>
</tr>
<tr>
<td>T0</td>
<td>5–25</td>
<td>625</td>
<td>590</td>
<td>626</td>
<td>640</td>
<td>570</td>
<td>527a</td>
</tr>
<tr>
<td>T1</td>
<td>5–25</td>
<td>720</td>
<td>630</td>
<td>728</td>
<td>729</td>
<td>735</td>
<td>689b</td>
</tr>
<tr>
<td>T2</td>
<td>5–25</td>
<td>679</td>
<td>731</td>
<td>701</td>
<td>800</td>
<td>847</td>
<td>750b</td>
</tr>
<tr>
<td>G0</td>
<td>0–5</td>
<td>ND^</td>
<td>685</td>
<td>703</td>
<td>651</td>
<td>603</td>
<td>725a</td>
</tr>
<tr>
<td>G1</td>
<td>0–5</td>
<td>ND</td>
<td>1179</td>
<td>1326</td>
<td>1431</td>
<td>1064</td>
<td>1086b</td>
</tr>
<tr>
<td>G2</td>
<td>0–5</td>
<td>ND</td>
<td>2335</td>
<td>2821</td>
<td>2184</td>
<td>2216</td>
<td>1913c</td>
</tr>
<tr>
<td>G0</td>
<td>5–25</td>
<td>ND</td>
<td>637</td>
<td>593</td>
<td>598</td>
<td>500</td>
<td>616a</td>
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<tr>
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<td>5–25</td>
<td>ND</td>
<td>719</td>
<td>674</td>
<td>689</td>
<td>639</td>
<td>676a</td>
</tr>
<tr>
<td>G2</td>
<td>5–25</td>
<td>ND</td>
<td>778</td>
<td>720</td>
<td>687</td>
<td>642</td>
<td>698a</td>
</tr>
</tbody>
</table>

^T = poplar tree and G = switchgrass; 0 = zero application, 1 = low biosolids application rate, and 2 = high biosolids application rate. For a given depth increment and vegetation, data with same letter in a column are not significantly different at 0.05 significant level. ND = not determined.
Table 4. Mass balance of applied P. Values in parentheses represent fractions of the total P applied in a given treatment.

<table>
<thead>
<tr>
<th>P Pools</th>
<th>Amount of P in Each Pool</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pools</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Applied biosolids</td>
<td></td>
</tr>
<tr>
<td>0–5 cm of soil</td>
<td></td>
</tr>
<tr>
<td>5–25 cm of soil</td>
<td></td>
</tr>
<tr>
<td>Above ground biomass of plants</td>
<td></td>
</tr>
<tr>
<td>Leachate to 50 cm</td>
<td></td>
</tr>
<tr>
<td>Remainder</td>
<td></td>
</tr>
</tbody>
</table>
The variation of total P among blocks was large; total P varied within blocks and even within plots at the research site. There was some spatial variation of total P at the research site even before biosolids was applied. Total P of soil samples collected at single points in 1990 was 694 mg kg\(^{-1}\) at 0–14 cm in block 1, 696 mg kg\(^{-1}\) at 0–31 cm in block 2, 763 mg kg\(^{-1}\) at 0–33 cm in block 3, and 895 mg kg\(^{-1}\) at 0–18 cm in block 4. Soil samples were not collected from all plots before biosolids were applied, so we do not know how total P varied within blocks. There is also the possibility that the biosolids may not have been uniformly applied to the soil surface, causing additional spatial variation of total P in soil.

Regression analysis of the data from four blocks in 1996 suggested a linear relationship between total soil P at both 0–5- and 5–25-cm depths and the amount of P applied with biosolids (P<0.05) (Table 5). Moreover, the increase in total P in soil with an increase of one unit of P applied with biosolids (given by the slope of the model) was not the same at the two depths. The slope of the model for the 0–5-cm depth (1.23) was almost nine times greater than that for the 5–25-cm depth.

**Mass Balances of P in Poplar Plots**

Table 4 shows the distribution of P in biosolids-amended poplar tree plots. The amounts of P accumulated in above-ground biomass by poplar trees were estimated to be 17 and 30 kg ha\(^{-1}\), respectively, in low and high biosolids treatments from 1991 to 1996. These quantities represented 2% of the P applied with biosolids. Phosphorus leached in soil solution from 1991 to 1996 and collected by ZTLs in the low and high rate plots was calculated to be 18 and 12 kg ha\(^{-1}\), respectively. The amount of P leached to 50 cm accounted for 2% and 1% of the P applied with biosolids at low and high application rates, respectively. Therefore, the
Table 5. Linear regression expressions that describe the change in concentration of total soil P (Y, mg kg\(^{-1}\)) as a function of cumulative P added in biosolids (X, kg ha\(^{-1}\)).

<table>
<thead>
<tr>
<th>Vegetation and depth</th>
<th>Linear regression expression(^\dagger)</th>
<th>R(^2)</th>
<th>Level of significance(^\ddagger)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Poplar</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–5-cm depth</td>
<td>(Y = 1.23 \times + 787)</td>
<td>0.79</td>
<td>*</td>
</tr>
<tr>
<td>5–25 cm depth</td>
<td>(Y = 0.14 \times + 537)</td>
<td>0.87</td>
<td>**</td>
</tr>
<tr>
<td><strong>Switchgrass</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–5-cm depth</td>
<td>(Y = 1.11 \times + 635)</td>
<td>0.80</td>
<td>*</td>
</tr>
<tr>
<td>5–25 cm depth</td>
<td>(Y = 0.04 \times + 628)</td>
<td>0.53</td>
<td>NS</td>
</tr>
</tbody>
</table>

\(^\dagger\) n = 12, i.e., 4 replications in each of 3 levels of biosolids

\(^\ddagger\) ***P < 0.001, **P < 0.01, *P < 0.05, NS P > 0.05.
total P accumulated in above-ground biomass and leached in the soil solution was small, estimated to be <5% of the total P applied.

In the poplar plots, about 50% of P applied with biosolids accumulated in the top 5 cm of the soil, and about 37% (low application rate) and 25% (high application rate) of the P applied with biosolids accumulated in the 5–25-cm depth (Table 4). The observation that proportionately less P moved into the 5–25-cm depth of soils in the high-rate plots than in the low-rate plots could be the result of several factors. It may be due to the thicker litter layer (about 6 cm) in the high-rate plots. The thicker litter layer could retain more of the solid fraction of biosolids than would the thinner litter layer (~3 cm) in the low-rate plots. In addition, more dissolved salts were applied with biosolids in the high-rate treatment, resulting in a consistently greater electrical conductivity (EC) in soil solution collected by the ZTLs (data not shown here). The greater EC implied a higher ionic strength in the soil solution, which could decrease desorption from or increase sorption of P by the solid phase of soil and biosolids (Ryden et al., 1977; Barrow et al., 1980). The fraction of P termed "remainder" (Table 4) included P accumulated by roots, P that moved to the 25–50-cm zone of the soil, P accumulated in the litter layer (Brockway, 1983), or P lost by runoff water and eroded soil.

Annual Changes in Total P in Poplar Plots

In the previous section, we considered soil P after 6 years of biosolids applications. In this section, we discuss how soil P varied on a year-by-year basis. Over this shorter temporal scale, variations in total soil P were not always consistent with our expectations. Our analysis in this section is limited to replications 1 and 2, from which we collected soil samples each year.
Total P in the 0–5-cm depth of soil in the control treatment changed little from 1990 to 1992, increased from 1992 to 1993, then remained constant from 1993 to 1996 (cf. Table 1 and Table 3). We are uncertain why there was an increase in total P in the control plots from 1992 to 1993, but it could have been due to an unrecorded accidental application of biosolids to the control plots under poplars sometime in 1993. Except for 1994, total P at the 0–5-cm depth of both low- and high-rate treatments increased dramatically each year from 1991 to 1996 because of the addition of P with biosolids (Table 3). There was a decline in total P in both low- and high-rate treatments in 1994. We do not know why this decrease occurred. Between fall of 1993 and spring of 1994, the amount of biosolids applied was smaller than in other years. We expected this smaller application simply to cause a smaller increase in total soil P rather than a large decrease. Judged on the basis of the small amounts of P estimated to have been leached or taken up by trees over 6 years (Table 4), neither leaching nor accumulation of P in above-ground biomass is likely to have been significant enough to account for the large decline in total P at the soil surface in that single year.

For the 5–25-cm depth (Table 3), total P in both the control treatment and the biosolids treatments varied irregularly over time. Some of this variation could be attributed to inherent spatial variability of soil P at the research site or accidental application, as discussed above. Some variation could be attributed to P uptake by plants and losses through soil water as well as to downward movement of P applied with biosolids on the soil surface.

Even with the uncertainties regarding annual variations in total P in the research plots, regression analysis with data from only blocks 1 and 2 indicated a significant (P<0.01) linear relationship between total P at both the 0–5- and 5–25-cm depths and the amount of P applied with biosolids at both low and high rates from 1990 to 1996 (Table 6). The slopes of
Table 6. Linear regression expressions that describe the change in concentration of total soil P (Y, mg kg\(^{-1}\)) in poplar plots as a function of P added annually in biosolids (X, kg ha\(^{-1}\)).

<table>
<thead>
<tr>
<th>Treatment and depth</th>
<th>Linear regression expression (^\dagger)</th>
<th>R(^2)</th>
<th>Level of significance(^\ddagger)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low biosolids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>treatment</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–5-cm depth</td>
<td>(Y = 1.18 \times X + 680)</td>
<td>0.84</td>
<td>***</td>
</tr>
<tr>
<td>5–25 cm depth</td>
<td>(Y = 0.07 \times X + 665)</td>
<td>0.67</td>
<td>**</td>
</tr>
<tr>
<td>High biosolids</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>treatment</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–5-cm depth</td>
<td>(Y = 1.49 \times X + 484)</td>
<td>0.66</td>
<td>**</td>
</tr>
<tr>
<td>5–25 cm depth</td>
<td>(Y = 0.11 \times X + 630)</td>
<td>0.76</td>
<td>**</td>
</tr>
</tbody>
</table>

\(^\dagger\) n = 6, i.e., 2 replications in each of 3 levels of biosolids

\(^\ddagger\) ***p < 0.001, **p < 0.01, *p < 0.05, \text{NS} p > 0.05.
the two equations for the 0–5-cm and 5–25-cm depths in both biosolids application rate treatments are different. The slope of the model reflects the rate of the increase of total soil P over time. The larger the slope, the faster the soil P increased; so the annual rate of the increase of soil P was larger at the 0–5-cm depth than at the 5–25-cm depth.

**Mobility of P Applied with Biosolids in Soils under Switchgrass**

In the switchgrass plots in the fall of 1996, the mean values of soil P at the 0–5-cm depth in low- and high-rate treatments were 1086 and 1913 mg kg\(^{-1}\), increasing 50% and 164%, respectively, compared with 725 mg kg\(^{-1}\) in the control treatment (Table 3). Total P at the 0–5-cm depth was significantly affected by the biosolids amendment (P<0.01). The amounts of P at the 0–5-cm depth increased by 164 and 473 kg ha\(^{-1}\), respectively, accounting for 28% and 45% of the P applied with biosolids (Table 4).

At the 5–25-cm depth in switchgrass plots, total P concentration was 676 mg kg\(^{-1}\) in the low treatment and 698 mg kg\(^{-1}\) in the high treatment, increasing 10% and 13%, respectively, compared with 616 mg kg\(^{-1}\) in the control treatment (Table 3). The total P concentration in this depth was not significantly affected by biosolids amendment (P>0.2). When compared to the control treatment, the amounts of P at the 5–25-cm depth increased 108 and 134 kg ha\(^{-1}\), respectively, in low and high treatments, accounting for 18% and 13% of the P applied (Table 4).

A linear relationship between total soil P in the switchgrass plots and the amount of P applied with biosolids was found at the 0–5-cm depth (P<0.05), but not at the 5–25-cm depth (P>0.05) as it was in the tree plots (Table 5). The lack of a statistically significant effect of biosolids amendment on soil P at the 5–25-cm depth of the switchgrass plots could be related to two factors. First, biosolids applications to the switchgrass plots ended in 1994 and there
was less P available to be transported. Second, switchgrass roots were more concentrated near the soil surface than were tree roots; thus they probably intercepted more of the applied P at that depth than did the tree roots.

**Mass Balances of P under Switchgrass**

The amounts of P taken up by switchgrass was estimated to be 150 kg ha\(^{-1}\) at both low and high rates from 1991 to 1996, i.e., 26% and 14% of the P applied with biosolids in the respective treatments (Table 4). The average P uptake by switchgrass was estimated to be at least five times more than that taken up by poplars each year.

Under switchgrass from 1991 to 1996, the P in soil solution that was leached to a depth of 50 cm and collected by ZTLs in the low and high treatments was estimated to be 32 and 30 kg ha\(^{-1}\), respectively, accounting for 5% and 3% of the P applied. Although the average P concentration in soil solution collected by ZTLs was slightly larger under poplar trees than under switchgrass (data not shown), more P was leached under switchgrass than under poplars, because more soil solution was collected by ZTLs under switchgrass than under poplars.

The relative accumulation of P at 0–5- and 5–25-cm depths was smaller in switchgrass plots than in poplar plots (Table 4). This is probably because the amounts of P taken up by switchgrass and leached by soil solution were estimated to be larger than in poplar plots. Because there was not a thick litter layer at the surface of the switchgrass plots, most of the P in the fraction termed "remainder" probably included (1) P that moved to the 25–50-cm depth of soil as well as (2) P that accumulated in switchgrass roots.
CONCLUSIONS

Biosolids amendments at two rates significantly ($P<0.01$) increased total $P$ concentration at the 0–5-cm depth of soils under both poplar trees and switchgrass. Total $P$ concentrations at the 5–25-cm depth also increased after the biosolids amendments, but the increase was much smaller than at the 0–5-cm depth. Total $P$ concentrations at the 5–25-cm depth of the soils were significantly influenced by biosolids amendments to poplar plots ($P<0.01$) but not by amendments to switchgrass plots ($P>0.2$).

Phosphorus concentrations at the 0–5-cm depth of soil under both poplars and switchgrass in 1996 were linearly related to the amount of $P$ applied with biosolids. In poplar tree plots only, there was also a linear relationship between $P$ concentration at the 5–25-cm depth and the amount of $P$ applied with biosolids. On an annual basis from 1990 to 1996, there was also a significant linear relationship between soil $P$ content at both depths and the amount of $P$ applied with biosolids.

