

**PHOSPHORUS SPECIATION IN BIOSOLIDS-AMENDED
SOILS: CORRELATING PHOSPHORUS DESORPTION,
SEQUENTIAL CHEMICAL EXTRACTIONS,
AND PHOSPHORUS-XANES SPECTROSCOPY**

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ABSTRACT

This study was conducted to compare the speciation and behavior of P in soils receiving either different biosolids or inorganic fertilizer, as assessed by sequential chemical extractions, phosphate desorption, and synchrotron X-ray absorption near edge structure (XANES) spectroscopy. The objectives of this study were to i) measure the total amount of organic and inorganic phosphorus removed by chemical extraction method ii) investigate how P desorption kinetics are influenced in biosolids amended soils compared to inorganic fertilizer amended soils; and iii) perform solid state speciation of soil samples before and after chemical extraction and desorption with P K-edge XANES spectroscopy. Soil samples were analyzed that received three different rates of biosolids (16.8, 33.6, and 67.2 Mg ha⁻¹ yr⁻¹) and one inorganic fertilizer application (336 kg N, 224 kg P, and 112 kg K ha⁻¹ yr⁻¹) for 32 years. Both sequential chemical extraction and XANES analysis showed that total amount of P increased in biosolids amended soils (from 5292 to 10945 mg P kg⁻¹) and that it increased with increasing application rate. Sequential chemical extractions showed that the labile portion of total P in inorganic fertilized soil (40 %) was larger than in biosolids applied soils (39 to 27 %). Results from both sequential chemical extraction and XANES analysis showed that NaOH extraction removed the highest amount of P from all biosolids applied soils (from 1857 to 2600 mg P kg⁻¹).

The amount of desorbed P decreased as the soil:solution ratio increased from 0.005 to 100 g L⁻¹ for both soils and the desorption was typically higher in inorganic fertilizer applied soil than in biosolids applied soil. The effect of pH on P desorption was pronounced, and desorption was higher at pH 5 than pH 7.5 for both soils. A continuous flow desorption method was also used to measure cumulative P desorption over time. Cumulative P desorption in inorganic fertilizer applied soil (894.5 mg P kg⁻¹) was higher than in the biosolids amended soils (572.9 mg P kg⁻¹) over 20 hr period time. First-order and parabolic diffusion kinetic equations were used to model the desorption data from the continuous flow technique. This revealed that the P desorption rate was faster (and chemically-controlled) at initial stages and slower (and diffusion-limited) at later stages. The desorption rate was much faster in inorganic fertilizer applied soil than in biosolids applied soil.

XANES analysis of the fractions removed in sequential chemical extractions suggested that the predominant form of P was poorly crystalline dicalcium phosphate in biosolids applied

soils, and labile, sorbed forms as well as some apatite-type calcium phosphate was present in inorganic fertilizer applied soil. The combined results from sequential chemical extraction and XANES analysis indicate that P in inorganic fertilizer and biosolids-applied soils behave differently. There were larger amounts of low crystallinity phosphates in the biosolids samples, and much higher apatite content in the inorganic fertilizer amended soil.

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Bertrand Russell, once defined the Good Life as one “inspired by love and guided by knowledge.” What Russell said about a Good Life may equally apply to a good teacher. A good teacher, besides having other qualities, should have genuine care for students. A teacher’s love for students must also be supplemented by knowledge and insight in his/her areas of expertise. Dr. Derek Peak, I strongly believe, is such a teacher. He meant so much to me that any note of acknowledgement will limit his contribution to my emotional and intellectual growth. His encouragement, his understanding, and most of all, his patience, are greatly appreciated. I am truly grateful for his mentorship and dedication.

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectroscopy
Al	Aluminum
ANOVA	Analysis of variance
Ca	Calcium
CSRF	Canadian synchrotron radiation foundation
DCM	Double crystal monochromator
EC	Electrical conductivity
Fe	Iron
LC	Linear combination
LSD	Least significant difference
MAP	Monoammonium phosphate
OC	Organic carbon
P	Phosphorus
PCA	Principal component analysis
P _i	Inorganic phosphorus
P _o	Organic phosphorus
P _t	Total inorganic and organic phosphorus
P _T	Total extractable phosphorus
SPSS	Statistical package for the social sciences
SRC	Synchrotron radiation centre
TEY	Total electron yield
TG-MAP	Technical-grade monoammonium phosphate

UHV	Ultra high vacuum
USEPA	United state environmental protection agency
XANES	X-ray absorption near edge spectroscopy

1. Introduction

Knowledge of phosphorus (P) dynamics in soil is essential for predicting its bioavailability and for assessing the risk of P transfer from soil to water bodies. Phosphorus is a valuable nutrient in natural and agricultural ecosystems because it is a key requirement to produce many important cellular compounds in plants and animals.

Biosolids, a by product of waste water treatment plants, are a good source of plant macro and micro nutrients (Rostagno and Sosebee, 2001). Biosolids usually contain 8 to 62 g kg⁻¹ P on a dry weight basis, primarily in an inorganic form (Sommers, 1977; Commission on Geosciences, Environment, and Resources, 1996). Phosphorus is known to accumulate in soil when biosolids are applied at agronomic rates based on crop N requirements (Shober and Sims, 2003). Many researchers (Chang et al., 1983; Clapp et al., 1994; Frossard et al., 1994) have also found that long-term application of biosolids to soils often increased total and available soil P. Over time, this can increase the risk of P transport to water bodies through leaching, erosion, and runoff (Sims et al., 1998; Sharpley and Tunney, 2000; Hooda et al., 2001). The problem arises through the run-off loss of desorbed P as well as erosion of P containing soil solids to bodies of water. This problem commonly leads to eutrophication and severely affects aquatic life. Eutrophication is a process whereby water bodies, such as lakes or slow-moving streams, receive excess nutrients that promote excessive plant growth.

Water-soluble P is the most bioavailable form and is the fact in prone to leaching in biosolids (Elliott et al., 2002; Huang et al., 2007). However, the availability and mobility of soluble P in biosolids can be reduced by adding Fe and Al at the waste water treatment plant. Corey (1992) found that the availability of P decreased with the increase in (Al+Fe)/P in biosolids. Fractionation of P in the form of soluble P, Al-P, Fe-P, and Ca-P can be useful in predicting the potential availability and mobility of P in soils (Maguire et al., 2000).

Therefore, in this project, the P in soils amended with inorganic fertilizer and different rate of biosolids was separated into inorganic and organic forms by sequential chemical extraction with various extractants. This method can separate P into fractions of differing solubility but cannot identify the specific chemical form of P species present in soil (Toor et al., 2005). The potential availability and mobility of P fractions by two different desorption methods were also estimated.

The quantification and identification of individual P compounds present in soils require advanced molecular-scale spectroscopic techniques such as X-ray Absorption Spectroscopy (Fendorf et al., 1994; Hesterberg et al., 1999; Beauchemin et al., 2003; Shober et al., 2006), Differential X-Ray Diffractometry (Ippolito et al., 2003; Huang and Shenker, 2004), and Nuclear Magnetic Resonance Spectroscopy (Hinedi et al., 1989; Frossard et al., 1994; Shober et al., 2006). In this study, it was X-ray Absorption Near Edge Structure (XANES) spectroscopy to identify P species (Fendorf et al., 1994; Shober et al., 2006). The XANES spectroscopy is a relatively new analytical method (Toor et al., 2005), which has been successfully used to identify P species in soils (Fendorf et al., 1994; Hesterberg et al., 1999; Beauchemin et al., 2003; Shober et al., 2006).

The objectives of this study were to i) measure the total amount of soil organic and inorganic phosphorus removed by chemical extraction methods, ii) investigate how P desorption kinetics are influenced by biosolids amendment compared to inorganic fertilizer amended soils; and iii) perform solid state speciation of soil samples before and after chemical extractions and desorption with P XANES spectroscopy. The experimental approach for this research was to combine traditional sequential chemical extractions and phosphate desorption techniques with new P K-edge XANES spectroscopic technique to produce a better estimate of P availability in the environment.

2. Literature Review

2.1. Phosphorus Forms in Soils and Biosolids

Biosolids are good sources of P and contain a large amount of plant macro and micro-nutrients (Rostagno and Sosebee, 2001). Biosolids typically contain 10 to 20 g total P kg⁻¹ (USEPA, 1995; Peters and Basta, 1996). There is a lower risk of P transfer in land runoff following application of liquid anaerobically digested biosolids, or dewatered biosolids cake compared with other agricultural P amendments at similar P rates: triple super phosphate, and liquid cattle manure (Withers et al., 2001). Triple super phosphate P is four to seven times more available to plants than biosolids P and they attribute this in part to P speciation in sewage sludge compost (McCoy et al., 1986).

Biosolids and animal manure are usually applied according to crop N requirements as long as loading rates for some trace elements are not exceeded. Several researchers (Kelling et al., 1977; Kick, 1981; Angela et al., 2002) have shown that applying biosolids and animal manure following a N-based management plan will lead to an oversupply of P relative to crop requirement. This also increases risk of P losses to surface and ground water (Shober and Sims, 2003). The increase of soluble forms of P in the soil solution can enhance the loss of P in runoff and P movement below the root zone (Sui and Thompson, 2000). Thus, agricultural runoff can accelerate the eutrophication of P sensitive waters (U.S.Environmental Protection Agency, 1996). Garcia and Stores (1997) stated that the risk of eutrophication can be assessed by using a model that simulates the release of soil P and its transport in runoff.

2.1.1. Inorganic and organic phosphorus forms

Much research has shown that P is present in soil and biosolids in inorganic and organic forms. A sequential chemical extraction procedure developed by Hedley et al (1982) is commonly used to separate and quantify different forms of P present in soil. It is known that soils amended with biosolids and P fertilizer as triple super phosphate often have differing distributions of P species. Triple super phosphate contains four to seven times more plant-available P (McCoy et al., 1986) whereas most P in biosolids is commonly in the form of solid Fe, Al, and Ca phosphate (Soon and Bates, 1982). Therefore, the extraction technique is very

useful to determine inorganic (Pi) and organic (Po) forms of P in inorganic fertilizer and biosolids amended soils.

The sequential extraction technique first removes plant-available or labile P, which is commonly estimated using water extractable and bicarbonate Pi and Po (Bowman and Cole, 1978; Sui et al., 1999). The Pi fraction is typically considered to be sorbed onto more crystalline P compounds, sesquioxides, or carbonates (Mattingly, 1975). The hydroxide extractable Pi is associated with Fe- and Al-oxides (Sui et al., 1999) which have lower plant availability (Marks, 1977). The HCl extractable Pi is considered to be Ca-bound relatively insoluble apatite-type minerals (Williams et al., 1980).

Water extractable and bicarbonate Po are mostly labile Po forms (Bowman and Cole, 1978), while the more stable Po forms are associated with humic compounds (Bowman and Cole, 1978) and extracted with sodium hydroxide. Finally, the residual-P, removed by acid digestion method, contains the least soluble Pi and stable Po forms (Thomas et al., 1967). Thus, the major P forms are: the “labile” water and bicarbonate extractable P, sodium hydroxide extractable P, hydrochloric acid extractable P, and residual P.

For inorganic P, water and bicarbonate Pi are considered to be labile and readily available to plant. The sodium hydroxide Pi form is considered moderately labile (Qian and Schoenau, 2004), which is mostly Fe and Al-oxide associated (Hedley et al., 1982). Also considered moderately labile is the hydrochloric acid extractable Pi form, which is operationally defined as Ca-bound P. The quantity of Fe and Al-bound P is very high in biosolids-amended soils as Al and Fe are added during the wastewater treatment process (Soon and Bates, 1982). Ca-bound P is also often high in biosolids as a result of liming of biosolids for health reasons prior to application (Sui et al., 1999). The presence of large quantities of moderately labile P can affect the fate of biosolids P in soils (Maguire et al., 2000). The residual P fraction occurs as occluded P or as a highly recalcitrant Pi (Hedley et al., 1982), which is not easily available.

The organic P fractions in soils comprise the water-Po, bicarbonate-Po, hydroxide-Po, and HCl-Po. The Po extracted with water and bicarbonate is easily mineralizable and contributes to plant available P (Bowman and Cole, 1978), while the hydroxide-Po is moderately available. In contrast, Fine and Mingelgrin (1996) reported that mineralization plays a limited role in the Po phytoavailability in soils amended with biosolids. The HCl-Po is fairly stable and likely comes from particulate organic matter (Qian and Schoenau, 2000).

2.2. Phosphorus Loading Issues in Soils

Phosphorus is an essential nutrient for crop growth, and excess P accumulates when fertilizer application rates provide more P than is needed for optimum crop production (Pautler and Sims, 2000). Many studies have shown that organic fertilizer application based on crop N requirement can lead to accumulation of excess P in soils (Kelling et al., 1977; Kirk et al., 1981; Shober and Sims, 2003), which greatly increases the risk of P losses to surface and ground water (Shober and Sims, 2003). Pautler and Sims (2000) reported that over application of organic and inorganic fertilizers increase the percentage of total P in soluble and desorbable forms.

In acidic soils, the retention of P depends on the presence of Fe and Al oxides (Williams et al., 1971; Syers and Curtin, 1988; Mozaffari and Sims, 1996). These Fe and Al oxides are the major solid phase component in soils responsible for P sorption in acid soils (Reddy et al., 1998). On the other hand, Bertrand et al. (2003) found that P sorption behavior in alkaline and calcareous soils is the direct function of CaCO_3 content because P is sorbed on Ca minerals as dicalcium phosphate dihydrates, octocalcium phosphate, and ultimately hydroxylapatite (Lindsay, 1979; Sample et al., 1980; Freeman and Rowell, 1981). Hartikainen (1989) suggested that initial P sorption in soils occurred by reaction with Fe hydroxides, as the Fe-P is more stable than Al-P bonds, and that Al hydroxides sorb greater proportion of the added P only when P content of a soil increases and the Fe hydroxides become more saturated with P. Thus, soils amended with biosolids could significantly increase a soil's P retention power by increasing the content of P-sorbing solids (Lu and O'Connor, 2001).

2.3. Factors Affecting Phosphorus Availability and Mobility

Many soil properties influence P availability and mobility in both inorganic fertilizer and biosolids-amended soils (Kashem et al., 2004). The factors that affect P availability and mobility may include pH, the presence of hydrous oxides of iron and aluminum, calcium minerals, waste treatment, time, mineralization and organic matter content, application rate, and nature of inorganic and organic fertilizer.