The amounts of $P$ accumulated in the upper 5 cm of soil were greater than those accumulated in the underlying 20-cm depth increment in both poplar tree and switchgrass treatments. The estimated amounts of $P$ taken up by poplars into above-ground biomass were small and only accounted for 2% of $P$ added with biosolids. The estimated amount of $P$ taken up by switchgrass was at least five times more than that taken up by poplars, accounting for 26% of $P$ applied at the low biosolids application rate treatment and 14% of $P$ applied at the high biosolids application rate. The amounts of $P$ estimated to be leached with soil solution were also small and accounted for 2% or less of $P$ added with biosolids to poplar tree plots. More $P$ was estimated to have leached with soil solutions in switchgrass plots than in poplar
plots. The solid phase of the biosolids was probably retained by the litter layer under poplars, and that could account for much of the P not allocated to other pools.
EFFECTS OF BIOSOLIDS AMENDMENT ON P IN MOBILE SOIL SOLUTION IN A MOLLISOL AND IN GROUNDWATER

A paper to be submitted to Soil Science Society of America Journal

Yaobing Sui and Michael L. Thompson

ABSTRACT

P plays a key role in eutrophication of surface water bodies, and P losses in surface and subsurface runoff account for most of the P transported from terrestrial to aquatic environments. A field study was conducted on a Cumulic Endoaquoll in central Iowa to observe the effects of land-applied biosolids on P concentrations both in soil solutions collected by zero-tension lysimeters (ZTL) under switchgrass and poplar vegetation and in groundwater. A completely randomized block experiment was designed with four replications and three biosolids application rates (control: no biosolids applied; low application rate: 6.4 and 8.4 Mg dry matter ha⁻¹ yr⁻¹ to poplar and switchgrass plots, respectively; high application rate: about twice the low biosolids application rate). In each plot, a ZTL was installed about 50 cm below the soil surface. In a separate investigation, ZTLs were installed in a single plot at depths ranging from 15 to 65 cm. Groundwater samples were collected from piezometers installed ~6 m below the soil surface. In 1994, the numbers and volumes of soil solutions collected in ZTLs in switchgrass and poplar plots were significantly different. More and larger volumes of soil-solution samples were collected under switchgrass than under poplar trees. Under both switchgrass and poplars, the largest P concentrations were observed in the mobile soil solutions collected from the low rather than from the high biosolids treatment. P concentrations in soil solution also decreased
significantly with increasing soil depth (P<0.05). P in groundwater was not influenced by biosolids applications.

**INTRODUCTION**

Phosphorus has been associated with environmental pollution, primarily through the eutrophication of lakes, bays, and nonflowing water bodies (Potash & Phosphate Institute, 1987). Eutrophication is the result of algal blooms caused by the overenrichment of nutrients. In the eutrophication process, phosphorus plays a key role compared with other nutrients (Thomas, 1973).

P can be transported from terrestrial to aquatic environments by surface and subsurface runoff, wind erosion and groundwater. Of these pathways, P losses in surface and subsurface runoff account for most of the P transported compared with losses in wind erosion and groundwater. The concentration of P required to support algal growth is exceedingly low (0.015 to 0.05 mg L\(^{-1}\)) (Potash & Phosphate Institute, 1987), so even P losses in runoff from uncultivated or pristine land can be sufficient to cause eutrophication (Sharpley et al., 1995). Soil applications of P with fertilizers, manure, and sewage sludge in excess of plant requirements are, therefore, of environmental concern (Benckiser and Simarmata, 1994; Sharpley et al., 1994). Increases in the P concentration of surface and subsurface runoff caused by the accumulation of P in soils have been reported (Culley et al., 1983; Hawkins and Scholefield, 1996; Sharpley and Syers, 1979; Sharpley et al., 1995).

P loss in groundwater is usually considerably smaller because the high affinity of soils for P prevents its downward movement to groundwater. Webber (1981) and Furrer (1981) found that total P concentrations in soil leachates collected with laboratory lysimeters were not affected by biosolids applications to the top of soil columns, although accumulations of P
in the soil did occur. But increases in the P concentration of soil drainage waters in response to soil P accumulation in soil surface horizons have also been found (Heckrath et al., 1995; Smith et al., 1995; Hawkins and Scholefield, 1996). James et al. (1996) observed an increase in the concentration of extractable inorganic P in subsoil layers as deep as 210 cm under conditions of heavy manuring.

The transport of P added to soils with fertilizers, manure, and sewage biosolids can be influenced by many factors. The adsorption and desorption capacities of soils surely play a key role in the downward movement of P in soils (Parfitt, 1978; Sibbensen, 1981; Falkiner and Polglase, 1997). Those soil properties which influence water movement, such as texture and structure, may also have an effect on the transport of P in soils. For a specific soil, P concentration in soil water is mainly controlled by the rate, timing, and method of P fertilizer applications; the content and forms of P in the fertilizers; the amount, intensity, and timing of rainfall after application; and the vegetative cover (Sharpley et al., 1995). Sharpley (1997) observed that the P concentration of runoff from soil amended with poultry litter was affected by rainfall frequency. Surface microrelief (Trojan and Linden, 1992), agricultural management (Bicki and Guo, 1991; Unger, 1992; Edwards et al., 1992; Edwards et al., 1993), and initial soil moisture (Bowyer-Bower, 1993) have been found to affect water and solute movement in soils, and therefore P transport.

There have been few reports dealing with the effects of sewage biosolids amendment on P concentrations in mobile soil solutions collected by zero-tension lysimeters (ZTL) under field conditions or in groundwater. Soil solution can be collected by ZTLs, by tension lysimeters, or by centrifugation (Litaor, 1988; Hendershot and Courchesne, 1991; Giesler et al., 1996; Marques et al., 1996). The solution collected by the ZTL is gravitational water and
water that moves through macropores by preferential flow. Our objectives in this study were (1) to investigate how biosolids amendments to a Mollisol affected P concentrations in soil solutions collected by ZTLs under field conditions and (2) to monitor if P in groundwater was influenced by biosolids amendments.

**MATERIALS AND METHODS**

**Research Site**

The research site lies north of the Water Pollution Control Facility of Ames (Iowa). The soil in the study area, which is on the Skunk River floodplain, is classified as a fine-loamy, mixed, mesic Cumulic Endoaquoll. The surface horizon is massive in the upper 15 cm. From 15 cm to about 60 cm, the soil possesses fine and medium subangular blocky structure; medium prismatic structure occurs from about 60 cm to about 140 cm. Slope at the site is 0%, and groundwater depth is normally about 3.5 m below the surface of the soil. Selected properties of a representative pedon before biosolids application began are shown in Table 1.

**Experimental Design**

The study of P in soil solutions collected by ZTLs was carried out in a completely randomized block field experiment with four blocks and three biosolids treatments for each kind of vegetation. Two kinds of vegetation, hybrid poplar-cottonwood trees (*Populus × euramericana* – clone NC-5326) and switchgrass (*Panicum virgatum* L.), were paired adjacent to each other. The three biosolids treatments were: control (no biosolids applied), low biosolids application rate (average of 6.4 and 8.4 Mg dry matter ha⁻¹ yr⁻¹ to poplars and switchgrass, respectively), and high biosolids application rate (about twice the low biosolids...
Table 1. Selected chemical and physical characteristics of a representative pedon before biosolids was applied at the Water Pollution Control Facility research site

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>pH</th>
<th>Total P (mg kg$^{-1}$)</th>
<th>Sand (g kg$^{-1}$)</th>
<th>Silt (g kg$^{-1}$)</th>
<th>Clay (g kg$^{-1}$)</th>
<th>Organic C (g kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–14</td>
<td>6.2</td>
<td>694</td>
<td>250</td>
<td>350</td>
<td>400</td>
<td>25.9</td>
</tr>
<tr>
<td>14–28</td>
<td>6.0</td>
<td>645</td>
<td>270</td>
<td>350</td>
<td>380</td>
<td>24.5</td>
</tr>
<tr>
<td>28–54</td>
<td>6.0</td>
<td>468</td>
<td>310</td>
<td>320</td>
<td>370</td>
<td>16.3</td>
</tr>
<tr>
<td>54–142</td>
<td>6.2</td>
<td>302</td>
<td>420</td>
<td>280</td>
<td>300</td>
<td>6.4</td>
</tr>
<tr>
<td>142–148</td>
<td>6.2</td>
<td>306</td>
<td>640</td>
<td>190</td>
<td>170</td>
<td>3.1</td>
</tr>
</tbody>
</table>
application rate) (Table 2). Each experimental plot was 60 m long and 15 m wide; one ZTL was installed 50 cm below the soil surface near the center of each plot.

The biosolids suspension was surface-applied to the poplar and switchgrass plots in both spring and fall. Biosolids was first applied to blocks 1 and 2 in 1991 and then to blocks 3 and 4 in 1992. Biosolids application to switchgrass plots was stopped after 1993 because the switchgrass had limited tolerance to high rates of biosolids application and the heavy wheel traffic that occurred during application. Dry matter in biosolids ranged from 3.2 to 5.5%, and pH ranged from 7.2 to 7.6. The range of total P in the dry matter was 1.7 to 3.2%. Biosolids was applied by City of Ames personnel using large application trucks that sprayed the suspension on the soil surface.

**Lysimeters and Groundwater Monitoring**

Each ZTL consisted of a polycarbonate cylinder, 8 cm long and 8.9 cm in diameter. It was sealed to a polycarbonate base at the bottom and to a polyester screen (with 150-µm openings) at the top. To install the ZTLs so that the overlying soil remained undisturbed, a hydraulic soil coring and sampling machine (Giddings Machine Co., Ft. Collins, CO) was used to remove a 10-cm-diameter core of soil. The ZTL was placed at the bottom of the hole, and the core was replaced. Before placing the lysimeter in the ground, acid-washed, silica sand was placed onto the screen at the top of the cylinder to fill the cavity and provide hydraulic contact with the overlying soil. Sampling and vent tubes extended from the ZTL to the soil surface. A schematic diagram of the ZTL and more details about installation are given by Thompson and Scharf (1994).

Groundwater at the research site flows from northwest to southeast. A piezometer well located northwest of the research site was regarded as the control well, and a well located
Table 2. Annual amounts of biosolids and P applied to poplar and switchgrass plots

<table>
<thead>
<tr>
<th>Year</th>
<th>Dry Matter Applied</th>
<th>P Applied</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Poplar</td>
<td>Switchgrass</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>1991</td>
<td>8.3</td>
<td>17.2</td>
</tr>
<tr>
<td>1992</td>
<td>4.1</td>
<td>8.8</td>
</tr>
<tr>
<td>1993</td>
<td>11.1</td>
<td>19.9</td>
</tr>
<tr>
<td>1994</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>1995</td>
<td>3.9</td>
<td>7.8</td>
</tr>
<tr>
<td>1996</td>
<td>8.3</td>
<td>12.4</td>
</tr>
<tr>
<td>Mean</td>
<td>6.4</td>
<td>11.5</td>
</tr>
</tbody>
</table>

*NA = no application*
southeast of the site was the monitoring well. The distance between the two wells is about 1.5 km.

**Sampling of Soil Solutions and Groundwater**

Soil solution collected by each ZTL was removed by applying suction to the sampling tube with a hand pump (Mityvac, Neward Enterprises Inc., Cucamonga, CA) or a peristaltic pump (Portable MasterFlex, Cole-Parmer Instrument Comp. Chicago, IL). Soil solution in ZTLs was normally collected within 24 hours after each intense rainfall (> ~13 mm) or shortly after spring snowmelt. Solution samples were frozen immediately after being brought to the laboratory, then thawed before total P analysis. In general, groundwater samples were collected every 3 months from piezometers installed about 6 m below the soil surface. These samples were acidified, stored at 4°C, and analyzed within 28 days.

**Analytical Methods**

In soil solution samples, P was determined by inductively coupled plasma atomic emission spectrometry. For groundwater, samples were digested with ammonium persulfate and determined colorimetrically following Standard Methods for the Examination of Water and Wastewater (Methods 4500-P.B.5 and 4500-P.E of Greenberg et al., 1992) The data were statistically analyzed by the General Linear Model of the SAS Institute (1989).

**RESULTS AND DISCUSSION**

**Numbers and Volumes of Soil Solutions Collected by ZTLs**

Figures 1 and 2 show the numbers of soil solutions collected by ZTLs from 1992 through 1994. The numbers varied among years for an individual ZTL and among the ZTLs during an individual year. Whether soil solution was collected by a ZTL could have depended on many factors, such as the amount and the intensity of a rainfall event,
Fig. 1. Sample numbers of soil solutions collected by ZTLs in switchgrass plots from 1992 to 1994. S = switchgrass; 0 = zero-rate biosolids, 1 = low-rate biosolids, and 2 = high-rate biosolids; R1 = replication 1, R2 = replication 2, R3 = replication 3, and R4 = replication 4.
Fig. 2. Sample numbers of soil solutions collected by ZTLs in poplar plots from 1992 to 1994. T = poplar trees; the others as described in Fig. 1.
antecedent soil moisture, the size and density of soil pores and surface cracks, microrelief, the type of vegetation, and the presence of saturated zones in the soil. The groundwater was typically about 350 cm deep, so the groundwater level at the research site had little effect on the numbers and volumes of water samples collected by the ZTLs. No solution was found in any of the ZTLs when the rainfall event was \(<13\) mm (~0.5 inch), except under the conditions of snowmelt and flooding. On the other hand, a rainfall event \(>13\) mm did not guarantee that there would be solution in any of the ZTLs, either.

At the research site, where the soil clay content was \(\geq 37\%\) in the upper 50 cm and the clay was dominated by smectite, shrinkage cracks developed when the soil was dry, and the cracks closed when the soil became wet. During summer periods without significant precipitation, the density of cracks increased greatly and the width of the cracks enlarged. Cracks \(>1\) cm wide at the soil surface were common. During such dry periods, water could move into the ZTLs by preferential flow, particularly when the rainfall intensity was greater than the infiltration rate.

The mean number of water samples collected by each ZTL was 6, 12, and 8 under switchgrass and 6, 14, and 5 under poplars in 1992, 1993, and 1994, respectively. In 1992 and 1993 there was no effect of vegetation on the mean number of samples collected by the ZTLs. In 1992, the effect of vegetation on the number of water samples may have been small because the trees were small and the litter layers under the trees had not developed. The 1993 data do not reflect an “unbiased” effect of poplars on the number of soil solution collected by ZTLs, either, because of flooding at the site during the growing season. If only the data from 1994 are used for statistical comparison, the numbers of water samples collected by ZTLs under switchgrass and under poplars were significantly different (\(\alpha = 0.05\)). We believe that
the litter layer that formed under poplars could absorb water from less intense rainfall and prevent water from moving vertically. We observed visually that more cracks formed at the soil surface under switchgrass than under poplars, and these cracks may also have contributed to the greater number of soil solution samples collected under switchgrass plots.

The mean volumes of soil solution samples collected by the ZTLs varied with each ZTL (Figs. 3 and 4). All the factors that could influence the numbers of soil solution samples collected by ZTLs (as discussed above) could also account for variability in sample volumes. Thompson and Scharf (1994) reported that the mean sample volumes collected by ZTLs at this research site were less variable when the rainfall event exceeded about 60 mm. When precipitation was <60 mm in a 24- to 36-h period, the volumes of soil solutions may be influenced by some combination of all other factors such as rainfall intensity, initial soil moisture, soil macropores, the litter layer, and microrelief.

Larger volumes of soil solution samples were collected under switchgrass than under poplars. For example, the mean volume of soil solution collected by each individual ZTL in 1994 was 1283 mL (n = 12) under switchgrass and 695 mL (n = 11) under poplars, significantly different at α = 0.05. In 1994, there was a linear relationship between the total volume of soil solution samples collected by ZTLs and the number of samples collected (R^2 = 0.86*** in switchgrass plots and 0.80*** in poplar plots). Even though individual ZTLs collected soil solution samples in variable quantities throughout the year, the total volume collected reflected primarily the number of samples collected.
Fig. 3. The volume of soil solutions collected by ZTLs and its standard deviation in switchgrass plots in 1994.
Fig. 4. The volume of soil solutions collected by ZTLs and its standard deviation in poplar trees plots in 1994. The lysimeter installed in plot T1R1 did not function in 1994.
Temporal Variations. Figures 5 and 6 show the P concentrations of soil solutions from 1992 through 1994 in some representative ZTLs. For the other ZTLs not shown on the two graphs, the results were similar to those shown.

We make three observations: First, P concentration in the soil solutions collected by ZTLs from 1992 through 1994 did not follow a consistent trend. Many large differences in P concentration occurred in the samples from both low- and high-rate biosolids plots. Other researchers have found trends related to how application of a chemical is followed by a precipitation event. Sharpley (1997) found that the concentration of P in runoff decreased when the period between application of poultry litter and rainfall-runoff increased. The length of the time between atrazine application and rainfall was also found to affect the atrazine concentration in soil waters (Edwards et al., 1993). By inspecting our data, however, we concluded that the concentration of P in soil solution did not decrease with increasing period between biosolids application and rainfall event. Perhaps because the biosolids was applied to the soil surface and not mixed with the soil immediately after applications, less sorption occurred. We hypothesize that the period between P release from biosolids applied at the surface and P transport into ZTLs at 50 cm depth may play a key role in determining the concentrations of P in soil solutions. Second, P concentrations of soil solutions were smaller in the control plots than in plots amended with biosolids. Concentrations were generally less than 1.00 mg P L\(^{-1}\) in control plots, and their variations were smaller compared with the variations of P concentrations in both low and high biosolids plots (Figs. 5 and 6). Third, P concentrations of soil solutions in most cases were larger in low-rate plots than in high-rate plots. These observations will be discussed further later in this paper. Two
Fig. 5. P concentration in representative ZTLs installed in poplar plots.
Fig. 6. P concentration in representative ZTLs installed in switchgrass plots.
extremely high P concentrations appeared in the soil solutions, one in the solution collected from GS0R2 on June 8, 1994 (5.78 mg L\(^{-1}\)) and the other in the solution collected from GS1R2 on August 1, 1994 (26.30 mg L\(^{-1}\), not shown in Fig. 6).

**Comparison Among the ZTLs.** Figures 7 and 8 show the mean concentrations of P and their standard deviations in soil solutions collected by ZTLs under poplars and switchgrass, respectively. The mean concentration of P in soil solutions collected from the plots with the same biosolids application rate varied among the blocks. The variation of P concentrations in the soil solutions among blocks with both low and high application rates was large, perhaps because biosolids was not always uniformly applied and there was only one ZTL (with a surface area of 53 cm\(^2\)) in each experimental plot (900 m\(^2\)). Microrelief of the soil surface in the immediate vicinity of each ZTL varied, too, contributing to the variations of P concentrations in soil solutions among blocks with the same application rate. On the other hand, the variability of P concentrations among the blocks without biosolids application (G0, T0) was small.

Figure 9 shows the volume-weighted mean P concentrations of soil solutions in all treatments in 1994 and their standard deviations. A weighted mean P concentration of soil solution in each ZTL, \(C\), was calculated first by using the equation
\[
C = \frac{\sum(C_i \times V_i)}{\sum(V_i)}
\]
where \(C_i\) and \(V_i\) are the P concentration and volume of the individual soil solution collected from a plot ZTL, respectively. Then the weighted mean P concentration of soil solution for a treatment was obtained by averaging the weighted mean P concentrations of the four blocks. Biosolids applications with both low and high rates increased the P concentration in soil solution collected by ZTLs, under both poplars (\(P = 0.16\)) and switchgrass (\(P = 0.12\)).
Fig. 7. Unweighted mean P concentrations of soil solutions in ZTLs installed in switchgrass plots.
Fig. 8. Unweighted mean P concentrations of soil solutions in ZTLs installed in poplar tree plots.
Fig. 9. Weighted mean P concentration of soil solutions collected by ZTLs in 1994 and their standard deviations.
Phosphorus concentrations were greater in soil solutions collected from the low-rate biosolids plots than from high-rate biosolids plots under both poplars and switchgrass treatments. We hypothesize that this may be due to the larger amount of salts applied with the biosolids in high-rate biosolids plots than in low-rate biosolids plots. The larger amount of salts resulted in a higher electrical conductivity in water samples collected from the high-rate biosolids plots than in those from low-rate biosolids plots (data not shown here). Higher electrical conductivity implied a greater ionic strength in the soil solution, which could promote P sorption and limit P desorption (Ryden et al., 1977; Barrow et al., 1980). The same results can also be observed for P concentrations in individual ZTLs (Figs. 5 and 6). Because biosolids was not applied to the switchgrass plots after 1994 and because the amounts of biosolids applied to soils under switchgrass and poplars were not exactly the same before 1993, the P concentrations in soils solutions collected from biosolids-amended switchgrass and poplar plots cannot be strictly compared with each other to reveal the effect of vegetation on P mobility.

**Variation in P Concentrations of Soil Solutions with Depth**

In the summer of 1994, three ZTLs were installed at 15, 35, and 60 cm depths below the soil surface in a switchgrass plot not amended with biosolids. After the installation, soil solution samples were collected from each of the three ZTLs after four rainfall events in 1994. Figure 10 shows the mean P concentrations in soil solutions and their standard deviation. The P concentration in soil solution decreased with increasing depth. Statistically, the P concentrations in soil solutions collected from these three depths were significantly different (\(\alpha = 0.05\)). Marques et al. (1996) observed that P concentration in the soil solution collected by ZTLs remained fairly constant through the profile to a depth of 120 cm of a
Fig. 10. P concentrations in soil solutions collected from different depths and their standard deviations.
forest soil. They found that preferential flow was small and the solution collected had interacted with the soil matrix for a long time. The cracks that formed at the soil surface in the switchgrass plots in our study could transport large volumes of water into the ZTLs, reducing the interaction time between soil and solutes by preferential flow, similar to the findings of Trojan and Linden (1992). However, the longer interaction time between the biosolids and soil with increasing the depth could have increased sorption of P, resulting in the smaller P concentrations in water collected by the deeper ZTLs.

**Total P in Groundwater**

From 1992 to 1997, in both the northwest and southeast wells, the P concentration of groundwater varied without any consistent trend (Fig. 11). Phosphorus concentration in groundwater was not always less in the northwest well than in the southeast well, and the difference in P concentration between the two wells in most cases was small. The average P concentration of groundwater in both wells during the observation period was 0.3 mg L\(^{-1}\). We conclude that the P concentration in groundwater at a depth of about 350 cm was not influenced by six years of biosolids application to the research plots.

**CONCLUSIONS**

The numbers and volumes of soil solution samples collected by ZTLs under switchgrass and poplars were significantly different. More samples and greater volumes of sample were collected in the switchgrass plots. Because the amount of P leached in soil solution was determined by both P concentration and the volume of soil solution, more P was transported by soil solution under switchgrass than under poplars, even though the mean P concentrations in soil solution were not different.
Fig. 11. P concentrations in groundwater from 1992 to 1997.
P concentrations in soil solutions collected by individual ZTLs varied greatly over time, and there was no consistent trend for this variability. P concentrations in the soil solutions collected from the same biosolids treatment varied among blocks, but the variability of P concentration was smaller in the control plots than in the plots amended with biosolids.

P concentrations were smaller in soil solutions collected from control plots under both switchgrass and poplars than in those collected from biosolids amendment plots. But the largest P concentrations under both switchgrass and poplars were found in the soil solutions collected from low-rate biosolids plots rather than from high-rate biosolids plots, no matter whether unweighted or volume-weighted P concentration data were used for the comparison.

P concentrations in soil solutions collected by ZTLs decreased with increasing soil depth. P concentrations were significantly different among the soil solutions collected from 15, 35, and 60 cm depths below the soil surface. P concentrations in groundwater at the research site were not influenced by biosolids application during the period of this study.
FRACTIONATION OF PHOSPHORUS IN A MOLLISOL AMENDED WITH BIOSOLIDS

A paper submitted to Soil Science Society of America Journal
Yaobing Sui, Michael L. Thompson, Chao Shang

ABSTRACT

Information about soil P fractions is useful to predict the bioavailability of P in soil as well as to predict the likelihood of its transport. In this study, we used a sequential fractionation procedure to investigate the forms of P in a Mollisol amended at the soil surface with biosolids, i.e., anaerobically digested sewage sludge. Soil samples from three depths (0–5, 5–20, and 20–35 cm) were collected from a Cumulic Vertic Endoaquoll in a field experiment with three biosolids application rates, two vegetation treatments (poplars and switchgrass), and four replications per treatment. The Hedley fractionation scheme (dividing soil P into six empirical fractions [water soluble, NaHCO₃-soluble inorganic and organic P, NaOH-soluble inorganic and organic P; HCl-soluble P, and residual P]) was employed. After six years of continuous application of biosolids to poplar plots, the absolute concentrations of all P fractions at the 0–5-cm depth increased significantly (P<0.05). Some P fractions at the 5–20-cm depth increased significantly, whereas at the 20–35-cm depth, none of the fractions was affected by biosolids amendment. At the 0–5-cm depth of both poplar tree and switchgrass plots the relative concentrations of some of the P fractions (e.g., HCl-P, NaOH-OP, and residual-P) decreased rather than increased. Because NaHCO₃-IP and H₂O-P increased in the biosolids-amended soil at rates disproportionate to their concentrations in the biosolids, we hypothesize that HCl-P applied with biosolids was transformed to more labile
forms as a result of the complementary effect of a relatively low pH in the biosolids-amended soil.

INTRODUCTION

To investigate the effects of biosolids amendments, i.e., anaerobically digested sewage sludge, on forms of soil P, we would prefer to identify and quantify individual P compounds in biosolids and in soil. But because the chemistry of soil P is so complex, it is almost impossible to identify individual P compounds. Instead, classes of soil P compounds are often defined functionally by the extractants that remove them from soil material in a sequential fractionation scheme. Sequential fractionation procedures are based on the assumption that chemical extractants selectively dissolve discrete groups of P compounds, and such operationally defined soil P fractions are subject to broad interpretations.

Nevertheless, the information obtained from P fractionation schemes has been useful for interpretations of soil development (Walker and Syers, 1976; Smeck, 1973, 1985; Cross and Schlesinger, 1995; Nair et al., 1995) as well as plant availability of P (Tiessen and Moir, 1993; Cox et al., 1997).

Many sequential fractionation strategies have been developed to quantify different forms of P in soils. The method developed by Chang and Jackson (1957), with later modifications such as those of Petersen and Corey (1966) and Williams et al. (1967), has been widely used for investigations of the forms and transformations of soil P, although some problems in interpretation have been cited for this method (Williams and Walker, 1969). Another widely used sequential P-fractionation approach was developed by Hedley et al. (1982). This procedure aims at quantifying plant-available (H$_2$O- or NaHCO$_3$-extractable P),
Ca-associated (HCl-extractable), Fe-oxide- and Al-oxide-associated inorganic P (NaOH-extractable), as well as labile and stable organic P.

Losses of P in surface runoff and by subsurface transport via drainage tile normally occur in water-soluble and sediment-bound forms (Ryden et al., 1973; Sharpley et al., 1995). The extent to which these forms are bioavailable determines the degree to which they can stimulate eutrophication in surface water bodies. Biologically available P has been defined by Sonzogni et al. (1982) as “the amount of inorganic P a P-deficient algal population can utilize over a period of 24 h or longer”. Dorich et al. (1985) and Sharpley et al. (1991) reported that the fraction of P in soil and sediment extracted with 0.1 M NaOH under the conditions of 1000:1 or 500:1 solution:soil ratio and 16 h of shaking was correlated well with algal uptake of P. Sims (1993) has presented a detailed discussion of the importance of P in the soil environment. More information about the forms of P in biosolids-amended soils is needed to assess the environmental consequences of the very high levels of P that can occur in such soils.

Our objectives in this study were (1) to quantitatively document the effects of biosolids amendments on soil P fractions in a Mollisol and (2) to qualitatively investigate transformations among soil P fractions after biosolids application.