2.3.1. pH

It is generally recognized that soil phosphorus availability is greatest between pH 6.5 to 7.5. Truog (1948) reported that phosphorus becomes less available below pH 6.5 due to the

presence of iron and aluminum which combine with phosphorus to form less soluble iron and aluminum phosphates. This low solubility also limits the mobility of P due to leaching in most acidic soils (Tiessen and Stewart, 1983). Sui et al (1999) noted that the proportion of HCl-P (a relatively resistant form) concentration decreased and subsequently NaHCO₃-P (a relatively available form) concentration increased in the soil surface as a result of decreased soil pH caused by biosolids addition to a high pH soil. Researchers have also found that HCl-extracted P (Ca-bound) is higher in soil with pH 8 or above, which is reasonable considering that CaCO₃ and CaPO₄ minerals are dominant at that pH (Ippolito and Barbarick, 2004).

2.3.2. Presence of Fe and Al

Soil Fe and Al oxides play an important role in P availability and mobility in soil because the Fe and Al oxides or CaCO₃ increase P sorption and reduce P lability (Reddy et al., 1998). Pastene (1981) reported that P availability is higher in soils amended with biosolids when the molar ratio of Al and Fe to P is less than one. O'Connor et al. (2004) also reported that the availability of P decreases significantly with very high concentration of Al and Fe in biosolids amended soils. Day et al. (1987) found that P can be mobile in a fine particulate soil because of the presence of Fe and Al in soil and can be absorbed and retained by clay minerals as Fe and Al oxide.

2.3.3. Calcium minerals

Many researchers (Williams et al., 1971; Syers and Curtin, 1988; Mozaffari and Sims, 1996) have shown that P was present in acidic soils as Al and Fe-P, and Ca-P in calcareous soils. Afif et al. (1993) reported that soil properties affect the relative distribution of absorbed and precipitated P with different cations. In calcareous soils, P is adsorbed as orthophosphate and precipitated as Ca phosphates in lower concentration and higher concentration, respectively (Castro and Torrent, 1998; Tunesi et al., 1999) and organic P is much more mobile than Pi in calcareous soils (Schoenau and Bettany, 1987; Frossard et al., 1989). Downward P mobility in coarse-textured soils is potentially significant from organic wastes because of its lower P-sorbing capacity compared to inorganic phosphate (Eghball et al., 1996; Harris et al., 1996; Lu and O'Connor, 2001). Some researchers (Lindsay, 1979; Sample et al., 1980; Freeman and Rowell, 1981) showed that the low plant availability of applied P is due to the formation of dicalcium

phosphate dihydrate, octocalcium phosphate, and ultimately hydroxyapatite in highly calcareous soils. These precipitation reactions of P with Ca are a key mechanism controlling P availability and mobility in soil (Tunesi et al., 1999). Delgado and Torrent (2000) noted that large amounts of Al and Fe phosphates were present in limed acid soils and Ca phosphates in calcareous soils and those Ca phosphates can transform to labile-P in biosolids-amended acid soils. They also noted that plant available P was higher in limed acid soils than calcareous soils. Lookman et al. (1996) found that a significant amount of Ca phosphates was present in heavily fertilized acid soils and most stable Ca phosphate as hydroxyapatite was present as a product of the dissolution of superphosphates in acid and slightly acid soils (Kumar et al., 1994).

2.3.4. Waste treatment

The availability and mobility of P mostly depends on the individual forms of Pi in soils (Sharma and Verma, 1980; McCoy et al., 1986; Sudhir et al., 1987). Many researchers (Kelling and Walsh, 1977; Kirkham, 1982) have shown that land application of biosolids increases bioavailability of soil P and it varies from 10 to 100 % over and above an equal amount of soluble fertilizer (de Haan, 1981). It is believed that biosolids-P is less soluble and less plant available due to the addition of metal salts and lime at the waste water treatment plant (Kirkham, 1982; McCoy et al., 1986; Frossard et al., 1996a; Brandt et al., 2004). Huang and Shenker (2004) have shown that the P solubility decreased to as low as 2 to 3 % of its solubility relative to the untreated biosolids, after treating with different amounts of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ or CaO .

2.3.5. Time

Changes in P availability and mobility in soils also vary with time after application. Kashem et al. (2004) showed that the availability of H_2O -P in P fertilized soils decreased significantly and that this fraction was slowly being transformed to the NaHCO_3 -P extractable forms. They also showed that the relative concentration of the more stable (recalcitrant) P fractions decreased while the labile P fractions increased signifying a transformation of biosolids to more labile P fractions with time. Chang et al. (1983) found that 5 years of biosolids applications to calcareous soils changed the predominant form of soil P from Ca-P to Al-P and Fe-P. Syers and Walker (1969) also found that the total amount of P in the soil profile decreased

with increasing time of soil development in New Zealand. This decrease in total P was attributed to the free draining nature of the sandy soils.

2.3.6. Mineralization and organic matter content

Organic P mineralization affects P phytoavailability in soils (Sommers et al., 1976; Pierzynski et al., 1994). However, Fine and Mingelgrin (1996) found that the mineralization of Po had a limited effect on P phytoavailability in biosolids amended soils.

Ekholm et al. (1999) have shown that the large amounts of organic matter applied to soils increased soil P movement, because introduction of organic matter at the surface promotes the build up of soil macropores. These macropores are a critical element for the movement of Po (Akhtar et al., 2003).

2.3.7. Application rate

Amendment rate has a significant role on P availability and mobility in soil. Kashem et al. (2004) found that the proportion of labile P increased with application rate and decreased the proportion of recalcitrant P in manure and P fertilized soils. They also found that the labile P was increased to 20 % in biosolids soils and 37 % in fertilized soils at the highest rate of P additions. Based on total P applied in soil, the movement of P to surface water is less from biosolids amended soils than inorganic P fertilizer or manure (Shober and Sims, 2003).

2.3.8. Nature of inorganic and organic fertilizer

Phosphorus availability and mobility is strongly dependent on the form and nature of inorganic and organic fertilizers used, and P lability is higher in fluid P fertilizer than in granular P fertilizer (Lombi et al., 2006). Kashem et al. (2004) showed that plant available P was seven times lower in biosolids-amended soils than monoammonium phosphate (MAP) amended soils and four to seven times less than in triple super phosphate soils (McCoy et al., 1986). Holloway et al. (2001) showed that TG-MAP was 4 to 5 times more effective in increasing the grain yield of wheat than granular MAP. The P content, availability, and mobility in biosolids amended soils depend on biosolids treatment methods and nutrient removal processes (Frossard et al., 1996; Maguire et al., 2001; Penn and Sims, 2002). Biosolids generated via biological phosphorus removal had P that was as bioavailable as fertilizer P, but Fe and Al added biosolids showed

reduced P phytoavailability (O'Connor et al. 2004). Elliott et al. (2002) also reported that activated and anaerobically digested sewage sludge treated with high amount of Al and Fe contains a small proportion of labile P fractions.

2.4. Phosphorus Desorption

Much previous research has been conducted on P desorption and dynamics. This is not surprising as P desorption is a key process in P cycling in the subsoil. Bhatti and Comerford (2002) studied P dynamics on poorly drained spodosols of the lower coastal plain of the United States and found that P desorption is the major mechanism which defines the labile pool of spodic horizon inorganic P. Wang et al. (2001) found that plant absorption of P depends on desorption of P from soil. They also found that P desorption due to leaching from small aggregates was greater than release from large aggregates when P had been added to the bulk soil. The rate of P desorption can be a useful parameter to predict the P bioavailability, from both the soil and fertilizer material (Toor and Bhal, 1999)

The land application of large amounts of manure and biosolids has led to P saturation in soils, which increases the risk of P leaching. The result of one desorption study suggested that soils with high animal density were more at risk to leach P into drainage waters than low animal density or forest soils because of the large accumulation of P in soils (Beauchemin et al., 1996). In an increasing number of areas, the potential for P loss in runoff has been elevated by the continual land application of manure from intensive livestock operations (McFarland and Hauck, 1995; Sharply et al., 1996). Angela et al. (2002) conducted an experiment that showed that high P diet manure contributes more P into runoff than low P diet manure, in both simulated and natural runoff. The desorption of P is influenced by PO_4^{3-} concentration, pH, and period of reaction (Barrow, 1983). The rate of P desorption is initially fast and then continues to proceed slowly (Munns and Fox, 1976; Lookman et al., 1995; Toor and Bahl, 1999; Siddique and Robinson, 2004) but the total amount of P desorption increases with desorption time (Barrow, 1983). At high pH in the soil, phosphorus desorption often increases due to the increasing negative charge on Al and Fe oxide surfaces. Alternatively, at high pH, less desorption may occur if high pH leads to enhanced hydrolysis of hydroxyl-Al associated organic matter (Haynes and Mokolobate, 2001). The desorption of P is also influenced by the soil:solution ratio (Barrow

and Shaw, 1979; White, 1966). Some researchers (Fordham, 1963; Barrow et al., 1965; White, 1966) found that low soil:solution ratio favoured P desorption.

2.5. Objectives

The overall goal of this research was to perform solid state speciation of soil samples with P XANES spectroscopy to relate the chemical forms of P with the amount that is released by sequential chemical extractions and desorption methods. Specific objectives of this project were to: i) measure the total amount of organic and inorganic phosphorus removed by different extraction methods; ii) investigate how P desorption kinetics are influenced by biosolids amendment compared to inorganic fertilizer amended soils; and, iii) perform solid state speciation of soil samples before and after chemical extractions and desorption with P XANES spectroscopy.

It has been hypothesized that speciation with P K-edge XANES spectroscopy will better explain the results from sequential chemical extractions and desorption, and combining all three methods will provide better estimate of P availability in the environment.

3. PHOSPHORUS SPECIATION DIFFERENCES IN BIOSOLIDS AND FERTILIZER AMENDED SOILS DETERMINED USING SEQUENTIAL CHEMICAL EXTRACTIONS AND XANES SPECTROSCOPY.

3.1. Introduction

Phosphorus (P) is an essential plant nutrient for optimum crop yields. Phosphorus, along with nitrogen, potassium, sulfur, calcium, and magnesium is one of the major nutrients required by plants (Mckenzie, 1989). Biosolids have a significant inorganic fertilizer replacement value because they contain appreciable amounts of both N and P (Huang et al., 2007). However, the land application of biosolids for crop production is typically based on crop N requirement and supplies excess P to the soil. Several researchers (Chang et al., 1983; Clapp et al., 1994; Frossard et al., 1994) have found that overapplication of biosolids to soil increased both total and available soil P which increases the risk of P loss to surface waters (Sharpley et al., 1996; Sims et al., 2000).

Much research has been conducted to determine the P availability and potential P mobility in soils receiving manure and phosphorus fertilizer (Qian and Schoenau, 2000; Sharpley and Moyer, 2000). Most of this research has been done to determine the inorganic and organic fractions of P. Results from speciation experiments and bulk and sequential chemical extractions serve an important role in environmental risk assessment from increasing soil P concentration (Lanyon, 2000) due to excess application. Soil P fractions are very useful for predicting the bioavailability of P, but operationally separating P into pools based upon extractants can be complicated (Sui et al, 1999). Sequential extraction techniques have been widely used to separate soil P into inorganic and organic fractions (Hedley et al., 1982; Sui et al., 1999; Sharpley and Moyer, 2000; Buehler et al, 2002). It is also important to quantify and identify individual P compounds present in soils, but this requires more advanced molecular-scale spectroscopic techniques such as X-ray Absorption Spectroscopy (Fendorf et al., 1994; Beauchemin et al., 2003; Shober et al., 2006), differential X-Ray Diffractometry (Ippolito et al., 2003; Huang and Shenker, 2004), and Nuclear Magnetic Resonance Spectroscopy (Hinedi et al., 1989; Frossard et al., 1994; Shober et al., 2006).

Sequential P fractionation techniques use different chemical extractants to separate P in soils into various forms of inorganic P (Maguire et al., 2000) and labile and stable organic P (Sui

et al., 1999). The sequential P fractionation technique has been proven to provide reliable estimates of different P forms in soils (Chu et al., 1962; Chien et al., 1987; Loganathan and Sutton, 1987; Kumar et al., 1993). This procedure can operationally separate soil P into pools such as plant available, Ca-associated, Al-oxide and Fe-oxide-associated P (Sui et al, 1999) based upon solubilities (Chang and Jackson, 1957; Hedley et al., 1982). However, there is no direct proof that a particular form of P is consistently removed by the extractant (Toor et al., 2006).

X-ray Absorption Near Edge Structure (XANES) spectroscopy is a molecular-scale analytical technique that has been used to conclusively identify P minerals present in soils (Hesterberg et al., 1999; Beauchemin et al., 2003; Shober et al., 2006). Each chemical species has its own unique spectral characteristics and the spectrum of a mixture of two or more chemical species of an element will quantitatively reflect the amount of each species in the sample being measured. This allows XANES spectroscopy to quantitatively determine different chemical forms present in the sample (Fleet and Liu, 2001). Phosphorus K-edge XANES spectroscopy has been successfully used to characterize the nature of molecular scale interactions of P with organic and inorganic fractions of soils.

The overall goal for this study was to thoroughly compare the speciation of P in soils receiving either biosolids or inorganic fertilizer. The experimental approach for this research is to combine sequential chemical extractions experiments with P K-edge XANES spectroscopy at each step of the extraction process. It was hypothesed that the combination of these two techniques can produce a better estimate of P availability in the environment.

3.2. Materials and Methods

3.2.1. Field site and experimental description

Soil samples were provided from research plots of the Greater Chicago Water Reclamation District, U. S. A. This research site has undergone 32 years of a continuous corn cropping system with soils receiving either the recommended level of inorganic fertilizer (as a triple super phosphate) or various amounts of biosolids. This research is a Complete Randomized Block experiment with 4 replicate blocks containing three biosolids treatments and one inorganic fertilizer treatment. More details on the field design are shown in Appendix A (Figure A1). Biosolids were never applied in inorganically fertilized plots (T1 treatment). Biosolids were

applied in the three plots at rate of $16.8 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ (quarter-maximum), $33.6 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ (half-maximum), and $67.2 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ (maximum). Each plot received a fixed amount of potassium fertilizer at rates of $112 \text{ kg K ha}^{-1} \text{ yr}^{-1}$. Four composite soil samples were collected by combining samples from the four replications of each treatment from the surface layer (0-15 cm) of the experimental plots. The soil treatments are referred in this study as inorganic fertilizer, quarter, half, and maximum biosolids rate amended soils. The soil samples were air dried, ground, sieved, and stored in containers at room temperature. Soil texture was determined by Laser scattering particle size distribution analyzer (HORIBA[®] LTD. 2007). Electrical conductivity (EC) and pH were measured by glass electrode method using 1:2 soil:water suspension (Nelson and Sommers, 1982). Soil organic carbon was measured by combustion of 0.15 g of soil using the Leco C632 carbon combustion analyzer (LECO[®] Corporation 2007). Basic characteristics of experimental field site soil were given in Table 3.1.

Table 3.1 Basic characteristics of experimental field site soil.

Parameter	Value
pH	7.6
EC (dS m ⁻¹)	0.5
OC (%)	1.7
Sand (%)	35.3
Silt (%)	55.3
Clay (%)	9.3

EC = Electrical conductivity
OC = Organic carbon

3.2.2. Sequential chemical extractions

A modified scheme of the sequential extraction method of Hedley et al. (1982) was used to separate the soil P into fractions using a variety of different extractants. For the sequential extractions, 0.2 g of soil was added in a 50-mL centrifuge tube and initially P was extracted by end-over-end shaking with 40 mL of double distilled deionized water for 1 hour. The soil and water were separated via centrifugation (10,000 rpm), and then this extraction process was repeated every 20 hours using progressively stronger extractants. The extraction scheme utilized 40 mL of 0.5 M NaHCO₃, 0.1 M NaOH, and 1.0 M HCl. At the end, the remaining soil residue from all treatments was digested using a mixture of 30% H₂O₂ and concentrated H₂SO₄ to extract any residual P that remained (Hedley et al. 1982).

3.2.2.1 Quantitative analysis of phosphorus

An ascorbic acid reduction method (Murphy and Riley. 1962) was used to determine both inorganic and organic P in the various extracted supernatants (Qian and Schoenau. 2000). A 10 mL aliquot of the filtered extractant from each treatment was added into a 50 mL centrifuge tube to determine inorganic P. All of the aliquots except HCl extract were acidified to pH 1.5 using 5 mL of 0.9 M H₂SO₄ and stored in a refrigerator for 30 min. The aliquots were centrifuged at 10,000 rpm for 10 min at 0°C and the supernatant was then decanted into 50 mL volumetric flasks without disturbing the sedimented organic matter. The tubes were rinsed with acidified water, and then pH was adjusted to 5.0-5.5. Then, the inorganic P (Pi) was determined colorimetrically by the Murphy and Riley procedure (1962). The aliquot from the HCl extractant was not further acidified since the pH of the aliquot was below 1.5.

Another 10 mL of the same filtered extractants was added to a different 50 mL volumetric flask to determine total P (inorganic and organic). Then, 0.5 g of ammonium persulfate and 10 mL of 0.9 M H₂SO₄ was added into each flask. The flasks were then placed on a hot plate and were gently boiled until the solution evaporated and white fumes appeared. At this point only ~ 0.3 ml of solution remained. The flasks were removed and let to cool. After cooling, 10 ml of distilled water was added into each flask, the pH was adjusted to 1.5, and total P (Pt) was determined colorimetrically by the Murphy and Riley procedure (1962). The organic P (Po) in each extraction was calculated by subtracting the determined Pi concentration from the determined Pt concentration in each extraction.

3.2.3. Acid-digestion analysis

Total phosphorus in the soils was also determined by H₂SO₄-H₂O₂ digestion as described by (Thomas et al., 1967). For these measurements, 0.25 g of soil was weighed into volumetric digestion tubes, 5 ml of concentrated H₂SO₄ was added in each digestion tube, and this suspension was heated at 360°C for 30 min. The tubes were removed from the heater, kept at room temperature for 30 minutes to cool, and then 0.5 mL H₂O₂ was added and the soil was re-suspended with a vortex mixer. The tubes were placed on the heater again, and this digestion process was repeated total 10 times. Finally, samples were allowed to cool for 30 minutes and enough deionized water was added to reach a volume of 75 mL. Phosphorus in these extracts was analyzed colorimetrically by the Murphy and Riley procedure (1962).

3.2.4. Aluminum analysis

A subsample from the NaOH extractant from the sequential extraction method was used for Al determination. A 2 mL aliquot was pipetted into 50 mL volumetric flasks, 1 mL of 10 M NaOH was added, and the flasks were filled to volume with distilled deionized water (Kiso et al. 2005). These solutions were then analyzed with an AA 1275-Varian AAS using a nitrous-acetylene flame.

3.2.5. XANES analysis

Phosphorus K-edge X-Ray Absorption Near Edge Spectroscopy (XANES spectroscopy) was used to directly determine the chemical forms of P present in the soils. Phosphorus K-edge XANES spectroscopy was conducted at the University of Wisconsin's Synchrotron Radiation Center (ALADDIN) and at the Canadian Synchrotron Radiation Foundation's double crystal monochromator (DCM) beamline. Data was collected at the P K-edge (2148 eV) in fluorescence mode using a 9 element solid-state Ge detector (Canberra) tuned to the P edge. Multiple scans were averaged to obtain acceptable signal to noise ratios for spectral analysis. Different spectra were obtained by subtracting normalized spectra of each step of the extraction from one another. This produced a spectrum of the P removed by each step of extraction technique.

3.2.6. Statistical analysis

Statistics were conducted using the data analysis package in Microsoft Excel 2003 (Microsoft, Seattle, WA) and the Statistical Package of Social Science (SPSS 14 for windows, SPSS Inc., Chicago, IL, USA) to calculate means and standard errors and to test for significant difference of P using one way ANOVA (Tukey test) at significance level of $P < 0.05$ for inorganic fertilizer and biosolids amended soils.

3.3. Results

3.3.1. Sequential Chemical Extractions

The slightly modified sequential chemical extraction method of P fractions (Hedley et al., 1982) was used to partition soil P into different P_o and P_i fractions. Results from this fractionation showed that biosolids application had a strong effect on P levels in all soil fractions compared with the inorganic fertilizer amended soil.

3.3.1.1 Water extraction

Water-extractable P_i exhibited great differences among the treatments (Table 3.2). The water-extractable P_i level was significantly higher in the inorganic fertilizer applied soil (165 mg P kg⁻¹) than in the biosolids amended soils (66 to 106 mg P kg⁻¹). The water-extractable P_i level increased with increasing rate of biosolids application in the biosolids amended soils (Table 3.2). As shown in Table 3.2, different rates of biosolids amended soils contained lower levels of water-extractable P_i compared to the inorganic fertilizer amended soil. There was more P_o present in all of the biosolids amended soils than in the inorganic fertilizer amended soil (Table 3.2). Among the soils, the water-extractable P_o level was much lower in inorganic fertilizer amended soil than in biosolids amended soils (Table 3.2). For all soils, more of the water-extractable P was in organic rather than inorganic form.

3.3.1.2 Bicarbonate extraction

Bicarbonate- P_i levels (Table 3.2) showed little variation with treatment. The highest amount of bicarbonate- P_i was observed in maximum rate biosolids amended soil, but bicarbonate- P_i was similar in inorganic fertilizer and quarter biosolids amended soil.

Interestingly, the lowest level of bicarbonate-Pi was observed in half biosolids amended soil ($1216 \text{ mg P kg}^{-1}$) but there was no significant difference among treatments.

There were large differences in the bicarbonate-Po among the soils. The lowest level of Po was observed in inorganic fertilizer amended soil and bicarbonate-Po consistently increased with increasing biosolids application (Table 3.2). The highest level of bicarbonate extractable Po was observed in maximum biosolids amended soil (904 mg P kg^{-1}) among the treatments.

3.3.1.3 NaOH extraction

Biosolids amended soil had much higher NaOH-extractable inorganic P content than did the inorganic fertilizer amended soil (Table 3.2). The biosolids amended soils overall had a large effect on NaOH-Pi levels in comparison with inorganic fertilizer amended soil. The highest level of NaOH-Pi was observed in maximum biosolids amended soil ($3252 \text{ mg P kg}^{-1}$) and lowest level was observed in inorganic fertilizer amended soil ($1306 \text{ mg P kg}^{-1}$), a trend that was similar to the bicarbonate-Pi (Table 3.2) in inorganic fertilizer amended soil. NaOH-Pi levels in the quarter, half, and maximum biosolids amended soils were respectively 1.15, 1.99, and 2.5 times higher than the inorganic fertilizer amended soil. The NaOH-Po fractions (Table 3.2) showed similarities to the bicarbonate-Po fraction. Maximum biosolids amended soil had significantly higher NaOH-Po than the other three soils. The NaOH extraction removed more P than any other extractant, and the majority of the NaOH-P was inorganic.

3.3.1.4 HCl acid extraction

The maximum biosolids amended soil had significantly the highest HCl-Pi ($2221 \text{ mg P kg}^{-1}$) and residual-P fractions (655 mg P kg^{-1}) among all soils, whereas the lowest level of HCl-Pi and residual-P were observed in the quarter biosolids and inorganic fertilizer amended soils, respectively (Table 3.2). The contribution of residual soil P fraction was small, but the differences among the soils were significantly larger than inorganic fertilizer and quarter biosolids treatments.

The HCl-Po level was also higher in different biosolids amended soils than in the inorganic fertilizer amended soil and the highest levels of both HCl-Po and residual P were observed in maximum biosolids amended soil (Table 3.2).

Table 3.2 Sequential phosphorus forms extracted in soils amended with inorganic fertilizer and biosolids (mean \pm standard error).

P form		Inorganic fertilizer	Quarter rate biosolids	Half rate biosolids	Maximum rate biosolids
		P concentration (mg kg ⁻¹)			
Extractable P	Inorganic P				
	Water	165 \pm 14.6a*	66 \pm 12.9b	80 \pm 8.9b	106 \pm 4.9b
	Bicarbonate	1363 \pm 41.0a	1391 \pm 171.1a	1216 \pm 135.0a	1526 \pm 126.0a
	Hydroxide	1306 \pm 93.0c	1510 \pm 57.7c	2601 \pm 105.0b	3252 \pm 61.0a
	Acid	916 \pm 5.9c	717 \pm 11.4d	1138 \pm 1.9b	2221 \pm 57.1a
	Organic P				
	Water	215 \pm 20.7b	329 \pm 47.2ab	316 \pm 45.9ab	376 \pm 38.5a
	Bicarbonate	211 \pm 17.6c	293 \pm 92.5c	596 \pm 118.5ab	904 \pm 84.0a
Total P	Hydroxide	291 \pm 73.8b	347 \pm 60.7b	423 \pm 66.9b	948 \pm 109.3a
	Acid	131 \pm 11.4c	256 \pm 31.8c	563 \pm 97.4b	958 \pm 95.1a
	Inorganic P	3751 \pm 31.9c	3683 \pm 137.6c	5035 \pm 40.9b	7105 \pm 117.1a
	Organic P	848 \pm 24.1d	1230 \pm 110.8c	1898 \pm 91.6b	3185 \pm 108.3a
	Residual P	295 \pm 98.3b	379 \pm 54.9b	498 \pm 13.2ab	655 \pm 28.7a
	Total P (Extractions)	4894 \pm 7.8d	5292 \pm 26.8c	7431 \pm 132.5b	10945 \pm 8.9a
	Total digestible P	4869 \pm 19.7c	5353 \pm 100.7c	7559 \pm 108.5b	11252 \pm 297.2a

* P form means followed by different letters in a row are significantly different between inorganic fertilizer and different rates of biosolids treatments at $P < 0.05$.

3.3.1.5 Total extractable phosphorus

Analysis of total soil P fractions (P_T) (Table 3.2) by the sequential extraction method showed that biosolids application significantly ($P < 0.05$) increased P_T more than did inorganic fertilizer application to the soil. The largest total P concentration was observed in the maximum biosolids amended soil. Maximum biosolids yielded significantly higher P_T ($10945 \text{ mg P kg}^{-1}$), which was higher than the amount extracted from the inorganic fertilizer amended soil ($4894 \text{ mg P kg}^{-1}$). The amount for quarter and half biosolids amended soils were intermediate between maximum biosolids and inorganic fertilizer amended soils.

Most of the P in all soils was inorganic with smaller amounts of organic and residual forms (Table 3.2). Inorganic fertilizer amended soil had slightly larger proportion of P_i (77%) than the biosolids amended soils (65 to 70%). Overall, the distribution of inorganic and organic forms of P varies among the soils. In all biosolids amended soil, the highest amount of P was NaOH-extractable, with the maximum biosolids amended soil being the largest amount extracted ($4200 \text{ mg P kg}^{-1}$) among all the soils. The highest amount of HCl-extractable P was also observed in maximum biosolids amended soil ($3179 \text{ mg P kg}^{-1}$).

3.3.2. Total Digestible Phosphorus

As shown in Table 3.2, total digestible P contents varied from 4869 to $11252 \text{ mg P kg}^{-1}$ and total digestible P contents increased according to the increasing rate of biosolids application and the highest amount of total digestible P was observed in maximum biosolids amended soil ($11252 \text{ mg P kg}^{-1}$). The total digestible P was 2.31 times higher in maximum biosolids amended soil than inorganic fertilizer amended soil. The sum of the P fractions in the (total P extractions) sequential extractions was compared with total P after acid digestion and the two agreed very well (Figure A.2).

Figure 3.1a shows the results of the extraction expressed on a mg kg^{-1} basis, while Figure 3.1b shows the same results expressed as a percentage of P_T in the soils. Among the soils, the highest amount of P_T was present in maximum biosolids amended soil (Figure 3.1a). The P_T was 2.24 times higher in maximum biosolids amended soil than inorganic fertilizer amended soil. Interestingly, all soils that received biosolids had higher amount of P_T than the inorganic fertilized soils, and the amount of P_T levels gradually increased among the quarter, half, and maximum biosolids amended soils, respectively (Figure 3.1a). For inorganic fertilizer amended

soil, 8% of the P_T was extracted with water, 32% bicarbonate, 33% hydroxide, 21% acid, and 6% was residual. In maximum biosolids amended soil, 4% of P_T was extracted with water, 22% bicarbonate, 38% hydroxide, 29% acid, and 6% was residual (Figure 3.1b). Similar trends were observed to the maximum biosolids amended soil with all other biosolids amended soils. Although absolute value of plant available P (defined operationally as the sum of water and bicarbonate-extractable P) was higher in biosolids amended soils compared to inorganic fertilizer amended soil (Table 3.2 and Figure 3.1a), the important observation was that the plant available P comprised 40% of P_T in inorganic fertilizer amended soil and 39%, 30%, and 27% in the quarter, half, and maximum biosolids amended soils, respectively (Figure 3.1b).