MATERIALS AND METHODS

Research Site, Biosolids, and Soil Characteristics

Located on the Skunk River floodplain (about 2 km from the river), the soil in the study area is a fine, smectitic, mesic Cumulic Vertic Endoaquoll. Slope at the site is 0%, and groundwater depth is normally about 3.5 m. Before biosolids amendments began, the surface horizon of the soil was sampled at eight locations in the research plots. In the upper 30 cm at
those sites, the particle size distribution [determined by the pipette method of Gee and Bauder (1986)] was $216 \pm 42 \text{ g kg}^{-1}$ sand, $372 \pm 26 \text{ g kg}^{-1}$ silt, and $412 \pm 48 \text{ g kg}^{-1}$ clay.

The study was designed as a randomized complete-block experiment with four blocks and three biosolids treatments. Two types of vegetation, hybrid poplar-cottonwood trees (*Populus × euramericana* – clone NC-5326) and switchgrass (*Panicum virgatum* L.), were planted adjacent to each other in strips in each block in 1990. Three biosolids treatments included a control (no biosolids applied), a low biosolids application rate, and a high biosolids application rate (see rate details in a later paragraph).

Biosolids produced by the Ames Water Pollution Control Facility (Ames, Iowa) was sprayed as a suspension (~5% solids) on the soil surface with large application trucks. Because the vegetation was permanent, no tillage was used to incorporate the biosolids into the soil. The average amount of biosolids annually applied to switchgrass plots from 1991 to 1993 was $8.4 \text{ Mg (dry matter) ha}^{-1}$ for the low biosolids application rate and $14.6 \text{ Mg ha}^{-1}$ for the high biosolids application rate. After 1993, biosolids application to switchgrass was stopped because the switchgrass had limited tolerance to the highest application rate and to the heavy wheel traffic that occurred during biosolids application.

The average amount of biosolids annually applied to poplar tree plots from 1991 to 1996 was $6.4 \text{ Mg ha}^{-1}$ for the low biosolids application rate and $11.5 \text{ Mg ha}^{-1}$ for the high biosolids application rate. Dry matter in the biosolids ranged from 3.2 to 5.5%, and pH ranged from 7.2 to 7.6. The range of total P in the dry matter was 1.7 to 3.2%, and the calculated amounts of P applied in the biosolids are given in Table 1. These analyses of the biosolids were supplied to us by the Environmental Protection Agency–certified laboratory at the Ames Water Pollution Control Facility.
Table 1. Annual amounts of biosolids and P applied to poplar and switchgrass plots

<table>
<thead>
<tr>
<th>Year</th>
<th>Dry Matter Applied</th>
<th>P Applied</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Poplar Low</td>
<td>High</td>
</tr>
<tr>
<td>1991</td>
<td>8.3</td>
<td>17.2</td>
</tr>
<tr>
<td>1992</td>
<td>4.1</td>
<td>8.8</td>
</tr>
<tr>
<td>1993</td>
<td>11.1</td>
<td>19.9</td>
</tr>
<tr>
<td>1994</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>1995</td>
<td>3.9</td>
<td>7.8</td>
</tr>
<tr>
<td>1996</td>
<td>8.3</td>
<td>12.4</td>
</tr>
<tr>
<td>Mean</td>
<td>6.4</td>
<td>11.5</td>
</tr>
</tbody>
</table>

′NA = no application
We conducted two sampling campaigns in the fall of 1996. First, soil samples were collected at depths of 0-5 and 5-25 cm within each experimental plot (15 x 60 m). Four subsamples from the same depth were collected on a grid pattern in each plot and mixed to form a composite sample from that plot. The samples were air-dried and ground to pass a 2-mm sieve, and organic C and total N were determined by dry combustion with a CHN analyzer (Leco Corp., St. Joseph, MI). Total P was measured after digestion with H₂SO₄-H₂O₂-HF (Bowman, 1988). Soil pH was measured in a 1:1 soil:water suspension. For the P fractionation study reported in this paper, soil samples were also collected from the research plots at depths of 0–5, 5–20, and 20–35 cm. A procedure similar to that previously described was used to collect and composite soil samples from each plot.

**Sequential Fractionation of Soil P**

A modification of the methods of Hedley et al. (1982) and Tiessen and Moir (1993) was selected in this study to extract empirically defined pools of P. A diagrammatic representation of this scheme is given in Fig 1. A 0.5-g air-dried, <2-mm soil sample was placed in a 50-ml centrifuge tube and was sequentially extracted with 30 ml each of deionized water, 0.5 M NaHCO₃ (pH=8.2), 0.1 M NaOH, and 1 M HCl. Each extraction ran for 16 hr of end-to-end shaking. After each extraction, the tubes were centrifuged at 26,860 g for 15 min at 5°C. Then the supernatant was passed through a 0.2-µm filter. After the final extraction, residual P was determined in the soil material left in the centrifuge tubes by extraction with H₂SO₄-H₂O₂ (Tiessen and Moir, 1993). The procedure was performed in duplicate on each composite sample from each replication. Phosphorus in a sample of biosolids collected at the treatment facility was fractionated with the same procedure for comparison (Table 2).
Fig. 1. Sequential P fractionation scheme, modified from Hedley et al. (1982).
Table 2. Fractionation of P in a sample of biosolids from the Ames Water Pollution Control Facility

<table>
<thead>
<tr>
<th></th>
<th>H₂O-P</th>
<th>NaHCO₃-IP</th>
<th>NaHCO₃-OP</th>
<th>NaOH-IP</th>
<th>NaOH-OP</th>
<th>HCl-P</th>
<th>Residual-P</th>
<th>Total P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg P kg⁻¹ freeze-dried biosolids</td>
<td>mg P kg⁻¹ freeze-dried biosolids</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>-------</td>
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<td>---------</td>
</tr>
<tr>
<td>H₂O-P</td>
<td>238</td>
<td>2,326</td>
<td>137</td>
<td>7,509</td>
<td>863</td>
<td>6,852</td>
<td>4,165</td>
<td>22,090</td>
</tr>
<tr>
<td>(1%)</td>
<td>(11%)</td>
<td>(1%)</td>
<td>(33%)</td>
<td>(4%)</td>
<td>(31%)</td>
<td>(19%)</td>
<td>(100%)</td>
<td></td>
</tr>
</tbody>
</table>


Our procedure differed from the standard Hedley fractionation procedure in that we used H₂O as the first extractant instead of equilibrating the soil sample with an anion exchange resin. We found in a preliminary study that an anion exchange resin was not required to extract detectable levels of labile P from the soil samples of our study. This fraction is intended to represent the most labile P in the soil, and we believe that P in the H₂O extract would be more closely related to bioavailable P in surface runoff from a soil than would resin-exchanged P.

**Analytical Methods**

Total P in the filtrates of the NaHCO₃ and NaOH extracts was determined by digesting aliquots of those filtrates in an autoclave at 103.5 kPa and 121°C (60 min for the NaHCO₃ extract and 90 min for NaOH extract) with acidified ammonium persulfate (Method 4500-PB5) (Greenberg et al., 1992). Orthophosphate P in the initial filtrates and in the digests of each soil extract was determined colorimetrically by using the method of Murphy and Riley (1962). Absorbance was determined at a wavelength of 712 nm. The difference between total P and inorganic P in the extracts represents organic P. The data were statistically analyzed using the General Linear Model Procedure of SAS Institute (1989). Differences in each P fraction among the three biosolids treatments were examined by a standard analysis of variance procedure, with means separation by Tukey’s procedure.

**RESULTS AND DISCUSSION**

After six years of biosolids amendments, organic C, total N, and total P had increased significantly and pH had decreased significantly in the upper 5 cm of the amended plots (Table 3). The differences between the biosolids-amended and unamended soil were most pronounced in the poplar plots, because these plots received biosolids fully three years longer
Table 3. Total P in soil from 1992 to 1996, calculated with the data of blocks 1 and 2 from 1992 to 1995 and with the data of all 4 blocks in 1996.

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Total Soil P</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>cm</td>
<td>mg kg⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T0</td>
<td>0-5</td>
<td>694</td>
<td>880</td>
<td>870</td>
<td>879</td>
<td>873</td>
</tr>
<tr>
<td>T1</td>
<td>0-5</td>
<td>976</td>
<td>1446</td>
<td>1199</td>
<td>1506</td>
<td>1840</td>
</tr>
<tr>
<td>T2</td>
<td>0-5</td>
<td>1248</td>
<td>2177</td>
<td>1284</td>
<td>2667</td>
<td>3265</td>
</tr>
<tr>
<td>T0</td>
<td>5-25</td>
<td>625</td>
<td>590</td>
<td>626</td>
<td>640</td>
<td>570</td>
</tr>
<tr>
<td>T1</td>
<td>5-25</td>
<td>720</td>
<td>630</td>
<td>728</td>
<td>729</td>
<td>735</td>
</tr>
<tr>
<td>T2</td>
<td>5-25</td>
<td>679</td>
<td>731</td>
<td>701</td>
<td>800</td>
<td>847</td>
</tr>
<tr>
<td>G0</td>
<td>0-5</td>
<td>ND</td>
<td>685</td>
<td>703</td>
<td>651</td>
<td>603</td>
</tr>
<tr>
<td>G1</td>
<td>0-5</td>
<td>ND</td>
<td>1179</td>
<td>1326</td>
<td>1431</td>
<td>1064</td>
</tr>
<tr>
<td>G2</td>
<td>0-5</td>
<td>ND</td>
<td>2335</td>
<td>2821</td>
<td>2184</td>
<td>2216</td>
</tr>
<tr>
<td>G0</td>
<td>5-25</td>
<td>ND</td>
<td>637</td>
<td>593</td>
<td>598</td>
<td>500</td>
</tr>
<tr>
<td>G1</td>
<td>5-25</td>
<td>ND</td>
<td>719</td>
<td>674</td>
<td>689</td>
<td>639</td>
</tr>
<tr>
<td>G2</td>
<td>5-25</td>
<td>ND</td>
<td>778</td>
<td>720</td>
<td>687</td>
<td>642</td>
</tr>
</tbody>
</table>

¹T = poplar tree and G = switchgrass; 0 = zero application, 1 = low biosolids application rate, and 2 = high biosolids application rate. ²For a given depth increment and vegetation, data with same letter in a column are not significantly different at 0.05 significant level. ³ND = not determined.
than did the switchgrass plots. The addition of biosolids increased organic C, total N, and
total P at the depth of 5–25 cm in the poplar plots, too, but there was no statistical difference
between the plots receiving the two application rates. Application of biosolids had no effect
on the pH of the poplar plots at 5–25 cm. Similarly, at the 5–25-cm depth in the switchgrass
plots, there was no statistically discernible effect of three years of biosolids application on
any of the measured parameters.

Total P in the upper 5 cm of the soil of our study increased to levels as great as 2,833
mg kg\(^{-1}\) in the poplar plots and 1,913 mg kg\(^{-1}\) in the switchgrass plots that received the high
rate of biosolids. The low rate of biosolids application corresponded approximately to the
“agronomic rate” of biosolids application, defined by the content of plant-available N in the
biosolids. But even at this application rate, total P in the upper 5 cm of the soil increased to
1,810 mg kg\(^{-1}\) in the poplar plots and 1,086 mg kg\(^{-1}\) in the switchgrass plots.

**Absolute Concentrations of P Fractions**

Our main interest in this study was to document how the large amounts of P added to
the soil were distributed into the various fractions of soil P at three depths. At the 0–5-cm
depth in both poplar tree and switchgrass plots, the absolute concentrations of all P fractions
were significantly influenced by biosolids amendments, at least at the high application rate
(Tables 4 and 5). In contrast, at the deepest sampling increment (20–35-cm) of both
vegetation treatments, none of the P fractions was substantially affected by biosolids
application. At the intermediate soil depth sampled (5–20 cm), the influence of biosolids
amendments was variable. For example, at the 5–20-cm depth of poplar tree plots, the
absolute concentrations of all *inorganic* P fractions increased after biosolids applications,
although some of the increases were not statistically significant. In the switchgrass plots, the
Table 4. Absolute concentrations of soil P fractions in poplar plots

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Depth</th>
<th>H$_2$O-P</th>
<th>NaHCO$_3$-IP</th>
<th>NaHCO$_3$-OP</th>
<th>NaOH-IP</th>
<th>NaOH-OP</th>
<th>HCl-P</th>
<th>Residual P</th>
<th>Total P (sum)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T0</td>
<td>0-5</td>
<td>21a$^d$</td>
<td>91a</td>
<td>23a</td>
<td>104a</td>
<td>124a</td>
<td>157a</td>
<td>146a</td>
<td>666a</td>
</tr>
<tr>
<td>T1</td>
<td>0-5</td>
<td>111b</td>
<td>319b</td>
<td>39ab</td>
<td>363a</td>
<td>315a</td>
<td>314b</td>
<td>203a</td>
<td>1664b</td>
</tr>
<tr>
<td>T2</td>
<td>0-5</td>
<td>165b</td>
<td>479c</td>
<td>47b</td>
<td>928b</td>
<td>483a</td>
<td>530c</td>
<td>216a</td>
<td>2848c</td>
</tr>
<tr>
<td>T0</td>
<td>5-20</td>
<td>3a</td>
<td>23a</td>
<td>24a</td>
<td>59a</td>
<td>98a</td>
<td>114a</td>
<td>136a</td>
<td>457a</td>
</tr>
<tr>
<td>T1</td>
<td>5-20</td>
<td>15ab</td>
<td>62ab</td>
<td>23a</td>
<td>100b</td>
<td>101a</td>
<td>137b</td>
<td>152a</td>
<td>590b</td>
</tr>
<tr>
<td>T2</td>
<td>5-20</td>
<td>19b</td>
<td>89b</td>
<td>26a</td>
<td>127b</td>
<td>99a</td>
<td>158c</td>
<td>157a</td>
<td>675b</td>
</tr>
<tr>
<td>T0</td>
<td>20-35</td>
<td>2a</td>
<td>8a</td>
<td>21a</td>
<td>33a</td>
<td>67a</td>
<td>80a</td>
<td>148a</td>
<td>359a</td>
</tr>
<tr>
<td>T1</td>
<td>20-35</td>
<td>4a</td>
<td>24a</td>
<td>20a</td>
<td>54a</td>
<td>83a</td>
<td>110a</td>
<td>155a</td>
<td>450a</td>
</tr>
<tr>
<td>T2</td>
<td>20-35</td>
<td>3a</td>
<td>17a</td>
<td>24a</td>
<td>47a</td>
<td>77a</td>
<td>106a</td>
<td>165a</td>
<td>439a</td>
</tr>
</tbody>
</table>