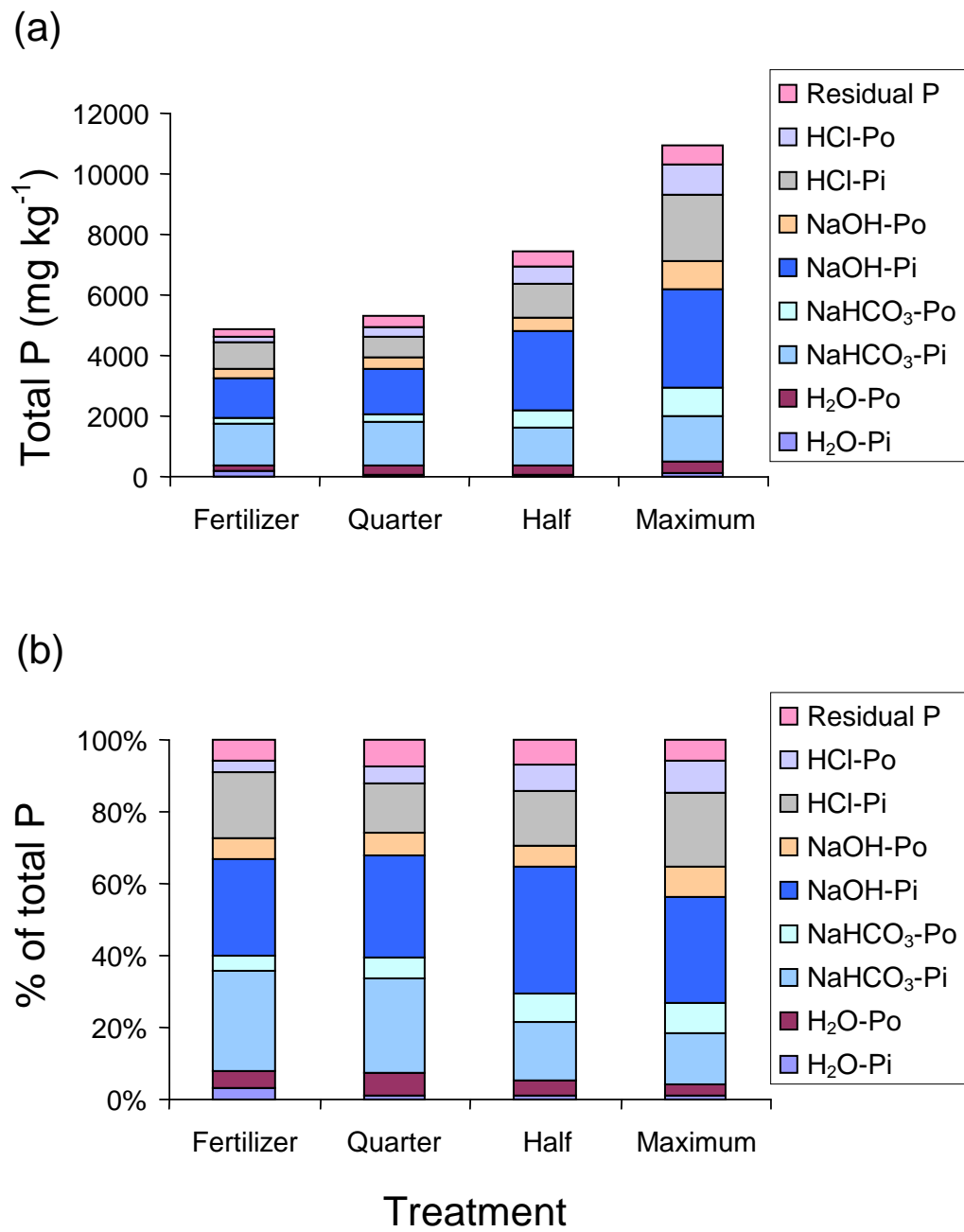


Figure 3.1 Phosphorus concentrations (a) and proportion of total phosphorus (b) contained into different fractions of the treatments.

3.3.3. XANES Results

Figure 3.2 shows P K-Edge XANES spectra collected from the solids after each step of the sequential chemical extraction process. These spectra were background-subtracted but not normalized so that the relative peak heights and intensity still correspond to the amount of P in the soil samples. The results of these experiments are consistent with the wet chemical analysis of the extracts. First of all, there is a larger total amount of P in the biosolids-amended soils (absorbance maximum is over twice as large in the biosolids amended soils). For both soils, the change in absorbance between H₂O extraction and HCO₃ extraction is relatively small. Additionally, it is observed that the largest intensity difference is between the HCO₃ and NaOH spectra for the inorganic fertilizer amended soil and between the NaOH and HCl extractions for the maximum biosolids amended soil. These observations are all in agreement with the quantitative analyses of the extracts.

In general, the spectra of all soil samples do not have sharp peaks or structural features that would make identification of the forms of P in them simple to perform. However, the spectra after NaOH extraction step do appear to have some post-edge features that are characteristic of CaPO₄ minerals (e.g. apatite, monetite, CaH₄PO₄). To more clearly determine how the speciation of phosphate is changing in the samples after extractions, different spectra were produced by subtracting spectra from successive steps of the extraction procedure from one another. The results of this are shown in Figure 3.3.

Since the amount of P removed by each step was substantially different, each different spectrum was normalized to a maximum absorbance value of 1 to facilitate comparison. Different spectra in Figure 3.3 are noisier than the spectra in Figure 3.2 because they are the difference of two fairly diluted samples. Nonetheless, clear differences in P speciation can be observed in these soils. These different spectra were compared to common phosphate standards in Figs 3.4 to 3.6.

Figure 3.4 shows the HCO₃-NaOH different spectra of the inorganic and biosolids amended soils. This different spectrum represents the forms of phosphate removed by the NaOH extraction step. For the inorganic fertilizer, there are no spectral features that stand out in the spectrum, and the majority of extracted P can be described as “sorbed” since it corresponds very well with phosphate adsorbed on an iron oxide standard.

Previous studies (Peak et al. 2001; Toor et al. 2005, 2006) have shown that adsorbed phosphate and aqueous phosphate all look very similar at the P K-edge, and so this fraction is probably best described as “labile” P. For the biosolids soils, spectra appear very different from the inorganic fertilizer amended soil. There is a small pre-edge feature that seems consistent with that observed in Fe(III)-PO₄ minerals, and a post-edge feature that corresponds fairly well with a feature common to AlPO₄ minerals such as variscite. The shape and size of the postedge peak is somewhat distorted, so there is some uncertainty in the assignment of this as an aluminum phosphate. However, high levels of Al³⁺ (2300 mg L⁻¹) were also detected in the extract for the maximum biosolids amended soil, and the water treatment facility is known to add aluminum sulfate during the treatment process. Given these facts, it seems reasonable that the NaOH step removes both Al and Fe phosphates from the biosolids amended soil.

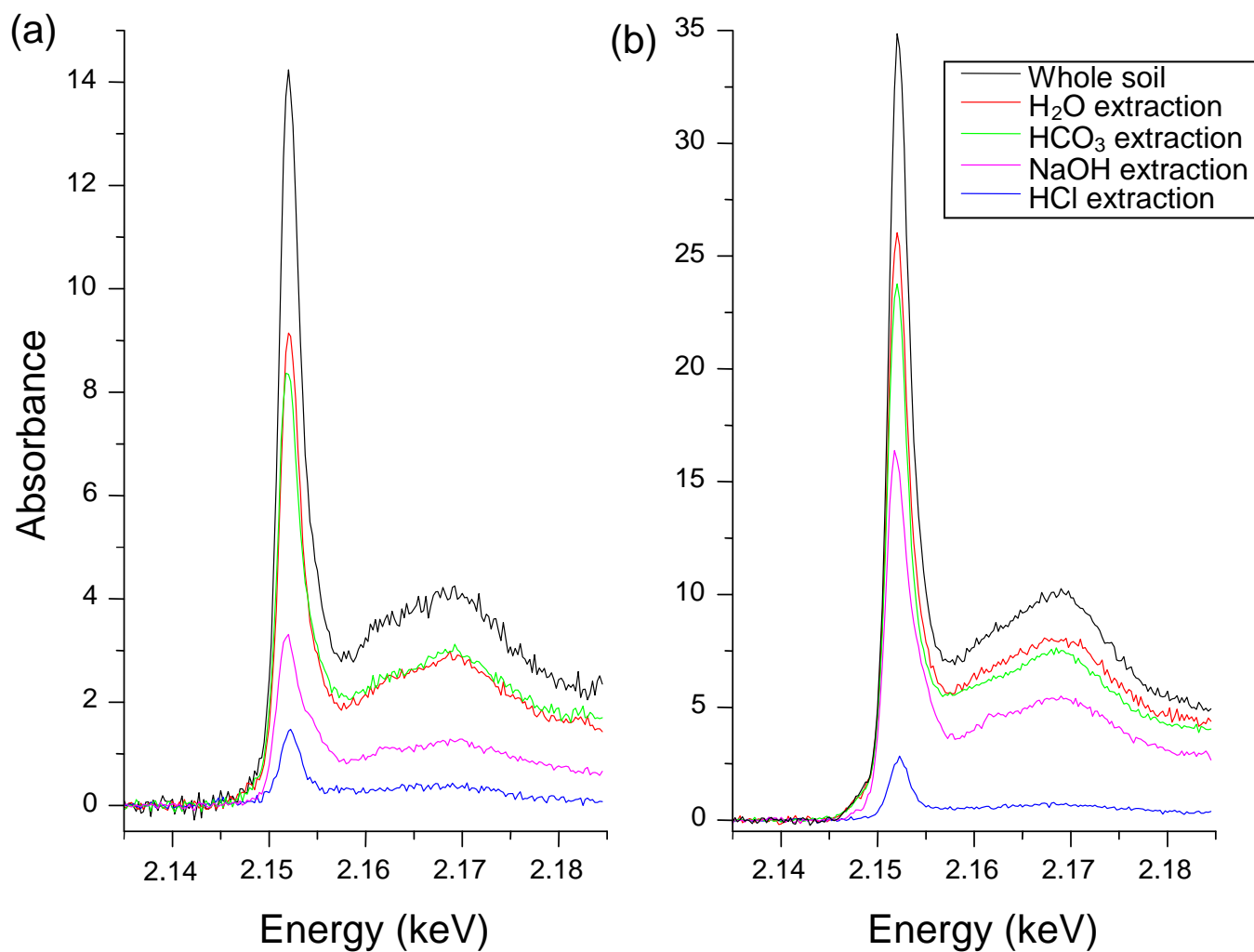


Figure 3.2 Background subtracted P K-Edge XANES spectra of soil receiving inorganic fertilizer (a) and the maximum biosolids application (b) after each step in a sequential chemical extraction. Spectra are whole soil, and the solid phase residual from H₂O, HCO₃, NaOH, and HCl extractions.

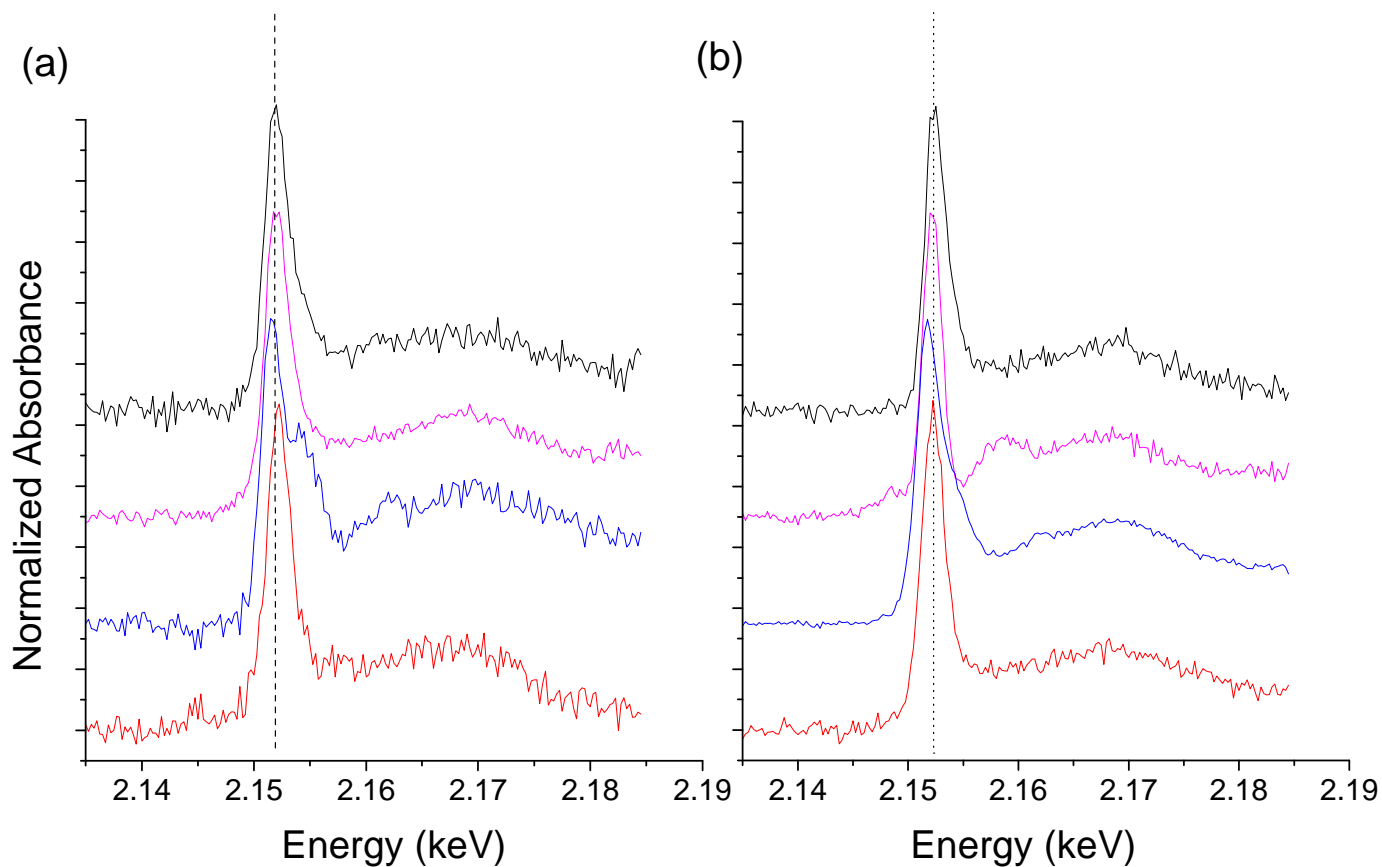


Figure 3.3 Difference spectra obtained by subtracting spectra of successive steps of the sequential extractions from one another for the inorganic fertilizer application (a) and the maximum biosolids amendment (b). These spectra show the species of PO_4^{3-} that was removed by each step in the extraction routine. Difference spectra are as follows: Whole Soil – H_2O (black), NaOH-HCO_3 (pink), HCl-NaOH (blue), and Residual after HCl (red).