$^d$Data are the means of four replications. T = poplar; 0 = zero application, 1 = low biosolids application rate, and 2 = high biosolids application rate. $^4$Data with same letter in a column at the same depth are not significantly different at 0.05 significant level.
Table 5. Absolute concentrations of soil P fractions in switchgrass plots

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Depth</th>
<th>H2O-P</th>
<th>NaHCO$_3$</th>
<th>NaHCO$_3$</th>
<th>NaOH</th>
<th>NaOH</th>
<th>HCl-P</th>
<th>Residual P</th>
<th>Total P</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G0</td>
<td>0-5</td>
<td>9a</td>
<td>50a</td>
<td>19a</td>
<td>84a</td>
<td>98a</td>
<td>189a</td>
<td>274a</td>
<td>723a</td>
</tr>
<tr>
<td>G1</td>
<td>0-5</td>
<td>38b</td>
<td>135b</td>
<td>30a</td>
<td>193a</td>
<td>164a</td>
<td>238a</td>
<td>300ab</td>
<td>1098a</td>
</tr>
<tr>
<td>G2</td>
<td>0-5</td>
<td>76c</td>
<td>295b</td>
<td>52b</td>
<td>595b</td>
<td>209a</td>
<td>429b</td>
<td>382b</td>
<td>2038b</td>
</tr>
<tr>
<td>G0</td>
<td>5-20</td>
<td>5a</td>
<td>44a</td>
<td>28a</td>
<td>68a</td>
<td>107a</td>
<td>166a</td>
<td>200a</td>
<td>618a</td>
</tr>
<tr>
<td>G1</td>
<td>5-20</td>
<td>9a</td>
<td>47a</td>
<td>25a</td>
<td>78a</td>
<td>112a</td>
<td>144a</td>
<td>199a</td>
<td>614a</td>
</tr>
<tr>
<td>G2</td>
<td>5-20</td>
<td>16a</td>
<td>78a</td>
<td>26a</td>
<td>98a</td>
<td>119a</td>
<td>181a</td>
<td>213a</td>
<td>731a</td>
</tr>
<tr>
<td>G0</td>
<td>20-35</td>
<td>3a</td>
<td>23a</td>
<td>12a</td>
<td>35a</td>
<td>76a</td>
<td>135a</td>
<td>195a</td>
<td>479a</td>
</tr>
<tr>
<td>G1</td>
<td>20-35</td>
<td>3a</td>
<td>22a</td>
<td>16a</td>
<td>37a</td>
<td>79a</td>
<td>109a</td>
<td>186a</td>
<td>452a</td>
</tr>
<tr>
<td>G2</td>
<td>20-35</td>
<td>3a</td>
<td>24a</td>
<td>15a</td>
<td>40a</td>
<td>81a</td>
<td>129a</td>
<td>204a</td>
<td>496a</td>
</tr>
</tbody>
</table>

Data are the means of four replications. G = switchgrass; 0 = zero application, 1 = low biosolids application rate, and 2 = high biosolids application rate. Data with same letter in a column from the same depth are not different at 0.05 significant level.
absolute concentrations of P fractions at the 5–20-cm depth increased slightly in the biosolids-amended plots, but none of the increases was significant, according to the standard analysis of variance procedure.

*Organic* P fractions (extracted by NaHCO₃ and NaOH) at the 5–20-cm depth tended to increase with the level of biosolids amendment, but the increases were not statistically significant (Tables 4 and 5). Several studies (Hannapel et al., 1964; Frossard et al., 1989; Eghball et al., 1996; Chardon et al., 1997) have reported that the translocation of organic P fractions can contribute to the transport of P in soil. But in our study, the concentration of organic forms of P in the biosolids was small, and we cannot unequivocally conclude that downward movement of organic P fractions occurred. It is likely that some of the increases in organic P forms in our study were indirectly related to biosolids additions through the stimulation of plant growth, root development, and other biological activity in the soil that comes with large additions of C and N.

Our results are similar to those of Sharpley and Smith (1995), who studied forms of P in soils that had received large amounts of animal manures over periods as long as 30 years. They also reported that the inorganic forms of P increased more than did the organic forms of P in the surface horizons of the soils. They found that the quantity of HCl-extractable P increased the most, whereas our results indicate that NaOH-IP was dominant in the biosolids-amended soils. In our soils, NaOH-OP also increased to levels generally much higher than those reported by Sharpley and Smith (1995). Their study differs from ours in that the manure had been incorporated into the soil during the production of agronomic crops, whereas there was no tillage at our site.
Poplar and switchgrass plots differed considerably in the amounts of labile P (H₂O-soluble and NaHCO₃-soluble) that occurred at the 0–5-cm depths. This difference was especially evident in the control plots where labile P was more concentrated at the surface of the tree plots than the switchgrass plots. Switchgrass roots were abundant very close to the soil surface, and as a result bioavailable P at that depth was probably taken up more effectively than in the poplar plots. In the plots amended with biosolids, translocation of labile P may have occurred more readily in the poplar plots because intercepting roots were less abundant near the surface than they were in the switchgrass plots.

Regression Analyses

We used a linear regression analysis to define the relationship between the absolute concentration of a soil P fraction and the amount of P applied with the biosolids. As shown in Table 6, at the 0–5-cm depth in both poplar and switchgrass plots, concentrations of several P fractions were linearly related to the cumulative amount of P added with biosolids amendments (P<0.05). For the poplar plots, the linear relationships between the fractions of H₂O-P and NaHCO₃-IP and the amount of P applied with biosolids were very significant (P<0.001).

In the linear models of Table 6, the slope of each equation reflects the increase in the concentration of a soil P fraction with each increment of P applied with biosolids. So, the greater the slope, the greater was the rate of increase for a particular fraction of P. At the 0–5-cm depth in the poplar plots, the order of the rates of increase in concentrations of P fractions was NaOH-IP > NaHCO₃-IP ≈ HCl-P > NaOH-OP > H₂O-P > residual-P > NaHCO₃-OP. At the 0–5-cm depth in switchgrass plots, the order of the rates was identical, except that the H₂O-soluble fraction did not increase as rapidly as the residual fraction of P.
Table 6. Linear regression expressions that describe the change in concentration of each P fraction at 0–5-cm depth (Y) as a function of cumulative P added in biosolids (X).

<table>
<thead>
<tr>
<th>Treatment and fraction</th>
<th>Linear regression expression</th>
<th>$R^2$</th>
<th>Level of significance$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Poplar</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_2O\text{-}P$</td>
<td>$Y = 0.09X + 23$</td>
<td>0.92</td>
<td>***</td>
</tr>
<tr>
<td>$NaHCO_3\text{-}IP$</td>
<td>$Y = 0.24X + 93$</td>
<td>0.92</td>
<td>***</td>
</tr>
<tr>
<td>$NaHCO_3\text{-}OP$</td>
<td>$Y = 0.01X + 24$</td>
<td>0.81</td>
<td>*</td>
</tr>
<tr>
<td>$NaOH\text{-}IP$</td>
<td>$Y = 0.50X + 45$</td>
<td>0.64</td>
<td>*</td>
</tr>
<tr>
<td>$NaOH\text{-}OP$</td>
<td>$Y = 0.18X + 131$</td>
<td>0.61</td>
<td>*</td>
</tr>
<tr>
<td>$HCl$</td>
<td>$Y = 0.23X + 142$</td>
<td>0.84</td>
<td>**</td>
</tr>
<tr>
<td>Residual P</td>
<td>$Y = 0.04X + 24$</td>
<td>0.80</td>
<td>*</td>
</tr>
<tr>
<td><strong>Switchgrass</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_2O\text{-}P$</td>
<td>$Y = 0.06X + 6$</td>
<td>0.92</td>
<td>***</td>
</tr>
<tr>
<td>$NaHCO_3\text{-}IP$</td>
<td>$Y = 0.23X + 34$</td>
<td>0.89</td>
<td>***</td>
</tr>
<tr>
<td>$NaHCO_3\text{-}OP$</td>
<td>$Y = 0.03X + 17$</td>
<td>0.58</td>
<td>NS</td>
</tr>
<tr>
<td>$NaOH\text{-}IP$</td>
<td>$Y = 0.47X + 32$</td>
<td>0.76</td>
<td>**</td>
</tr>
<tr>
<td>$NaOH\text{-}OP$</td>
<td>$Y = 0.11X + 99$</td>
<td>0.67</td>
<td>*</td>
</tr>
<tr>
<td>$HCl$</td>
<td>$Y = 0.22X + 164$</td>
<td>0.67</td>
<td>*</td>
</tr>
<tr>
<td>Residual P</td>
<td>$Y = 0.10X + 263$</td>
<td>0.68</td>
<td>*</td>
</tr>
</tbody>
</table>

$^+ n = 12$, i.e., 4 replications in each of 3 levels of biosolids
$^+ *P < 0.001, **P < 0.01, *P < 0.05, NS P > 0.05.$
These rates of increase reflect the dominance of inorganic P in the biosolids (Table 2). But the relatively large rate of increase in NaHCO₃-IP is not consistent with its abundance in the biosolids and suggests that its concentration may have increased as a result of direct transformation from other P forms.

At the 5–20-cm depth in the poplar tree plots, the order of the rate increases in concentrations of P fractions was NaOH-IP = NaHCO₃-IP > HCl-P > H₂O-P = Residual-P > NaHCO₃-OP (Table 7). At the 5–20-cm depth in switchgrass plots, the order of increase in absolute concentrations of P was NaOH-IP = NaHCO₃-IP > HCl-P = NaOH-OP = H₂O-P = Residual-P = NaHCO₃-OP (Table 7). The rates of increases of all P fractions were less at the 5–20-cm depth than at the 0–5-cm depth. For example, in poplar plots the rates of increase in H₂O-P and NaHCO₃-IP at the 0-5 cm depth were 9-and 6-fold, respectively, those at the 5–20-cm depth.

Therefore, the effect of biosolids amendments on soil P fractions at the 5–20-cm depth can be interpreted differently, depending on which statistic is used. The standard analysis of variance for the 5–20-cm depths indicated that the absolute concentrations of all P fractions in switchgrass plots and of some fractions in poplar tree plots were not significantly increased by biosolids application (P>0.05) (Tables 4 and 5). On the other hand, regression analysis indicated that, although the concentration increases were small, biosolids amendments did increase most of the P fractions (P<0.05) at a linear rate at the 5-20 cm depth in both poplar and switchgrass plots (Table 7).

Transformations of P Applied with Biosolids

Because the portion of applied biosolids captured by the litter layer and not mixed with the underlying soil in the plots is unknown, our data do not allow us to quantify
Table 7. Linear regression expressions that describe the change in concentration of each P fraction at 5-20 cm depth (Y) as a function of cumulative P added in biosolids (X).

<table>
<thead>
<tr>
<th>Treatment and fraction</th>
<th>Linear regression expression</th>
<th>$R^2$</th>
<th>Level of significance$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Poplar</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_2O$-P</td>
<td>$Y = 0.01X + 4$</td>
<td>0.77</td>
<td>*</td>
</tr>
<tr>
<td>NaHCO$_3$-IP</td>
<td>$Y = 0.04X + 24$</td>
<td>0.86</td>
<td>**</td>
</tr>
<tr>
<td>NaHCO$_3$-OP</td>
<td>$Y = 0.00X + 23$</td>
<td>0.58</td>
<td>NS</td>
</tr>
<tr>
<td>NaOH-IP</td>
<td>$Y = 0.04X + 60$</td>
<td>0.88</td>
<td>**</td>
</tr>
<tr>
<td>NaOH-OP</td>
<td>$Y = 0.00X + 99$</td>
<td>0.42</td>
<td>NS</td>
</tr>
<tr>
<td>HCl</td>
<td>$Y = 0.03X + 113$</td>
<td>0.95</td>
<td>***</td>
</tr>
<tr>
<td>Residual P</td>
<td>$Y = 0.01X + 138$</td>
<td>0.72</td>
<td>*</td>
</tr>
<tr>
<td><strong>Switchgrass</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_2O$-P</td>
<td>$Y = 0.01X + 6$</td>
<td>0.62</td>
<td>*</td>
</tr>
<tr>
<td>NaHCO$_3$-IP</td>
<td>$Y = 0.03X + 39$</td>
<td>0.67</td>
<td>*</td>
</tr>
<tr>
<td>NaHCO$_3$-OP</td>
<td>$Y = 0.00X + 27$</td>
<td>0.28</td>
<td>NS</td>
</tr>
<tr>
<td>NaOH-IP</td>
<td>$Y = 0.03X + 99$</td>
<td>0.43</td>
<td>NS</td>
</tr>
<tr>
<td>NaOH-OP</td>
<td>$Y = 0.01X + 109$</td>
<td>0.81</td>
<td>**</td>
</tr>
<tr>
<td>HCl</td>
<td>$Y = 0.01X + 157$</td>
<td>0.67</td>
<td>*</td>
</tr>
<tr>
<td>Residual P</td>
<td>$Y = 0.01X + 198$</td>
<td>0.96</td>
<td>***</td>
</tr>
</tbody>
</table>

$^+ n = 12$, i.e., 4 replications in each of 3 levels of biosolids

$^* P < 0.001$, $** P < 0.01$, $* P < 0.05$, $NS P > 0.05$
transformations of P fractions applied with biosolids. But changes in the relative concentrations of soil P fractions (i.e., the proportion of each fraction in the total amount of P) at the 0–5 and 5–20-cm depths in both poplar and switchgrass plots suggest that transformation of P did occur concomitant with biosolids amendments (Tables 8 and 9). If there had been no transformation of biosolids-applied P from one fraction to another, then we might expect that a large amount of a given P fraction in the biosolids would increase the proportion of that fraction of P in the amended soil. For example, the relative concentrations of NaOH-IP and HCl-P were high in the biosolids (Table 2). Thus the proportion of NaOH-IP and HCl-P at the 0–5-cm depth of the biosolids-amended plots might be expected to increase in comparison to the control plots.