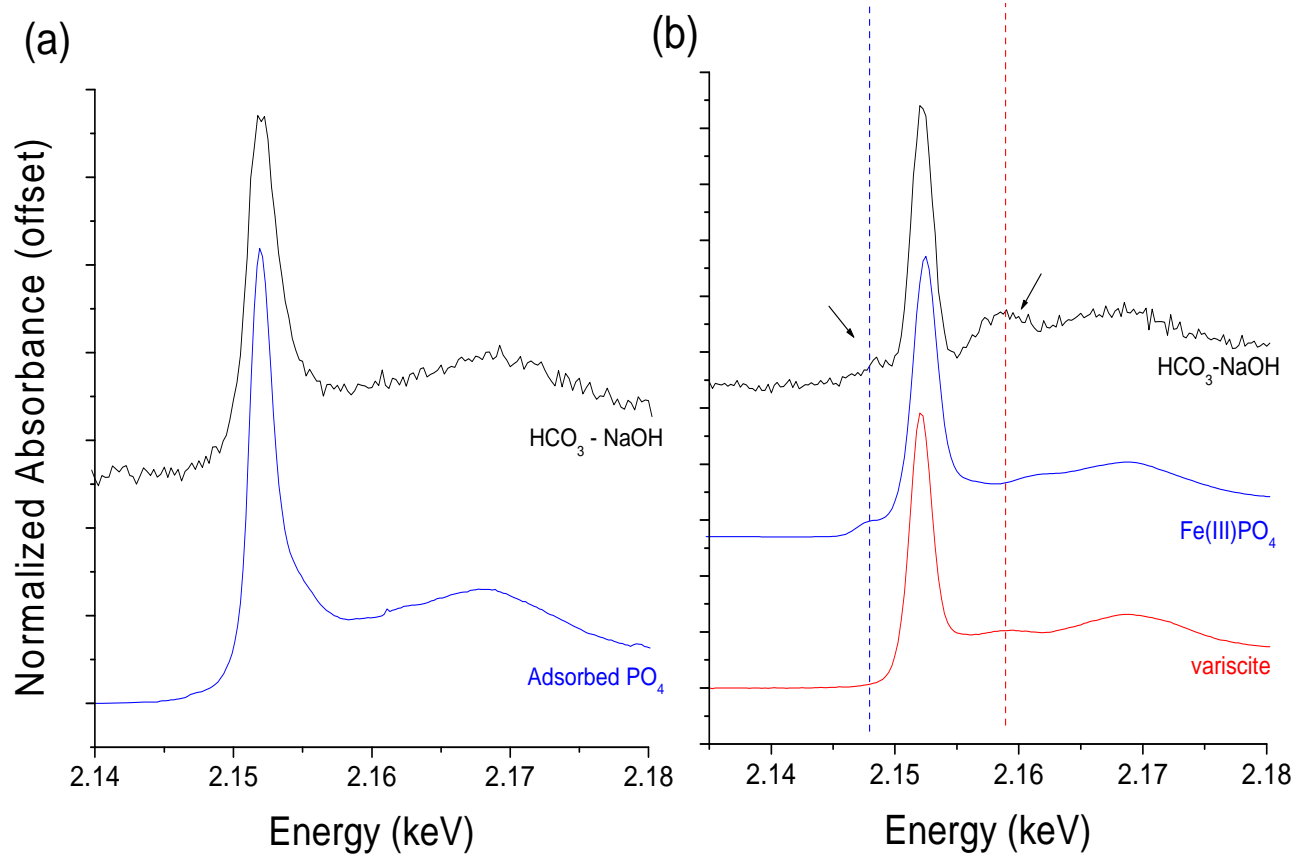


Figure 3.4 Comparison of the $\text{HCO}_3^- - \text{NaOH}$ difference spectra for the (a) inorganic fertilizer and (b) maximum biosolids samples to different phosphate standards. The $\text{HCO}_3^- - \text{NaOH}$ spectrum is the form of P removed by the NaOH step. Arrows in (b) denote spectral features consistent with metal phosphate solids and are discussed in the text.

The NaOH-HCl spectra of inorganic and maximum biosolids amended soil are shown in Figure 3.5. The NaOH-HCl spectrum is the form of P that was removed by the HCl extraction step. Both soils have spectral features that are consistent with calcium phosphate standards. However, the calcium phosphate structure is surprisingly different. For the inorganic fertilizer amended soil, the spectrum is a good match to apatite, but for the biosolids amended soil, brushite, a hydrated dicalcium phosphate, is much more consistent with the extracted soil. This is interesting because it suggests that while calcium phosphate is removed in both soils by the HCl extraction, that the true solubility of phosphate in the soils would be very different due to differences in crystal structure.

The XANES spectra of the PO_4 that remains after the final HCl step of the extractions are shown in Figure 3.6. The spectra from both inorganic and biosolids amended soils appear quite similar. The white line energy (denoted with a dashed line) aligns precisely with a Fe(III)- PO_4 standard. The position of the white line energy is specific to the number of electrons in a 3d transition metal (Okude et al., 1999). However, it is not known whether this is the true residual species or if a small amount of entrained aqueous phosphate might be re-adsorbing to crystalline iron oxides in this extraction step. Interestingly, there is no evidence of Po in the residue since the white line energy does not match with organic P standards. Some previous sequential extraction studies (Dobermann et al., 2002) have operationally defined the residual fraction as being Po forms.

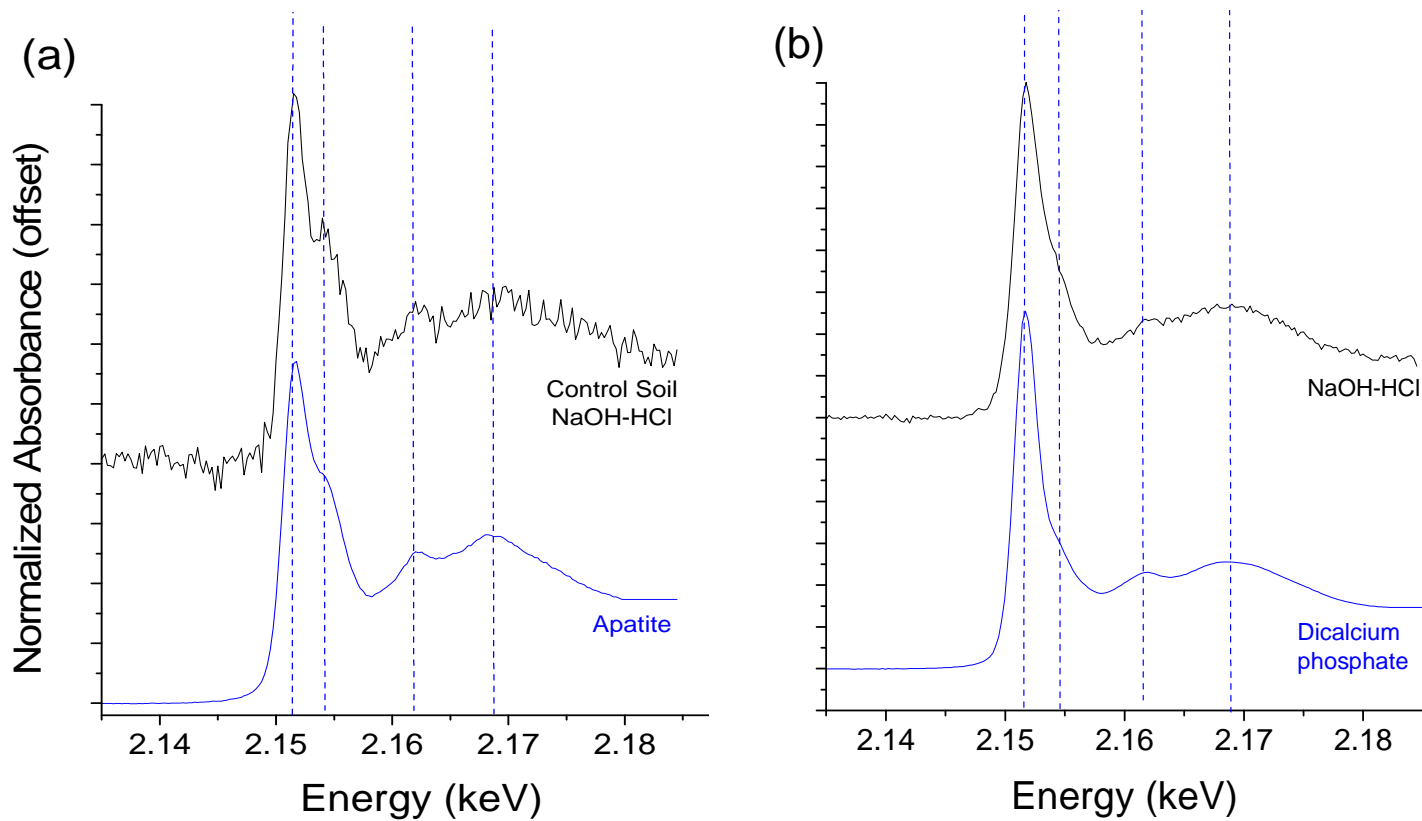


Figure 3.5 Comparison of the NaOH – HCl difference spectra for the inorganic (a) and maximum biosolids (b) samples to calcium phosphate standards. The NaOH-HCl spectrum is the form of P removed by the HCl step.

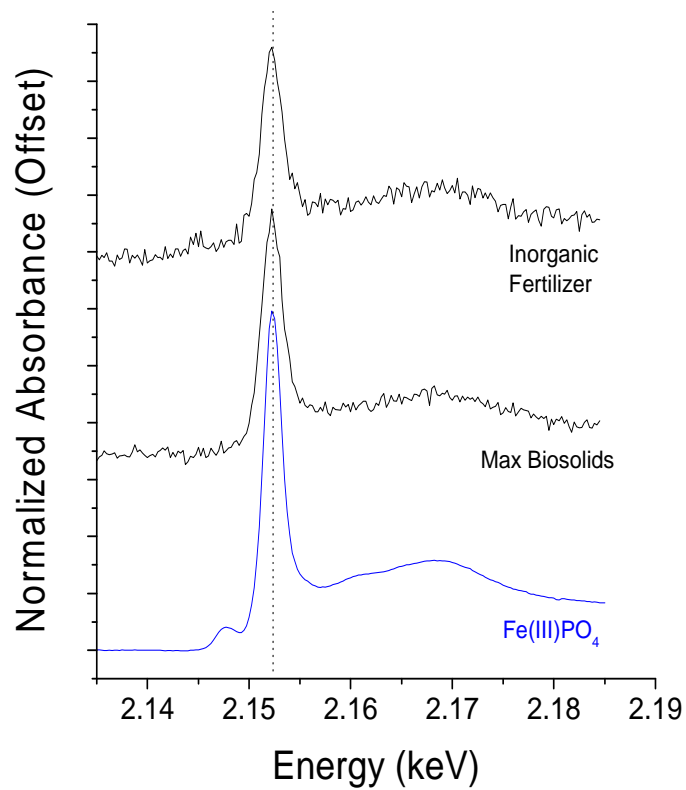


Figure 3.6 Comparison of the residual spectra for the inorganic and maximum biosolids samples to an iron (III) phosphate standard. This is the P that persists after the final HCl extraction step.

3.4. Discussion

In general, the results from the sequential extractions showed that the extraction steps removed different amounts of P from the soil depending upon the type of fertilizer amended. This experiment also showed that labile P, operationally-defined as both water and bicarbonate-P (Schoenau et al., 1989) percentages were higher in the inorganic fertilizer amended soil than biosolids amended soils, although total amount of P was higher in biosolids amended soils. This is consistent with the observation that triple super phosphate P is four to seven times more available to plants than common P forms in biosolids (McCoy et al., 1986). The relatively small percentages of labile P in biosolids amended soils may be due to the presence of different elements and surfaces that can potentially react with and fix phosphates (Coker and Carlton-Smith, 1986; Kyle and McClintock, 1995; Kashem et al., 2003). NaOH-extractable P, which is typically considered to be Fe and Al-associated P (McLaughlin et al., 1977; Bowman and Cole, 1978), was higher in all biosolids amended soil and the highest amount of Fe-Al-associated P was observed in maximum biosolids amended soil. The water treatment facility is known to add aluminum sulfate during the treatment process and high amount of extractable Al was also present in the NaOH extracts from all biosolids amended soils (data not shown). This suggests that the major portion of P in biosolids amended soil is present as Al-P and Fe-P. Surprisingly, HCl-extractable P was much higher than in the inorganic fertilizer amended soil into different rates of biosolids amended soils, which suggests that these may contain much more primary mineral P (Tiessen et al., 1984) and particulate organic matter (Qian and Schoenau, 2000). Smaller proportion of residual P in all soils compared to the P_T is probably due to the greater removal of P from the sequential chemical extraction process (Toor et al., 2005).

In general, the results from XANES analysis showed that the extraction steps do remove distinct chemical species of P from the soils. The H_2O and bicarbonate extractions represent a “labile” fraction of P, and the NaOH and HCl extractions remove more strongly bound forms. Some interesting observations from these experiments are that while the total amount of P in the biosolids amended soils was much larger than in the inorganic fertilizer amended soil, the majority was bound in a dicalcium phosphate solid fraction that was not removed with mild “labile” extractants. Additionally, the NaOH extraction removed mostly Al and Fe phosphate mineral phases in the biosolids amended soils, whereas in the inorganic sample adsorbed P was removed. This suggests that there is a trend in the biosolids amended soils towards different solid

precipitates of phosphate. In the biosolids amended soils, the calcium phosphates were much higher in concentration and poorly crystalline, but in the inorganic fertilizer amended soil, apatite was present at lower total amounts.