Indeed, the relative concentration of NaOH-IP did increase, but the proportion of HCl-P at the 0–5-cm depth of soil amended with biosolids in both poplar tree and switchgrass plots decreased (Tables 8 and 9). At the same time, the relative concentration of NaHCO₃-IP at the 0–5-cm depth of plots amended at the high rate of biosolids application increased from 14% to 17% in poplar plots and from 7% to 14% in switchgrass plots. Similarly, the relative concentration of H₂O-P at the 0–5-cm depth of plots amended at the high rate of biosolids application increased from 3% to 7% and from 1% to 4% in poplar and switchgrass plots, respectively. In the poplar plots, the relative concentration of H₂O-P also increased at the 5–20-cm depth.

We hypothesize that HCl-P in biosolids was dissolved and transformed into other P fractions, especially NaHCO₃-IP and H₂O-P. Soil pH may have influenced the transformation of biosolids-applied HCl-P into other P fractions. Although the pH of the applied biosolids was relatively high (7.2–7.6), soil pH at the 0–5-cm depth, after 6 years of biosolids
Table 8. Relative concentration of P fractions in poplar tree plots.

<table>
<thead>
<tr>
<th>Treatment†</th>
<th>Depth</th>
<th>H2O-P</th>
<th>NaHCO3-IP</th>
<th>NaHCO3-OP</th>
<th>NaOH-IP</th>
<th>NaOH-OP</th>
<th>HCl-P</th>
<th>Residual P</th>
</tr>
</thead>
<tbody>
<tr>
<td>T0</td>
<td>0-5</td>
<td>3</td>
<td>14</td>
<td>3</td>
<td>16</td>
<td>19</td>
<td>23</td>
<td>22</td>
</tr>
<tr>
<td>T1</td>
<td>0-5</td>
<td>7</td>
<td>19</td>
<td>2</td>
<td>22</td>
<td>19</td>
<td>19</td>
<td>12</td>
</tr>
<tr>
<td>T2</td>
<td>0-5</td>
<td>6</td>
<td>17</td>
<td>2</td>
<td>32</td>
<td>17</td>
<td>19</td>
<td>7</td>
</tr>
<tr>
<td>T0</td>
<td>5-20</td>
<td>1</td>
<td>5</td>
<td>5</td>
<td>13</td>
<td>21</td>
<td>25</td>
<td>30</td>
</tr>
<tr>
<td>T1</td>
<td>5-20</td>
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<td>10</td>
<td>4</td>
<td>17</td>
<td>17</td>
<td>23</td>
<td>26</td>
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<tr>
<td>T2</td>
<td>5-20</td>
<td>3</td>
<td>13</td>
<td>4</td>
<td>19</td>
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<td>1</td>
<td>2</td>
<td>6</td>
<td>9</td>
<td>19</td>
<td>22</td>
<td>41</td>
</tr>
<tr>
<td>T1</td>
<td>20-35</td>
<td>1</td>
<td>5</td>
<td>5</td>
<td>12</td>
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<td>35</td>
</tr>
<tr>
<td>T2</td>
<td>20-35</td>
<td>1</td>
<td>4</td>
<td>5</td>
<td>11</td>
<td>18</td>
<td>24</td>
<td>37</td>
</tr>
</tbody>
</table>

†T = poplar tree; 0 = zero application, 1 = low biosolids application rate, and 2 = high biosolids application rate.
Table 9. Relative concentration of P fractions in switchgrass plots

<table>
<thead>
<tr>
<th>Treatment†</th>
<th>Depth cm</th>
<th>H₂O-P</th>
<th>NaHCO₃-IP</th>
<th>NaHCO₃-OP</th>
<th>NaOH-IP</th>
<th>NaOH-OP</th>
<th>HCl-P</th>
<th>Residual P</th>
</tr>
</thead>
<tbody>
<tr>
<td>G0</td>
<td>0-5</td>
<td>1</td>
<td>7</td>
<td>3</td>
<td>12</td>
<td>13</td>
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<td>38</td>
</tr>
<tr>
<td>G1</td>
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<td>12</td>
<td>3</td>
<td>18</td>
<td>15</td>
<td>22</td>
<td>27</td>
</tr>
<tr>
<td>G2</td>
<td>0-5</td>
<td>4</td>
<td>14</td>
<td>3</td>
<td>29</td>
<td>10</td>
<td>21</td>
<td>19</td>
</tr>
<tr>
<td>G0</td>
<td>5-20</td>
<td>1</td>
<td>7</td>
<td>5</td>
<td>11</td>
<td>17</td>
<td>27</td>
<td>32</td>
</tr>
<tr>
<td>G1</td>
<td>5-20</td>
<td>1</td>
<td>8</td>
<td>4</td>
<td>13</td>
<td>18</td>
<td>24</td>
<td>32</td>
</tr>
<tr>
<td>G2</td>
<td>5-20</td>
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<td>13</td>
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</tr>
<tr>
<td>G0</td>
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<td>5</td>
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<td>7</td>
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<td>27</td>
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</tr>
<tr>
<td>G1</td>
<td>20-35</td>
<td>1</td>
<td>5</td>
<td>4</td>
<td>8</td>
<td>17</td>
<td>24</td>
<td>41</td>
</tr>
<tr>
<td>G2</td>
<td>20-35</td>
<td>1</td>
<td>5</td>
<td>3</td>
<td>8</td>
<td>16</td>
<td>26</td>
<td>41</td>
</tr>
</tbody>
</table>

†G = switchgrass; 0 = zero application, 1 = low biosolids application rate, and 2 = high biosolids application rate.
amendments at the high rate, had decreased from 6.2 to 5.0 under poplar and to 5.8 under switchgrass. These declines in pH values of the biosolids-amended soils most likely occurred when NH₄⁺-N and organic N applied in the biosolids were oxidized to NO₃⁻. We suggest that the relatively low soil pH favored conversion of the biosolids-applied HCl-P into more labile forms that could be more easily translocated to the 5–20-cm depth.

Another interpretation is possible: The large addition of nutrients in the biosolids could have stimulated biological activity in the soil sufficiently that the increase in labile forms of P originated not directly from dissolution of HCl-P but from mineralization of organic forms of P. We reject this alternative, reasoning from the model of McGill and Cole (1981) that significant release of inorganic P from organic matter in the soil occurs only when the supply of inorganic P is limited. Such was certainly not the case in the soils of this study.

**CONCLUSIONS**

The effect of biosolids amendments on soil P fractions was greater at the soil surface where biosolids was applied than it was deeper in the soil. After 6 years of continuous biosolids applications to poplar plots and after 3 years of biosolids applications to switchgrass plots, the absolute concentrations of all P fractions at the 0–5-cm depth increased. Concentrations of inorganic P fractions (NaOH-IP, NaHCO₃-IP, HCl-P) increased the most as a result of biosolids amendments. At the 5–20-cm depth in poplar tree plots, H₂O-P, NaHCO₃-IP, NaOH-IP, and HCl-P were significantly increased by biosolids amendments. On the other hand, at the 20–35-cm depth of both poplar tree and switchgrass plots, none of the soil P fractions was influenced by biosolids amendments during the period of our study.
At the 0–5-cm depth of both poplar tree and switchgrass plots the relative concentrations of all P fractions except NaHCO$_3$-OP changed after the biosolids amendments. The relative concentrations of NaOH-OP, HCl-P, and residual-P decreased, whereas those of H$_2$O-P, NaHCO$_3$-IP, and NaOH-P increased after the biosolids amendments. At the 5–20-cm depth of the poplar plots, the relative concentrations of all P fractions except NaHCO$_3$-OP changed after the biosolids amendment, and the trends were similar to those at the 0–5-cm depth. We hypothesize that HCl-P applied with biosolids was transformed to more labile forms (NaHCO$_3$-IP and H$_2$O-P) as a result of the relatively low pH of the biosolids-amended soil. This suggests that careful management of pH in biosolids-amended soils may be important to prevent the accumulation of bioavailable forms of P that might otherwise threaten surface water supplies.
ABSTRACT

When biosolids is applied to a soil, the soluble forms of P in the biosolids interact with the soil and become less soluble. From the agronomic point of view, P becomes less available for plant uptake when strongly retained by soil. But from the environmental point of view, strong retention of P by soil may prevent its loss in runoff water as well as movement to groundwater. In this study, the effects of biosolids amendments on P sorption potential and buffering capacity in a Mollisol were investigated by using sorption isotherm experiments. The P sorption maxima of biosolids-amended soil as well as the binding energies of P sorption were calculated by using the two-surface Langmuir equation. The P equilibrium buffering capacity (PEBC) and equilibrium P concentration (EPC) were obtained from quantity/intensity (Q/I) plots. The effects of sorption period and liquid/solid ratio on P desorption from a soil with and without biosolids applications were also compared. For the wide range of standard P concentrations used in our sorption isotherm experiment, the P sorption potentials of soils decreased after biosolids amendment, even though the calculated maximum P sorption potential was increased by the high rate of biosolids amendment. The addition of biosolids to the soil significantly decreased both the high- and low-affinity bonding energies of P sorption. The PEBC of the soil significantly decreased and the EPC of the soil significantly increased after the biosolids amendments. The effects of extraction time, liquid/solid ratio, and their interaction on the desorption of P from the soils amended with
and without biosolids were not same. The amount of P desorbed from the soil with and without biosolids amendment increased by increasing the liquid/solid ratio and the extraction time. Although the P sorption potential increased in the soil amended with the high rate of biosolids, all the other effects of biosolids amendments on P sorption, and desorption, as well as P buffering capacities, imply a large increase in the P concentration of soil solution. The increase of P in soil solution could enhance the losses of soluble P in runoff water and movement to groundwater by preferential flow.

INTRODUCTION

When a material containing phosphorus is applied to a soil, the soluble forms of P react quickly with the soil to form less soluble components which become increasing insoluble over time (Holford et al., 1997). From the agronomic point of view, P becomes relatively unavailable for plant uptake when soluble P is strongly retained by soil. But from the environmental point of view, strong retention of P by soil may prevent losses of soluble P in runoff water as well as movement to groundwater. Thus, sorption/desorption and precipitation of P as well as P buffering capacities of soils may play an important role in both agronomic and environmental aspects of P.

Sorption of P on soil minerals and organic compounds initially proceeds by a rapid exothermic ligand-exchange reaction with surface groups (Frossard et al., 1995). Following the rapid reaction, slow endothermic reactions such as solid state diffusion (Barrow, 1985). Unfortunately, it is extremely difficult to distinguish precipitation of insoluble phosphate salts from sorption of phosphate. In this paper, we use the term sorption to cover both types of retention mechanisms.
The quantity of P sorbed by a soil will depend on the number of sorption sites in the soil. Al and Fe oxides in soils are the most important components determining the soil sorption capacity (Ellis and Truog, 1954; Holford and Mattingly, 1975a; Parfitt, 1978; Ryan et al., 1984; Hamad et al., 1992; Van der Zee and Van Riemsdijk, 1991). The maximum amount of additional P that might be adsorbed by a soil is a useful value, particularly when the soil already has a high level of P. We refer to this value as the P sorption potential of a soil.

Sorption of P by soil compounds is influenced by many other factors, as well. Bowden et al. (1980) and Barrow et al. (1980) reported that the sorption of P on oxides was influenced by pH and electrolyte. Bowden et al. (1977) showed that the sorption of P on oxides was a function of the electrostatic potential in the plane of adsorption. Organic anions that compete with orthophosphate for sorption sites have been identified (Nagarajah et al., 1970; Kafkafi et al., 1988; Geelhoed et al., 1998). Complexes of humic compounds with Al and Fe may sorb P, too (Levesque, 1969; Borie and Zunino, 1983). The specific surface areas of soil components (Borrero et al., 1988), temperature, and reaction time (Barrow, 1983) also influenced the sorption of P.

Sorption isotherm techniques have been widely used for studying the sorption of P in soils. The data obtained from sorption isotherms can be compared more readily by fitting them to adsorption equations such as the Langmuir, or Freundlich equations. The Freundlich equation often fits experimental data well (Barrow, 1978; Ratkowsky, 1986), but it can not predict sorption maxima. The Langmuir equation can be used for calculating the parameters like the P adsorption maxima as well as an affinity constant. The use of the Langmuir equation in describing P sorption, however, has been questioned (Harter and Baker, 1977;
Harter and Smith, 1981), because the theoretical assumptions of the equation are not met in soil systems. Adsorption maxima estimated by the Langmuir equation could be in error by more than 50% if the entire isotherm is not used in calculating sorption parameters (Harter, 1984). Because the Langmuir equation might inaccurately describe P adsorption by soil when surfaces have more than one type of elementary space (i.e., sites with different adsorption energies), a “two-surface” Langmuir equation has been used for P adsorption study (Syers et al., 1973; Holford et al., 1974). A complete derivation of the two-surface Langmuir equation has been given by Sposito (1982).

The P buffering capacity of a soil is the ability of a soil to resist a change in the P concentration in the solution phase. Peaslee and Phillips (1981) gave a detailed illustration of P buffering capacity by using P quantity/intensity (Q/I) relationships. The advantage of using Q/I relationships is that they provide information about both P fixation and the release capacities of soils (Kpomblehou-A and Tabatabai, 1997). The P buffering capacities of soils are important to plant nutrition as well as to environmental pollution related to P (Peaslee and Phillips, 1981). The Q/I relationship can be determined by either adsorption or desorption experiments. But because of the adsorption/desorption hysteresis, the P buffering capacity values obtained from adsorption curves and from desorption curve are generally different (Peaslee and Phillips, 1981; Okajima et al., 1983). Hartikainen (1991) and Kpomblehou-A and Tabatabai (1997) used low concentrations of P in solution to yield a single straight Q/I line that crossed sorption and desorption ranges in order to overcome the discrepancies created by sorption/desorption hysteresis.

Barrow (1979) showed that P desorption from soils was influenced by desorption time and the liquid/solid ratio. He also found that the effects of these factors on P desorption from
soils incubated with phosphate for different periods were not same. Similar data are, however, scanty with regard to the effects of desorption time and liquid/solids ratio on P desorption from soils amended with biosolids. On the other hand, investigating the effects of desorption time and liquid/solids ratio on P desorption from biosolids-amended soils could help us better predict the extent of P desorption under varied environmental conditions, such as flooding, different rainfall intensities as well as rainfall duration.

The objectives of this study were (1) to investigate the effects of biosolids amendments on P sorption potential and P buffering capacities in a Mollisol, and (2) to compare the effects of sorption time and liquid/solid ratio on P desorption from a soil with and without biosolids amendment.

**MATERIALS AND METHODS**

**Soils and Biosolids**

The soil in the study area, located on the Skunk River floodplain (about 2 km from the river), is classified as a fine, smectitic, mesic Cumulic Vertic Endoaquoll. The study was designed as a randomized complete-block experiment with four blocks and three biosolids treatments. The three biosolids treatment were a control (no biosolids applied), a low biosolids application rate, and a high biosolids application rate. Poplar trees (*Populus x euramericana* – clone NC-5326) were planted in each plot before biosolids was applied. In the determination of P sorption capacities and P buffering capacities, soil samples were collected at the depth of 0–10 cm in the fall of 1997. Soil samples used for the P desorption study were collected at a depth of 0–5 cm in the fall of 1996. To decrease sampling errors, four subsamples from the same depth were collected on a grid within each plot and were
mixed to form a composite soil sample. Soil characteristics are shown in Table 1. Soil samples were air-dried and ground to pass a 2-mm sieve before being used.

Biosolids produced by the Ames Water Pollution Control Facility (Ames, Iowa) was sprayed as a suspension (~5% solids) on the soil surface with large application trucks. Because the vegetation was permanent, no tillage was used to incorporate the biosolids into the soil. The average amount of biosolids annually applied to poplar tree plots from 1991 to 1996 was 6.4 Mg ha⁻¹ for the low biosolids application rate and 11.5 Mg ha⁻¹ for the high biosolids application rate. Dry matter in the biosolids ranged from 3.2 to 5.5%, and pH ranged from 7.2 to 7.6. The range of total P in the dry matter was 1.7 to 3.2%. These analyses of the biosolids were supplied to us by the Environmental Protection Agency–certified laboratory at the Ames Water Pollution Control Facility.

**Sorption Isotherm of P**

A 1.5-g air-dried, <2-mm subsample of soil was placed in a 50-mL centrifuge tube with screw cap and was equilibrated with 30 mL of one of 13 P solutions: 0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.8, 2.2, and 2.6 mM (equal to 0, 31, 62, 124, 248, 372, 496, 620, 744, 868, 1116, 1364, and 1612 mg P kg⁻¹ soil). The P solutions were prepared with monobasic potassium phosphate (KH₂PO₄) and 0.01 M CaCl₂. Three drops of chloroform were added each tube to inhibit microbial activity prior to end-to-end shaking of the tubes for 24 h. After the equilibration, the tubes were centrifuged at 26,860 g for 15 min at 25°C. Then the supernatant was passed through a 0.4-µm membrane filter, and the filtrate was analyzed for P as described later. Sorbed P was inferred from the difference between the concentration of soluble P in the initial solution and the concentration of P in the solution at equilibrium.
Table 1. Selected properties of soils (0-10 cm).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Organic C</th>
<th>Total N</th>
<th>Total P</th>
<th>pH-H$_2$O</th>
<th>pH-CaCl$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g kg$^{-1}$</td>
<td>mg kg$^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T0</td>
<td>23</td>
<td>2.3</td>
<td>649</td>
<td>6.22</td>
<td>5.71</td>
</tr>
<tr>
<td>T1</td>
<td>36</td>
<td>2.5</td>
<td>1455</td>
<td>5.51</td>
<td>5.29</td>
</tr>
<tr>
<td>T2</td>
<td>41</td>
<td>3.2</td>
<td>2427</td>
<td>5.41</td>
<td>5.21</td>
</tr>
</tbody>
</table>

T0 = no biosolids added, T1 = low rate of biosolids amendment, and T2 = high rate of biosolids amendment.
The procedure was performed in duplicate on each composite sample from each replicate plot.

The sorption isotherm of P was modeled with the standard Langmuir, the “two-surface” Langmuir, and the Freundlich equations. The Langmuir equation has the form:

$$Q = \frac{bkC}{(1+kC)},$$

where $Q$ and $C$ represent the P sorbed by soil (mg kg$^{-1}$) and P concentration in the equilibrium solution (mg L$^{-1}$) respectively; parameters $b$ (mg kg$^{-1}$) and $k$ (L mg$^{-1}$) represent the sorption maximum and a constant related to the energy of adsorption, respectively. The Freundlich equation is expressed as:

$$Q = kC^n,$$

where $Q$ is the amount of P sorbed by soil (mg kg$^{-1}$), $C$ is the equilibrium P concentration in solution (mg L$^{-1}$), $k$ and $n$ are adjustable parameters, and $n$ is allowed to range from 0 to 1.

The two-surface Langmuir equation is defined as:

$$Q = b_1k_1C/(1 + k_1C) + b_2k_2C/(1 + k_2C),$$

where $Q$ (mg kg$^{-1}$) and $C$ (mg L$^{-1}$) are the amount of P sorbed and the equilibrium P concentration, respectively; $b_1$ (mg kg$^{-1}$) and $b_2$ (mg kg$^{-1}$) are the high-and low-affinity maxima of P sorption respectively; $k_1$ (L mg$^{-1}$) and $k_2$ (L mg$^{-1}$) are the high-and low-affinity bonding energies of sorption of P respectively. Two straight lines can be obtained from a plot of $Q/C$ versus $Q$ if an isotherm sorption fits the equation well, and sorption parameters can be determined from the plot (Sposito, 1982).

**Desorption of P from Soils**

Our desorption study was a factorial experiment with two factors: desorption time and liquid/solid ratio. Nine desorption times (0.5, 1, 3, 6, 12, 24, 48, 72, 96 h) and 5 liquid/solid
ratios (10, 30, 60, 120, 240) were chosen by referring Barrow (1979), so there were a total of 45 treatments in this study. A 0.5-g subsample of the composite sample from each of the four replications (plots) (without biosolids amendment and with the high level of biosolids amendment) was put into a 50-mL centrifuge tube with screw cap or a 250-mL plastic bottle with a screw cap and was extracted with 5, 15, 30, 60, and 120 ml of 0.5 mM CaCl₂, respectively, setting up liquid/soils ratio of 10, 30, 60, 120, and 240. Each set of tubes or bottles with the same liquid/solid ratio were shaken end-to-end for each of the 9 periods of desorption time. After the extraction period, the tubes were directly centrifuged at 26,860 g for 15 min at 25°C; the suspensions in the plastic bottles were transferred into 50-mL centrifuge tubes, and then centrifuged. Then the supernatants were passed through a 0.4-μm membrane filter. The filtrates were reserved for P analysis. The procedure was performed in duplicate on each composite sample from each of the two biosolids treatments.

**Analytical Methods**

Total organic C and total N were determined by dry combustion with a CHN analyzer (Leco Corp., St Joseph, MI). Total P was measured after digestion with H₂SO₄-H₂O₂-HF (Bowman, 1988). Soil pH was measured in a 1:1 soil:water or soil:CaCl₂ suspension. Inorganic P in the filtrates of each soil extract was determined colorimetrically by using the method of Murphy and Riley (1962). Absorbance was determined at a wavelength of 712 nm. Dissolved organic C was determined in the extracts by using a Shimadzu carbon analyzer (Pt – catalyzed combustion at 650 °C).

The data were statistically analyzed using the General Linear Model Procedure of SAS Institute (1989). Differences in each P fraction among the three biosolids treatments were
examined by a standard analysis of variance procedure, with means separation by Tukey’s procedure.

RESULTS AND DISCUSSION

P Sorption Capacities of Soil

Sorption isotherms of P. Figure 1 shows the sorption isotherms of P. Each point shown on the figure represents a mean value from the four replicated plots. These samples had a very large capacities to sorb P. Other workers have estimated the maximum P sorption capacity of a soil sample by measuring the amount of P sorbed from a single addition of 1500 mg P kg\(^{-1}\) soil sample (Bache and Williams, 1971; Eghball et al., 1996; Indiati and Sharpley, 1997). The last point in our sorption series represented 1612 mg P kg\(^{-1}\) soil. But according to the sorption isotherm in Figure 1, it seems unlikely that the soil samples in our study had reached a true sorption maximum even at this high level of added P. In general, over the large range of standard P concentrations used in this study, biosolids amendment decreased the P sorption potential of the soil. Both P and organic matter were introduced when the soil was amended with biosolids, and both could have diminished the amount of additional P that could be sorbed from solution. First, water-soluble P in the biosolids (or P transformed from more insoluble fractions of P in the biosolids) could occupy the P sorption sites in the soil. Thus, the degree of saturation of P sorption sites probably increased so that the potential for additional sorption of P decreased. Second, organic anions applied to soils in biosolids could result in the decrease of P sorption potential of the soil samples by competing with P for similar sorption sites (Nagarajah et al., 1970; Kafkafi et al., 1988, Geelhoed et al., 1998).

When the initial solution P concentration was <1.0 mM (620 mg P kg\(^{-1}\) soil), P sorption was least in the samples collected in the plots amended with the high rate of biosolids. When
Fig. 1. Sorption isotherms of P. T0 = no biosolids applied, T1 = low rate of biosolids amendment, and T2 = high rate of biosolids amendment
the initial solution P concentration was >1.8 mM (1116 mg P kg⁻¹ soil), P sorption was least in the samples collected in the plots amended with the low rate of biosolids. Between the initial solution P concentrations of 1.0 and 1.8 mM, the P sorption by soils amended with low and high biosolids application rates were almost the same. Overall, the difference in P sorption between the plots amended with biosolids was smaller than the difference between the plots with and without any biosolids amendments.

**Sorption parameters of P.** Figures 2, 3, and 4 show the Langmuir, Freundlich, and two-surface Langmuir equations by plotting C/Q versus Q, log Q versus log C, and Q/C versus Q, respectively. The sorption isotherm of P in this study did not fit the Langmuir equation (Fig. 2) but it did fit the Freundlich equation (Fig. 3). The sorption isotherm data were fit by the two surface Langmuir equation (Fig. 4) better than by the simple Langmuir equation. Because a prediction of the maximum sorption potential cannot be obtained from the Freundlich equation and the sorption isotherm data of P in this study did not fit the simple Langmuir equation well, the maximum P sorption potentials of the soil samples were determined from Figure 4 according to Sposito (1982). The sorption parameters of P obtained from the two-surface Langmuir equation are given in Table 2.

Predicted maximum P sorption potentials of the soil were 819, 718, and 880 mg kg⁻¹ in the control, low biosolids, and high biosolids treatments, respectively (Table 2). The reversal in P sorption potential of the biosolids-amended samples is likely to be the result of more than one type of reaction. These isotherms suggest that the intensity of sorption (inferred from the slope of the line) may be related to the amount of organic acids applied and generated by the biosolids amendment. Traina et al. (1986a) found that organic acids can extract metallic ions from the surface of an acidic, montmorillonite soil, and so create new P
Fig. 2. Sorption isotherm plotted according to the Langmuir equation. T0 = no biosolids added, T1 = low rate of biosolids amendment, and T2 = high rate of biosolids amendment.
Fig. 3. Sorption isotherm plotted according to the Freundlich equation. $T_0$ = no biosolids added, $T_1$ = low rate of biosolids amendment, and $T_2$ = high rate of biosolids amendment.
Fig. 4. Sorption isotherm plotted according to the two-surface Langmuir equation (soil without biosolids amendment).
Table 2. P sorption and buffering parameters of soils (0-10 cm).

<table>
<thead>
<tr>
<th>Treatment</th>
<th>b₁</th>
<th>b₂</th>
<th>b</th>
<th>k₁</th>
<th>k₂</th>
<th>PEBC</th>
<th>EPC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg kg⁻¹</td>
<td>L mg⁻¹</td>
<td>L kg⁻¹</td>
<td>mg L⁻¹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T0</td>
<td>243a†</td>
<td>576a</td>
<td>819a</td>
<td>0.07a</td>
<td>0.07a</td>
<td>309a</td>
<td>0.00a</td>
</tr>
<tr>
<td>T1</td>
<td>210a</td>
<td>508a</td>
<td>718a</td>
<td>0.6b</td>
<td>0.05b</td>
<td>88b</td>
<td>1.18b</td>
</tr>
<tr>
<td>T2</td>
<td>299a</td>
<td>581a</td>
<td>880a</td>
<td>0.3b</td>
<td>0.03c</td>
<td>49b</td>
<td>2.30c</td>
</tr>
</tbody>
</table>

Data with same letter in each column are not different at the 0.05 level of significance. b₁, b₂, k₁, and k₂ were calculated according to the two-surface Langmuir equation, b is the sum of b₁ and b₂; PEBC and BPC were obtained from the Q/l relationship curve.
sorption sites. In the present study, the addition of biosolids not only directly introduced organic acids to soil but probably also stimulated the microbial activities in both litter layer and surface soil as well, which could produce even more organic acids. If, in the plots amended with the high rate of biosolids, the sorption sites for P created by organic acids were more than those sorption sites to be occupied by the P introduced, then the sorption potential could be greater in the high-rate plots than in the low-rate plots. Thus, the P sorption capacities of soil could increase because of the biosolids even though the biosolids amendments did not increase the P sorption of soil in the low P standard solutions.

The soil in the research site is a fine, smectitic, mesic Cumulic Vertic Endoaquoll. Clay minerals in the soil are dominated by smectite. The quantity of P sorbed to smectite has been shown to be strongly affected by free iron and aluminum oxides (Coleman, 1944; Chatterjee and Datta, 1951; Ellis and Truog, 1954) and by the valence and hydration energy of cations on the clay surface (Ellis and Truog, 1954; Coleman et al., 1960; Traina et al., 1986b). But because the contents of free iron and aluminum oxides are usually relatively low and the total P concentration is usually relatively large in Mollisols, the degree to which P saturates potential sorption sites in this soil may be high.

On the other hand, because organic matter concentration was high both in the soil and biosolids, ligand exchange of P for organic anions might play an important role in the sorption of P. In our study, the average dissolved organic carbon (DOC) extracted when the initial solution P concentration was zero was 69, 151, and 191 mg DOC kg⁻¹ of soil in samples from the control, low, and high biosolids treatments, respectively. By subtracting those DOC values from DOC amounts extracted with the series of solutions containing different concentrations of P, we found that the amount of P sorbed was correlated well with
the net amount of DOC desorbed (Fig. 5). So, ligand exchange of P for organic anions might be a significant mechanism of P sorption in this soil.