Overall, it was found that very different phases are present in biosolids *vs.* inorganic fertilizer amended soils. This makes it difficult to perform quantitative XANES analyses (PCA, LC-XANES) on natural samples of whole soils since the fertilizer source and other chemical parameters will greatly affect the speciation. This fact also makes operational definitions of sequential chemical extractions more difficult to assign. For example, the same extractant (HCO_3) removed very different phases in inorganic *vs.* biosolids amended soils.

3.5. Conclusions

The results of the present study demonstrate that long-term biosolids amendments do affect soil P fractions compared to the use of an inorganic fertilizer. Sequential chemical extractions showed that labile fraction of P percentages in inorganic fertilizer amended soil was larger than biosolids amended soils though both sequential chemical extractions and XANES analysis showed that the total amount of P in biosolids amended soils was much larger than in the inorganic fertilizer amended soil. The results also showed that Ca-associated P was very high in biosolids amended soil. The results of the XANES spectroscopic study showed that much of the P in biosolids amended soils was in a dicalcium phosphate solid form, with some aluminium and iron phosphate forms. However, in inorganic fertilizer amended soils, most of the P was present as labile and sorbed forms with some apatite-type calcium phosphate. Overall, the results indicate that speciation of P in inorganic fertilizer and biosolids amended soils is quite different. Additionally, one might infer that the impact of P on the environment from biosolids amended soils may be considerably less than expected based upon their total P levels due to the majority of P being present in less labile fractions.

4. PHOSPHORUS DESORPTION STUDIES IN BIOSOLIDS-AMENDED AND INORGANICALLY-FERTILIZED SOILS.

4.1. Introduction

Knowledge of phosphorus (P) dynamics in soil is essential for predicting its bioavailability and for assessing the risk of P transfer from soil to water bodies. Phosphorus is known to accumulate and release in soil when it is applied in excess of the crop removal, as is common in areas with high density livestock confinement operations and in biosolids amended soil. Over time, this can increase the risk of P transport to water bodies through leaching, erosion, and runoff (Sims et al., 1998; Sharpley and Tunney, 2000; Hooda et al., 2001; Koopmans et al., 2004). The problem arises through the run-off loss of both dissolved P and P-rich solids to bodies of water. This problem commonly leads to eutrophication and can severely affect aquatic life.

Release of P in soil is strongly influenced by chemical factors such as phosphate concentration, pH, and period of reaction (Barrow, 1983). The rate of P release (desorption) is initially fast and then proceeds slowly (Munns and Fox, 1976; Lookman et al., 1995; Toor and Bahl, 1999; Siddique and Robinson, 2004), but the total amount of P desorption increases with time (Barrow, 1983). At high pH in the soil, phosphorus desorption often increases due to the increasing negative charge on Al and Fe oxide surfaces because organic acids and soluble humic and fulvic acids released during the decomposition of organic matter which increases the desorption of added phosphate by competing for binding sites of the soil colloids (Sibanda and Young, 1986; Bhatti et al., 1998; Haynes and Mokolobate, 2001). But at high pH, less desorption may occur if the pH leads to enhanced hydrolysis of hydroxyl-Al associated with organic matter (Haynes and Mokolobate, 2001). The desorption of P is also influenced by the soil:solution ratio (White, 1966; Barrow and Shaw, 1979). Some researchers (Fordham, 1963; Barrow et al., 1965; White, 1966) found that low soil:solution ratios favoured P desorption but in contrast, Hope and Syers (1976) found that high soil:solution ratios favoured P desorption.

Two common experimental techniques that have been used to measure P desorption are continuous flow and infinite dilution methods. The continuous flow method (as shown in Sparks et al, 1980) is used to remove the desorbed species from the substrate (Quaghebeur et al., 2005) in a flow through system and monitor the desorbed concentration in the effluent over time (Bar-

Tal et al., 1995). This method has also been used to study the kinetics of P desorption from a variety of soil types. Many researchers (Elkhatib and Hern, 1988; Bahl, 1990; Yang and Skogley, 1992) have explained the kinetics of P desorption and it was concluded that P desorption can be modeled clearly using various kinetic equations. In this study, the two most common ones, the first-order kinetics and the parabolic diffusion equation, have been used to model the relationship between P desorption and time.

It is known that the chemical form of P in soils will have a large effect on the rate and extent of desorption. X-ray Absorption Near Edge Structure (XANES) spectroscopy is a molecular-scale spectroscopic technique that has been used to identify P minerals present in whole soils (Hesterberg et al., 1999; Beauchemin et al., 2003; Shober et al., 2006). Phosphorus K-edge XANES spectroscopy should be able to monitor the changes in speciation of P in soil samples after desorption studies are completed.

The overall goals for this chapter were to (i) compare P desorption kinetics in biosolids applied soils to inorganic fertilizer amended soil; (ii) investigate the effects of soil to solution ratios and pH on P desorption from soils amended with inorganic fertilizer and biosolids; and, (iii) perform solid state speciation of soil samples before and after desorption with P XANES spectroscopy to determine how P desorption affects speciation. It was hypothesized that this combined experimental approach will produce a better estimate of P availability compared to any single experimental technique.

4.2. Materials and Methods

4.2.1. Field study and experiment

The inorganic fertilizer and maximum biosolids applied soils were used in this study. Soil samples were collected from four replications of inorganic fertilizer and maximum rate biosolids amended soils. Two composite soil samples were collected by mixing four replications of each treatment from the surface layer (0-15 cm) of the soil for desorption experiments. The details of the field study and experiment of provided soil were given in section 3.2.1 (Chapter 3).

4.2.2. Desorption studies

In the environment, desorbed P can enter to the surface and ground water through leaching, lateral water movement, and erosion. In the laboratory, the rate of desorption of P was

evaluated from the two soils using two different methods: continuous flow and infinite dilution method. These two methods were applied to investigate how P desorption kinetics are affected by amendment with biosolids vs. inorganic phosphorus fertilizer. Continuous flow and infinite dilution methods approximate P losses due to leaching and lateral water movement in stationary soil and P release from a soil particle that enters surface waters via erosion, respectively. Continuous flow results can be modeled to describe the kinetics of P desorption with time and the infinite dilution method can be used to study the effects of different soil:solution ratio and solution pH on P desorption from the soil samples.

4.2.2.1 Infinite dilution analysis

The dilution method was conducted by varying the soil: solution ratio at pH 5.0 or 7.5 using two composite soil samples from the inorganic fertilizer and maximum biosolids treatments. Forty mL of distilled deionized water was placed in each centrifuge tube with varying amount of soil added. Ten soil/solution suspensions were prepared with the amount of soil varied from 0.005 to 100 g L⁻¹. End-over-end shaking was applied for 4 days to reach equilibrium conditions. At the end of 4 day, soil solutions were centrifuged at 10,000 g for 10 min, filtered with 0.45 µm filter paper, and analyzed using the colorimetric method of Murphy and Riley (1962) for phosphate levels. To verify that 4 days was sufficient time for equilibrium, preliminary experiments were conducted with sample collection done every 24 hours for 6 days (Figure A4). Collected extractants were centrifuged, filtered, and analyzed using colorimetric method and no change in P levels was observed after 4 days. Solution pH was adjusted to 5.0 and 7.5 with diluted HNO₃ and/or NaOH as necessary.

4.2.2.2 Continuous-flow method

Exactly 0.2 g of each soil sample was suspended in 20 mL of 0.01 M NaNO₃. This suspension was then injected into a 47 mm Nuclepore Swin-LokTM filter holder containing a 0.45-µm GelmanTM cellulose ester filter (Eick et al., 1998). The 0.01 M NaNO₃ solution was used as a desorbing solution and was adjusted to the original soil pH by HNO₃ and/or NaOH as necessary. The filter holder plus sample were weighed before and after the desorption experiment to determine the volume of entrained solution (Eick et al., 1998). The filter holder was then connected to a peristaltic pump to maintain a constant flow of 0.60 mL min⁻¹ of

solution through the thin disk. The solution was pumped through the thin disk and samples (12 mL) were collected at 20 min intervals for 20 hours with a fraction collector. The P concentration was measured to determine both the total P desorbed and the entrained concentration from all collected samples using the colorimetric method of Murphy and Riley (1962). The P concentration of the filtrate was also measured to determine the total P desorbed and the entrained concentration.

4.2.2.2.1 Kinetic modeling

Two kinetic models were applied to better understand the effects of inorganic fertilizer and biosolids amendment on desorption rates. The first order chemical reaction and parabolic diffusion equations were used in this study to model the experimental P desorption data obtained from the continuous flow method. These equations have been widely used in desorption studies of soils and soil components. The pseudo first order model is expected to describe the desorption data when the chemical reaction can be rate limited. The equation described by Sparks et al. (1980) was used to model the first order reaction. The equation is expressed as:

$$\ln (P_t/P_0) = -k_d (t)$$

where P_t is the amount of P sorbed at desorption time t ($P_0 - P_{\text{desorbed}}$), P_0 is the amount of P sorbed at time 0, t is time (m), and k_d is the apparent desorption rate constant (m^{-1}). A graph of $\ln (P_t/P_0)$ vs. t will yield a straight line of slope $-k_d$ when the reaction is first order (Eick et al., 1998).

The parabolic diffusion model by Hodges et al. (1987) is expected to describe desorption data when mass transfer is rate limiting. The parabolic diffusion equation is expressed as:

$$F_d = kt^{1/2}$$

where F_d is the fraction desorbed ($1 - P_t/P_0$), $t^{1/2}$ is the square root of time in minutes, and k is the diffusion rate constant (m^{-1}). A graph of F_d vs. $t^{1/2}$ will be linear, having slope k when the reaction is diffusion-controlled (Sparks et al., 1980).

4.2.3. XANES analysis

Phosphorus K-edge XANES spectroscopy was used to directly determine the chemical forms of P present in the samples. Remaining soil solids from the continuous flow desorption experiments were analyzed by P K-edge XANES spectroscopy. A small amount of air-dried, fine ground solid soil sample was placed on a piece of graphite tape and transferred into the ultra high

vacuum (UHV) chamber of the Canadian Synchrotron Radiation Foundation's (CSRF) beamline at University of Wisconsin Madison's ALADDIN synchrotron facility. The beamline was calibrated using P powder to the edge energy of 2145 eV in the total electron yield (TEY) spectrum (Toor et al., 2005). The electron storage ring was operated at 1 GeV for this experiment. Several (4-10) individual scans were taken and averaged for each soil sample (after correcting for edge shifts, if necessary) to improve the signal to noise ratio (Toor et al., 2005). Data was collected in fluorescence mode using a 9 element solid-state detector (Canberra) for all soil samples, and in TEY mode for concentrated standards to avoid self-absorbance effects. WinXAS v.3.1 software was used to process the P XANES spectra. The spectra were background subtracted using a first order polynomial over the pre-edge region, and unless noted, were normalized over the energy range of interest to an edge jump of 1.0 between 2.14 and 2.18 keV.

4.3. Results

4.3.1. Infinite dilution analysis

The soil:solution ratio had a significant effect on the total amount of P desorbed (Figure 4.1). In this experiment, a gradual decrease in P desorption with increasing soil:solution ratios was found from both inorganic fertilizer and maximum biosolids amended soil, although higher P desorption was observed in the inorganic fertilizer samples. The largest amount of P was desorbed at a soil:solution ratio of 0.005:1 and the smallest amount at a ratio of 100:1 g L⁻¹ for both soils (Figure 4.1). The P desorption at each soil:solution ratio was found to be much higher in inorganic fertilizer amended soil than maximum biosolids amended soil except the soil:solution ratio of 1:1 g L⁻¹ (Figure 4.1). In addition, pH had a large effect on P desorption in both soils. For example, desorption of P from both inorganic fertilizer and maximum biosolids amended soils was less at high pH (7.5) (Figure 4.1). A greater pH effect was observed with small soil:solution ratio but the impact of pH was decreased with increasing soil:solution ratio.

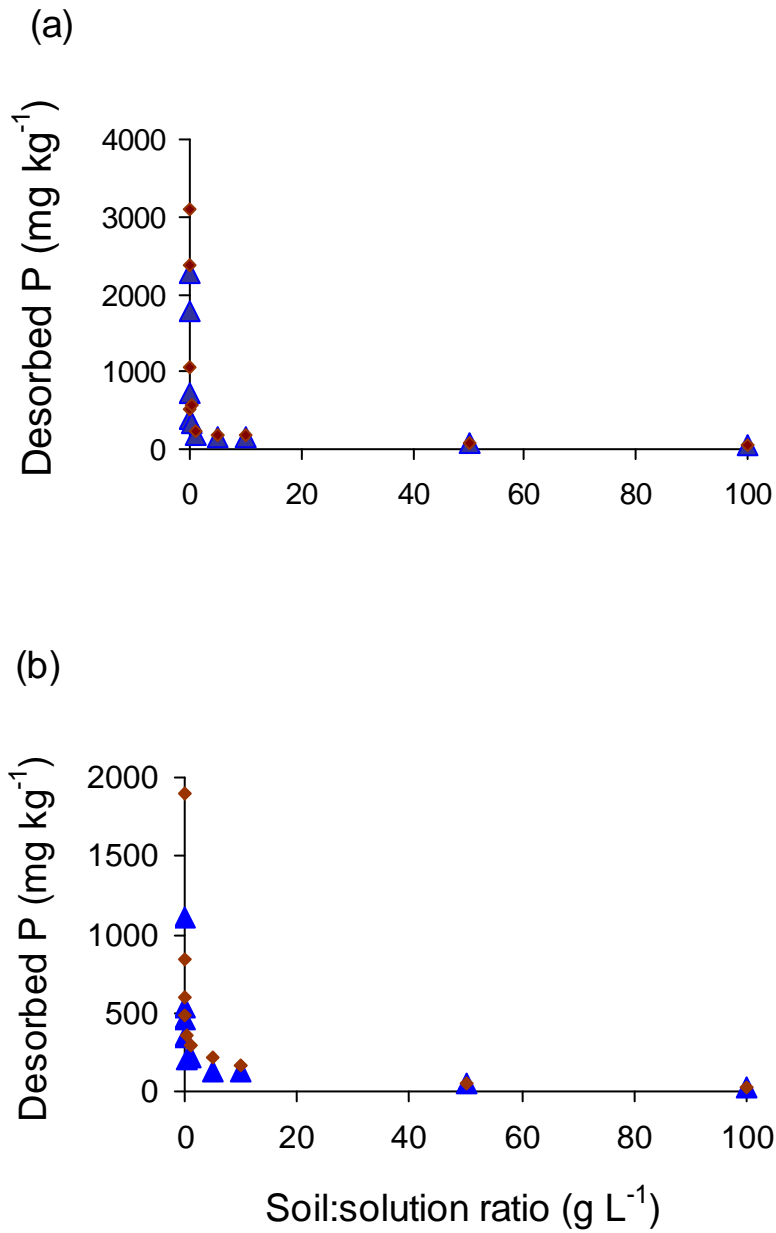


Figure 4.1 Phosphorus desorption affected by soil:solution ratio and pH for (a) inorganic fertilizer and (b) maximum biosolids amended soils.

4.3.2. Continuous flow analysis

Phosphorus desorption based on three replications of each of the two soil treatments conducted over 20 hr periods were summed and plotted against time (Figure 4.2). Initially, the rate of P release was rapid in all samples and then decreased gradually over time. Figure 4.2 showed that the initial high rate of desorption lasted more or less up to 8 hr, and then cumulative P desorption was slower over the remaining period. The cumulative P desorption in inorganic fertilizer amended soils was much higher than the biosolids amended soils. The mean total quantity of P desorbed over 20 hr periods using the 0.01 M NaNO₃ solution was 894.5 and 572.9 mg P kg⁻¹ from inorganic fertilizer and biosolids amended soils, respectively. The experiments were ended at 20 hr period due to limitations in equipment, but for most samples there was small but continued desorption even at the end of the experiment (Figure 4.2).

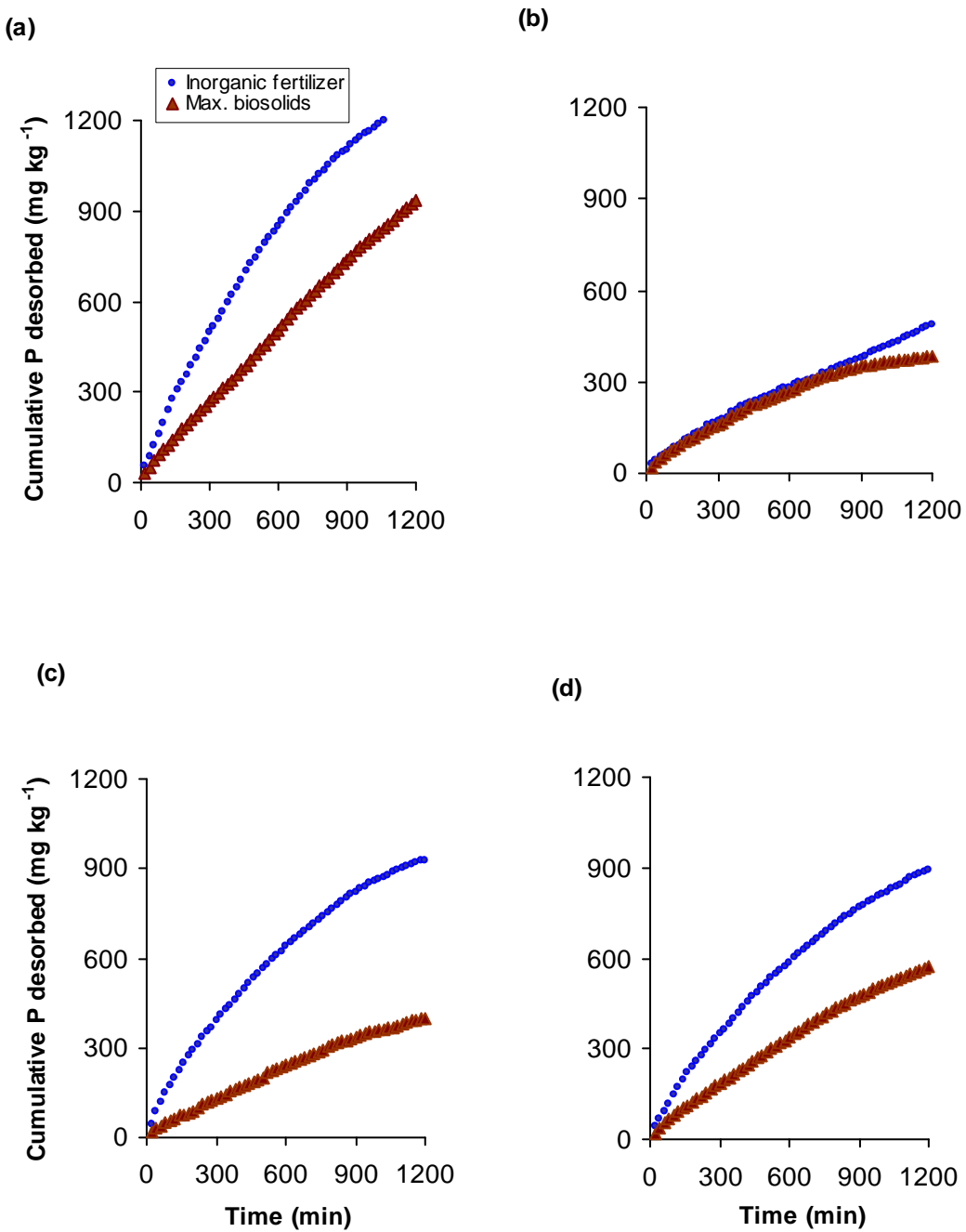


Figure 4.2 Cumulative phosphorus desorption from inorganic fertilizer and maximum biosolids amended soils with time using the continuous flow method. Data are presented here individually for the three replications (a, b, and c) and (d) the average P desorbed for each soil.

4.3.2.1 Kinetics modeling

The first order and parabolic diffusion equations were applied to describe the desorption kinetics of P from inorganic fertilizer and biosolids amended soils. These two equations were fitted to describe the P desorption data at the two different time periods. No single model performed well with the entire set of data for both soils; therefore, data sets were broken into two time range of periods: from 0-480 and 480-1200 min. The kinetic parameters calculated using two equations for P desorption data are given in Table 4.1, and Figure 4.3a shows the first-order model and Figure 4.3b shows the parabolic diffusion models. The first order model seemed the best fit with the first time period of data points, which indicates that the initial P desorption rate in both the inorganic fertilizer and biosolids amended soils may be chemically rate limited (Figure 4.3a). The parabolic diffusion model was the best fit with the second time period of data points, which suggests that at longer time diffusion may control the desorption rate (Figure 4.3b).

Table 4.1 Kinetics modeling parameters from first order and parabolic diffusion equations used to describe phosphorus desorption kinetics for soils amended with inorganic fertilizer and biosolids.

Treatment	Time (min)	<u>First-order</u>		<u>Parabolic diffusion</u>	
		$-k_d$	r^2	K	r^2
Inorganic fertilizer	0-1200	-2×10^{-4}	0.993	3×10^{-4}	0.975
	0-480	-2×10^{-4}	0.995	4×10^{-4}	0.993
	480-1200	-1×10^{-4}	0.992	2×10^{-4}	0.990
Maximum biosolids	0-1200	-4×10^{-5}	0.982	8×10^{-5}	0.992
	0-480	-4×10^{-5}	0.997	2×10^{-4}	0.997
	480-1200	-4×10^{-5}	0.991	7×10^{-5}	0.990

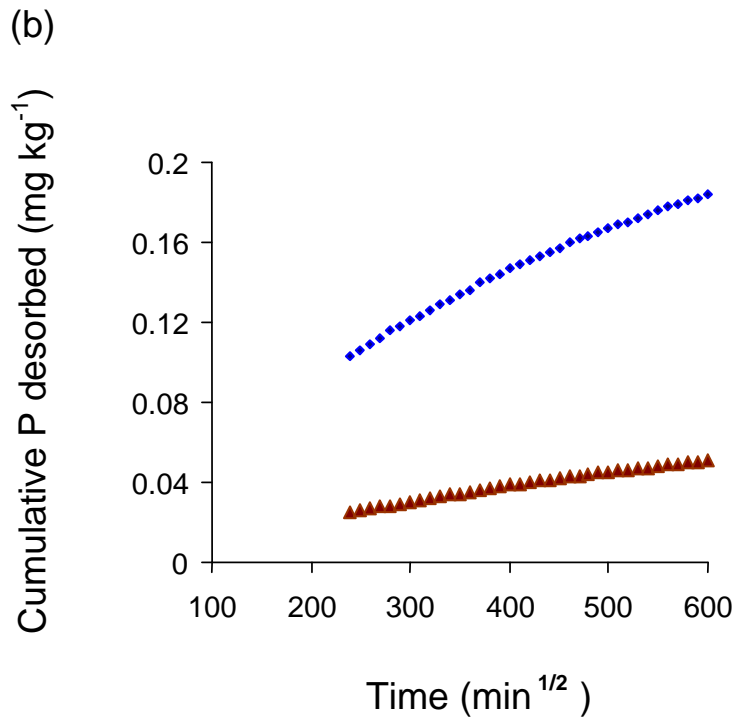
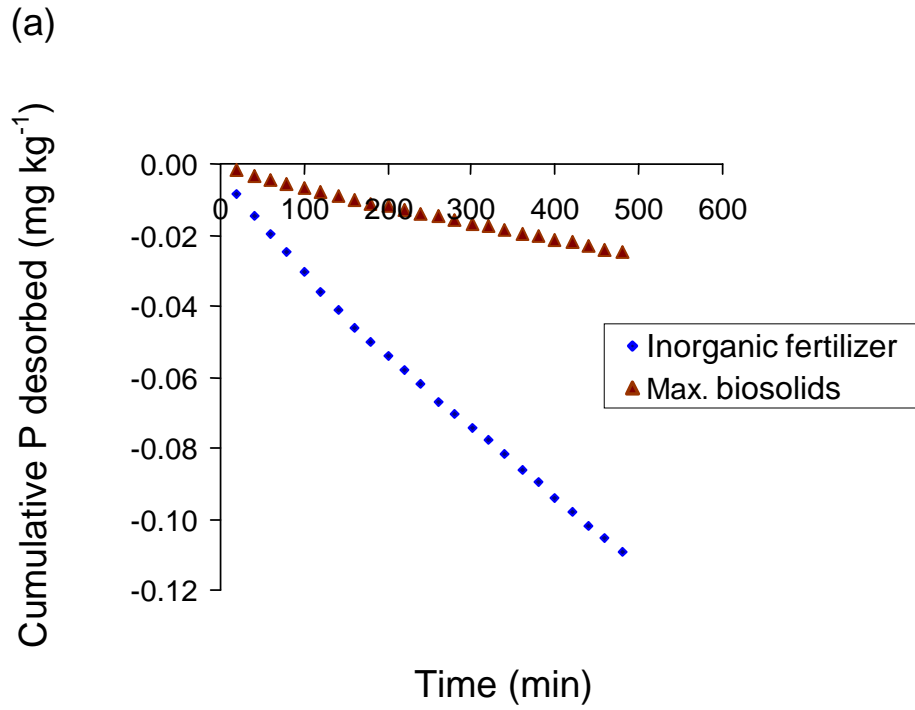


Figure 4.3 (a) First order and (b) parabolic diffusion models of mean phosphorus desorption for both inorganic fertilizer and maximum biosolids amended soils.

4.3.2.2 XANES results

Initially a variety of phosphate standards were analyzed with XANES to aid in interpreting peak positions and intensities for the samples. These are shown in Figure 4.4 and are offset for clarity. Standards were collected in total electron yield (TEY) mode to minimize self-absorption effects that can distort the spectra of concentrated samples.

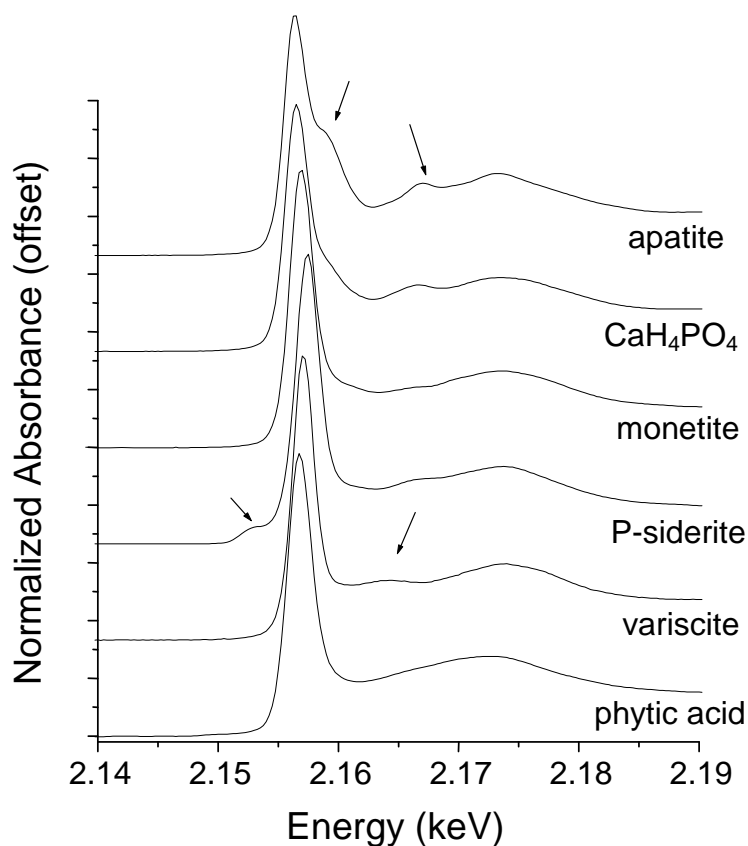


Figure 4.4 Phosphorus K-Edge XANES spectra of a variety of CaPO_4 minerals of differing structure (apatite, CaH_4PO_4 , and monetite), Fe(III) PO_4 (siderite), AlPO_4 (variscite), and an organic phosphate standard (phytic acid). All data were collected in Total Electron Yield (TEY) mode to minimize self absorption effects. The arrows note peaks that can distinguish Al, Fe(III), organic and Ca phosphates from one another.

From the standards, it is clear that there are some differences in main peak position for different phosphate minerals that can aid in identification. There are also changes in the number and position of pre-edge and post-edge peaks that can distinguish Al, Fe(III), organic, and Ca phosphates from one another. This has been shown in many previous studies (Hesterberg et al., 1999; Peak et al., 2002; Beauchemin et al., 2003).