At the 0-5 cm depth of soils sampled from the same experimental sites where our samples were collected, Han and Thompson (1999) observed that the hydrophilic fraction of soluble organic C was more abundant than the hydrophobic fraction. Hydrophilic DOC, which is likely to contain humic substances with low molecular weight and high COOH/C ratio, non-humic-polysaccharides, and simple organic acids (Qualls and Haines, 1991), can form moderate- to low-strength metal complexes with iron and aluminum oxides (Kuiters and Mulder, 1990). Orthophosphate-P can replace simple organic anions, such as acetate, citrate, oxalate, malate and amino acids, that are sorbed to the soil by ligand exchange (Bingham et al, 1964; Lopez-Hernandez et al., 1986; Kafkafi, et al., 1988; Violante et al., 1991; Violante and Gianfreda, 1993; Geelhoed et al., 1998). But whether phosphate is capable of replacing an organic anion by ligand exchange is determined by the relative stability of the Fe (or Al)--organic anion complex and the Fe (or Al)-phosphate complex (Nagarajah et al., 1970) and by the concentration of P in the solution (Geelhoed et al., 1998).

On the other hand, there was little evidence that the P sorption isotherms were approximating the maximum sorption level, even though a wide range of P standard solutions was used (Fig. 1). The differences between the calculated maximum P sorption potential and the amount of P sorbed from the solution with the highest concentration of P solution were 184, 192, and 285 mg kg⁻¹ for the control, low, and high biosolids treatments, respectively. A small shift of sorption isotherm points could result in a large change of the calculated maximum P sorption potentials. Because the amount of P sorbed in the largest concentration of P standard solution was far from approximating the maximum sorption possible, our
Fig. 5. The relationship between P sorbed and DOC desorbed.

\[ y = 4.4x + 39.2 \]

\[ R^2 = 0.92 \]
interpretations of the data must be made cautiously. It appears that the additions of biosolids into the soil significantly decreased both the high- and low-energy bonding energies for P sorption (Table 2), which may result from the competition of organic anions for sorption sites with P.

**P Buffering Capacities**

P buffering capacities can be obtained from P quantity/intensity (Q/I) diagrams (Peaslee and Phillips, 1981; Hartikainen, 1991; Kpomblekou-A and Tabatabai, 1997). Following the approaches of Hartikainen (1991) and Kpomblekou-A and Tabatabai (1997), Q/I diagrams were plotted by using the data obtained from low equilibrium P concentrations in the sorption isotherm, including both P sorption and desorption (Fig. 6). The slope of the straight line in Figure 6 represents the P equilibrium buffering capacity (PEBC), and the intercept of the x-axis indicates the equilibrium P concentration (EPC). P buffering parameters in the soils from three different biosolids treatments are shown in Table 2. The EPC of the soil was significantly increased by the biosolids applications (P<0.05), which implies that a large initial P concentration in the solution is required to start P sorption for the soil amended with biosolids. Biosolids amendments significantly decreased the PEBC of the soil (P<0.05).

**Desorption of P Affected by Extraction Time and Liquid/Solid Ratio**

The P desorbed from the soil samples collected from plots with and without biosolids amendment are given in Table 3 and 4, respectively. The effects of extraction period, liquid/solid ratio, and the interaction between extraction period and liquid/solid ratio on P desorbed from the soils with and without biosolids amendments were statistically significant (P<0.001). Because there was an interaction between sorption time and liquid/solid ratio,
Fig. 6. Q/I relationship. T0 = no biosolids added, T1 = low rate of biosolids amendment, and T2 = high rate of biosolids amendment.
Table 3. P desorption from soil (0-5 cm) without biosolids amendment

<table>
<thead>
<tr>
<th>Extraction Time</th>
<th>Liquid/Solid Ratio (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
</tr>
<tr>
<td>0.5 hr</td>
<td>2.5a</td>
</tr>
<tr>
<td>1 hr</td>
<td>2.9a</td>
</tr>
<tr>
<td>3 hr</td>
<td>2.2a</td>
</tr>
<tr>
<td>6 hr</td>
<td>2.9a</td>
</tr>
<tr>
<td>12 hr</td>
<td>2.0a</td>
</tr>
<tr>
<td>24 hr</td>
<td>2.1a</td>
</tr>
<tr>
<td>48 hr</td>
<td>2.7a</td>
</tr>
<tr>
<td>72 hr</td>
<td>2.4a</td>
</tr>
<tr>
<td>96 hr</td>
<td>2.6a</td>
</tr>
<tr>
<td>Average</td>
<td>2.4</td>
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Data followed by the same letter, within the same column, are not different at the 0.05 level of significance.
Table 4. P desorption from soil (0-5 cm) with biosolids amendment

<table>
<thead>
<tr>
<th>Extraction Time</th>
<th>Liquid/Solid Ratio</th>
<th></th>
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<td>hr</td>
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<td>10</td>
<td>30</td>
<td>60</td>
<td>120</td>
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<tr>
<td>0.5</td>
<td>23a†</td>
<td>54a</td>
<td>74a</td>
<td>103a</td>
<td>130a</td>
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<td>24a</td>
<td>56ab</td>
<td>81b</td>
<td>105a</td>
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<td>3</td>
<td>25a</td>
<td>59bc</td>
<td>89c</td>
<td>116b</td>
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<td>27a</td>
<td>66de</td>
<td>96de</td>
<td>129c</td>
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<td>98d</td>
<td>143d</td>
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<td>183d</td>
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<td>135e</td>
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<td>24</td>
<td>58</td>
<td>91</td>
<td>126</td>
<td>170</td>
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</tbody>
</table>

Data followed by the same letter, within the same column, are not different at the 0.05 level of significance.
we examined the effect of the different levels of one factor on P desorbed from soil by fixing the other factor at a certain value.

For any one extraction period, the P desorbed from the soil with or without biosolids amendment was significantly different among the five levels of liquid/solid ratio ($P<0.001$) (Tables 3 and 4). But P desorbed from the biosolids-amended soil was about 10-fold the P desorbed from the soil without biosolids amendment when the extraction period was similar. For the liquid/solid ratios 10, 30, 60, 120 and 240, the differences in the P desorbed from the soil samples with and without biosolids amendments increased as the liquid/solid ratio increased (22, 53, 83, 115, and 154 mg kg$^{-1}$, respectively).

When the liquid/solid ratio was 10, extraction time had no significant impact on the amount of P desorbed from the soils with or without biosolids amendments ($P>0.05$) (Tables 3 and 4). When the liquid/solid ratio was 30, the P desorbed from the soil without biosolids amendment was not significantly influenced by extraction time ($P>0.05$) (Table 3). On the other hand, P desorbed from the soil amended with biosolids was significantly influenced by extraction time ($P<0.05$) (Table 4). When the levels of liquid/solid ratio ranged from 60 to 240, the amount of P desorbed from samples both with and without biosolids amendment was influenced by the extraction period (Tables 3 and 4). In fact, at the liquid/solid ratio of 240, P desorbed from the soil amended with biosolids was significantly different for each of the nine levels of extraction times, except between 0.5 and 1 h and 12 and 24 h (Table 4).

These results indicate that the amount of P desorbed from soil is not influenced by extraction period when the liquid/solid ratio was small (10 for T2 and 30 for T0 at this study). When the liquid/solid ratio increased, extraction period did influence P desorption, perhaps because readsoption of soluble P occurred. Overall, the longer the soil was extracted
and the larger the liquid/solid ratio was used, the more P was desorbed. The interaction between extraction time and liquid/solid ratio was greater for P desorption from the biosolids-amended soil than from the unamended soil.

ENVIRONMENTAL IMPLICATIONS

Except for the fact that the P sorption potential increased in the soil amended with the high rate of biosolids, all the other effects of biosolids amendments on P sorption/desorption and P buffering capacities imply a large increase in the P concentration in soil solution. The increase of P in soil solution could enhance the losses of soluble P in runoff water and movement to groundwater by preferential flow.

For the wide range of soluble P concentrations used in our sorption experiment, P sorption potentials of soils decreased after biosolids amendment, even though the calculated maximum P sorption potential was increased by the high rate of biosolids amendment. The decrease in P sorption potential suggests that, if the same amount of soluble P were added to both soils, the amount of P sorbed by the biosolids-amended soil could be less that that sorbed by the unamended soil.

The additions of biosolids to the soil significantly decreased both the high- and low-affinity bonding energies of P sorption, which suggests that P sorbed by the soil amended with biosolids will be released into soil solutions easily than the P sorbed by the soil without biosolids amendment.

The PEBC of the soil was significantly decreased by the biosolids amendments, which implies that the ability of the soil to remove P from solution decreases after the biosolids amendment. The EPC of the soil was significantly increased by the biosolids amendment.
which implies that the instantly labile P in biosolids-amended soil surface horizons may be very great.

The effects of extraction time, liquid/solid ratio, and their interaction on the desorption of P from the soils with and without biosolids were not the same. The difference between the P desorbed from the soils with and without biosolids increased by increasing both the liquid/solid ratio and extraction time.
SUMMARY

Land application of biosolids is becoming more popular because it is an agronomically, environmentally, and economically acceptable means for biosolids disposal. When the amount of biosolids is applied to agricultural land according to N-based agronomic rate, however, the amount of P applied generally more than plants need. The subsequent accumulation and fate of P in soils is of environmental concern, because it could lead to eutrophication of water bodies if P is carried off-site in runoff water and eroded soils. Thus, a study on the fate of biosolids-derived P applied to a Mollisol was conducted in a completely randomized block experiment with three biosolids treatments (approximately 0, 7.4, and 13.0 Mg dry matter ha⁻¹ yr⁻¹) and four blocks. The objectives of this study were to observe the redistribution of biosolids-derived P, to examine the influence of land application of biosolids on P in soil solutions collected by zero-tension lysimeters and in groundwater, to assess the effects of land application of biosolids on P fractions, and to evaluate the effect of biosolids application on the P sorption, desorption, and buffering capacities.

After six years of continuous biosolids application to poplar tree plots, total P in soil increased significantly at both the 0-5- and 5-25-cm depths. Also at both depths, a linear relationship between total P in soil and the amount of P applied in biosolids was found. Because biosolids application to switchgrass plots was stopped since 1994, total P increased significantly at only the 0–5-cm depth. A linear relationship between total P in soil and the amount of P applied with biosolids was found at the 0–5-cm depth under switchgrass but not at the 5–25-cm depth. The amount of P accumulated was larger in the upper 5 cm thickness (0–5 cm) of soil than in the 20 cm thickness (5–25 cm) of soil below it. P that accumulated in the upper 5 cm of the soil accounted for ≥45% or more of the total P applied with biosolids,
except for the low biosolids application rates to switchgrass plots where the value was 28%.
The amount of P taken up annually by switchgrass was estimated to be 5 times more than
that taken up by poplars. The amount of P leached in the mobile soil solution of switchgrass
plots was estimated to be twice that leached in soil solution of poplar tree plots.

In the experiment examining the influence of land application of biosolids on P in soil
solutions collected by zero-tension lysimeters and in groundwater, a ZTL was installed about
50 cm below the soil surface in each plot. In a separate investigation, ZTLs were installed in
a single plot at depths ranging from 15 to 65 cm. Groundwater samples were collected from
piezometers installed ~6 m below the soil surface. In 1994, the numbers and volumes of soil
solutions collected in ZTLs in switchgrass and poplar plots were significantly different. More
and larger volumes of soil-solution samples were collected under switchgrass than under
poplar trees. Under both switchgrass and poplars, the largest P concentrations were observed
in the mobile soil solutions collected from the low rather than from the high biosolids
treatment. P concentrations in soil solution also decreased significantly with increasing soil
depth. P in groundwater was not influenced by biosolids applications.

The Hedley fractionation scheme (dividing soil P into six empirical fractions [water
soluble, NaHCO₃-soluble inorganic and organic P, NaOH-soluble inorganic and organic P;
HCl-soluble P, and residual P]) was employed to assess the effects of land application of
biosolids on soil P fractions. After six years of continuous application of biosolids to poplar
plots, the absolute concentrations of all P fractions at the 0–5-cm depth increased
significantly. Some P fractions at the 5–20-cm depth increased significantly, whereas at the
20–35-cm depth, none of the fractions was affected by biosolids amendment. At the 0–5-cm
depth of both poplar tree and switchgrass plots the relative concentrations of some of the P
fractions (e.g., HCl-P, NaOH-OP, and residual-P) decreased rather than increased. Because NaHCO₃-IP and H₂O-P increased in the biosolids-amended soil at rates disproportionate to their concentrations in the biosolids, we hypothesize that HCl-P applied with biosolids was transformed to more labile forms as a result of the complementary effect of a relatively low pH in the biosolids-amended soils.

P sorption and desorption experiments under various equilibrium times and liquid/solid ratios were conducted to evaluate the effect of biosolids application on the P sorption, desorption, and buffering capacities of the soil. The maximum P sorption potential and the affinity bonding energies of P sorption were obtained by fitting sorption isotherm into the two-surface Langmuir equation. The buffering parameters of P were calculated based on Q/I relationship. For the wide range of P concentrations used in our sorption experiment, P sorption potentials of soils decreased after the biosolids amendment, even though the maximum P sorption potential in the soil amended with the high rate of biosolids increased. The decrease in P sorption potentials of soils means that, if the same amount of soluble P were added to both soils, the amount of P sorbed by the biosolids-amended soil could be less than that sorbed by the unamended soil. The additions of biosolids to the soil significantly decreased both of the high- and low-affinity bonding energies of P sorption, which suggests that P sorbed by the soil amended with biosolids will be released into soil solutions more easily than the P sorbed by the soil without biosolids amendment. The PEBC of the soil was significantly decreased by the biosolids amendments, which implies that the ability of the soil to remove P from solution decreases after the biosolids amendment. The EPC of the soil was significantly increased by the biosolids amendment, which implies that a large initial P concentration in the solution is required to start P sorption for the soil amended with
biosolids. The effects of extraction time, liquid/solid ratio, and their interaction on the desorption of P from the soils with and without biosolids were not same. The difference between the P desorbed from the soil with and without biosolids increased by increasing the liquid/solid ratio and the extraction time.

Except for the fact that the P sorption potential increased in the soil amended with the high rate of biosolids, all the other effects of biosolids amendments on P sorption/desorption and P buffering capacities imply a large increase in the P concentration in soil solution. The increase of P in soil solution could enhance the losses of soluble P in runoff water and movement to groundwater by preferential flow.
LITERATURE CITED


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