The individual replicate samples were next analyzed from continuous flow desorption studies. Stacking their normalized spectra on top of one another allows for comparison of any changes in the samples that might be due to plot variability or experimental variability. The results are shown in Figure 4.5. There is very little difference in any of the individual samples, and an average spectrum is therefore acceptable to use as representative of the maximum biosolids and inorganically fertilized soil samples for future discussion.

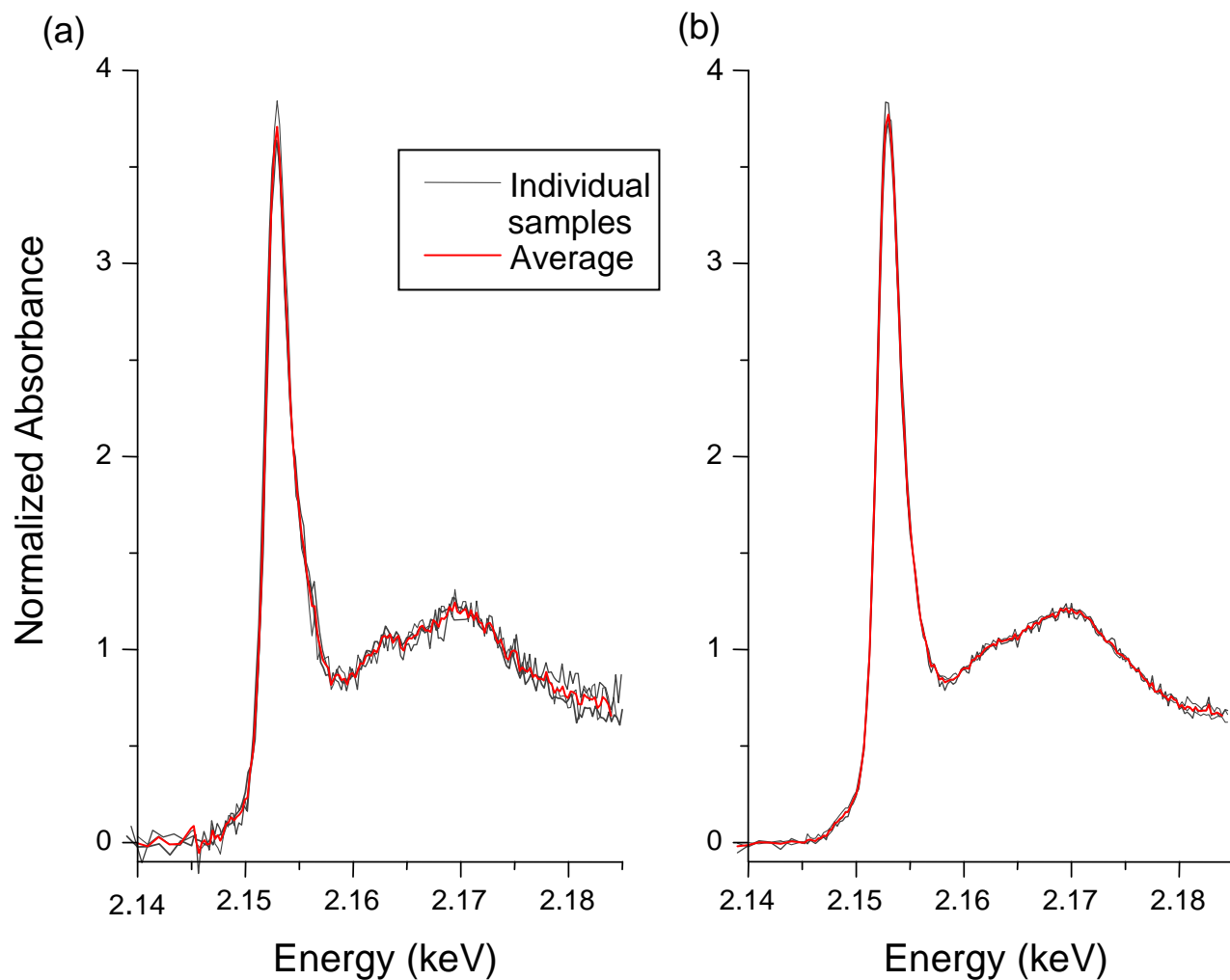


Figure 4.5 Phosphorus K-Edge XANES spectra of individual replicates after the continuous flow desorption experiments using inorganically fertilized soil (a) and soil receiving the maximum biosolids treatment (b). Individual replicates are shown in light grey, whereas the average scan is in red. No major differences in spectra were observed for any replicate.

Figure 4.6 compares background-subtracted XANES spectra of both of the unaltered soil samples to the composite average desorption spectra previously shown in Figure 4.5. From this Figure, it is clear that the intensity of the P signal has decreased (height of the main peak as well as overall intensity of the spectrum for desorption samples). It is also clear that some changes in the spectral features post-edge have occurred. For the inorganic-fertilized sample, peaks that are consistent with crystalline CaPO_4 minerals are more pronounced in the desorption sample. For the maximum biosolids sample, on the other hand, the spectral features post-edge became less pronounced after desorption and no clear evidence of crystalline minerals is observed.

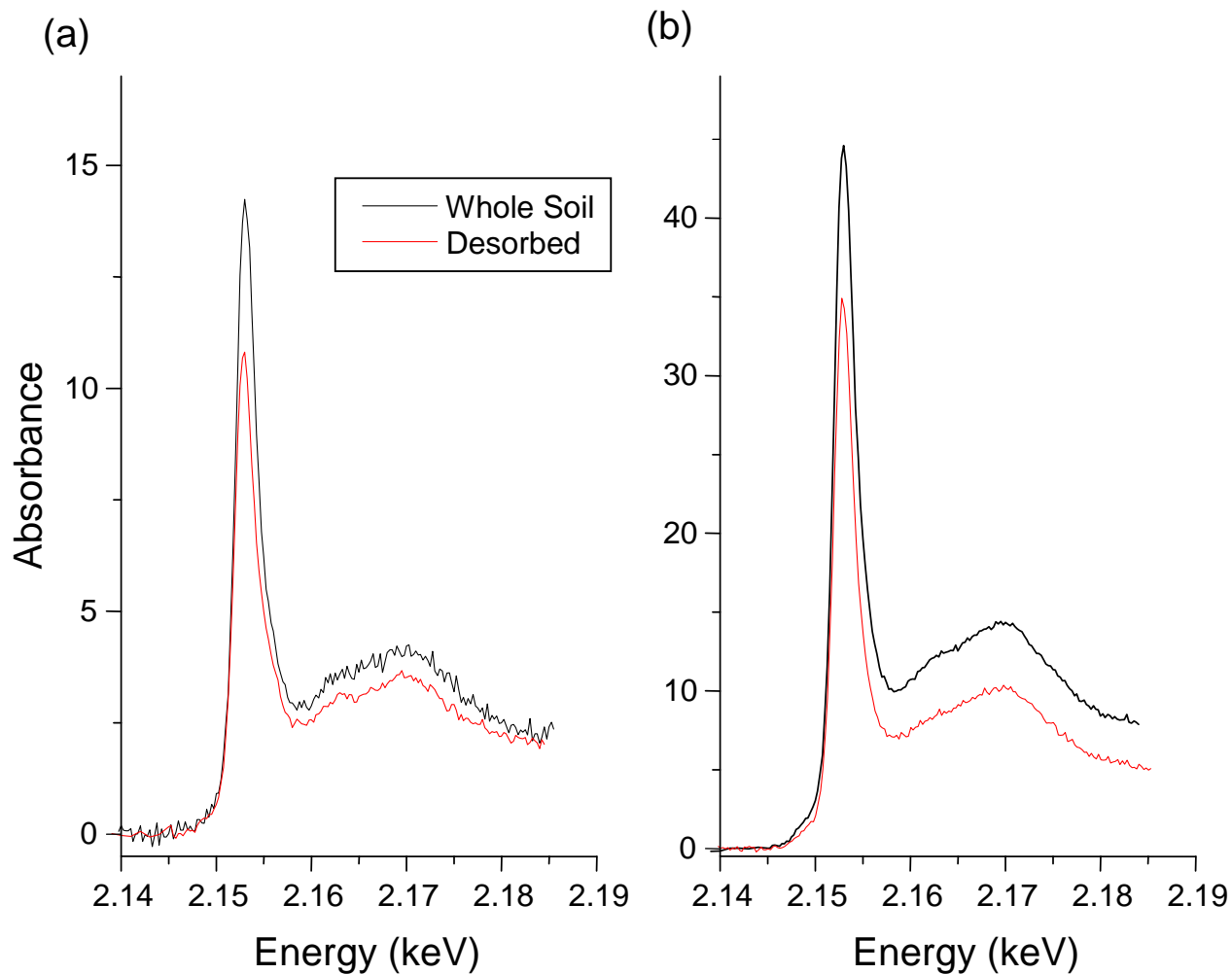


Figure 4.6 Comparison of whole soil spectra to post-desorption spectra for the continuous flow experiments using inorganically fertilized soil (a) and soil receiving the maximum biosolids treatment (b). The spectra shown are an average obtained from the three replicates as shown in Figure 4.6. Note that the absorbance scales on (a) and (b) are different.

Effects of desorption on P speciation in the samples can be more clearly observed when the spectra are stacked on top of one another for comparison (Figure 4.7).

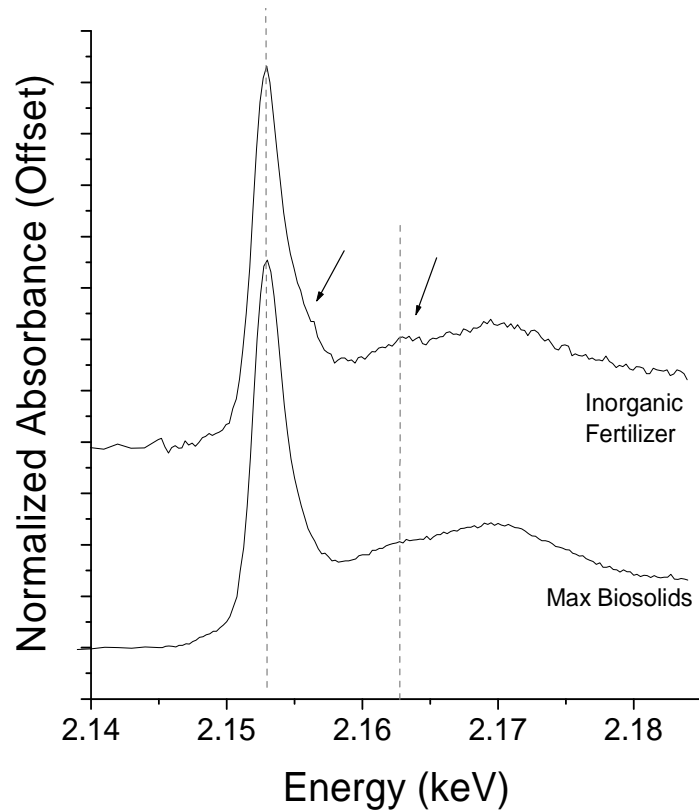


Figure 4.7 Comparison of normalized desorption spectra from the inorganically-fertilized and maximum biosolids treated soils. The arrows in the inorganic soil sample point towards peaks that are consistent with a larger proportion of crystalline CaPO_4 minerals in this sample.

As mentioned earlier, there are features (marked with arrows) in the inorganically fertilized samples that are consistent with crystalline PO_4 phases. Since the spectra are both normalized to the same step size, one can also observe far more noise in the inorganic sample. Probably, this observation relates to the fact that the overall signal is lower in the inorganic samples.

4.4. Discussion

The results obtained for the desorption of P at different soil:solution ratios indicate that these ratios do affect the extent of P desorption. Phosphorus desorption was higher with low soil:solution ratio as indicated in Figure 4.1. This suggests that at low soil:solution ratio, the exchange of phosphate per unit weight of soil with the solution increases (White, 1966). Increased microbial activity with increasing P concentration of the soil suspension can cause decreased P desorption (Larsen and Widdowson, 1964) and may be due to a lack of equilibrium condition in the soil (White, 1966). One of the factors governing phosphate exchange in solids and water is the pH of the solution. Phosphorus desorption rate decreased with the increased pH in both soils (Figure 4.1). High pH favors the formation of hydroxylapatite. This hydroxylapatite remains insoluble in soil at high pH (>7) and at high pH, P is absorbed on the high affinity sites of the Fe and Al oxides which is slowly transformed into Ca-phosphates (Freeman and Rowell, 1981; Castro and Torrent, 1998; Shober et al., 2006). In contrast, low pH increases the dissolution of Ca-P and desorbable P comes from active P fractions in Ca-P rich soil (Indiati and Sharpley, 1998).

The data collected from continuous flow experiment showed that initial P desorption was faster in inorganic fertilizer amended soils than biosolids amended soils and the rate decreased with time for both soils. The initial faster reaction suggests the rapid dissolution of amorphous phosphates present that are in greater abundance in inorganic fertilizer amended soils. These phosphates are metastable and ultimately converted to crystalline forms such as octocalcium phosphate and calcium hydroxyapatite (Griffin and Jurinak, 1974). The slow down in rate of desorption with time may be due to the slow dissolution of the crystalline phosphate compounds in soils (Toor and Bahl, 1999). The initial faster P desorption was also consistent with the presence of more labile P in soil and the replacement of solution phosphate ions with higher surface coverage of absorbed soil P, which can be the reason of initial faster P desorption (Kuo and Lotse, 1974; Toor and Bahl, 1999). Results from the continuous flow method, show that

cumulative P desorption was higher in inorganic fertilizer amended soils. These results are similar to results published by McCoy et al. (1986), who found that triple super phosphate released four to seven times more available P than biosolids P. Phosphorus in biosolids is commonly present in the form of Fe-P and Al-P, as the water treatment facility that produced these biosolids is known to add Fe and Al during the treatment process (Soon and Bates, 1982). Aluminum oxides are well known to be responsible for reducing P desorption by precipitation or sorption reactions in some other systems (Staats et al., 2004).

Much faster release of P occurred in the first 480 min of desorption, and a first order model fitted the data well from this initial reaction for both soils. This suggests that a first order reaction may be controlling the kinetics of release initially. Staats et al. (2004) have shown that P desorption is usually faster in initial stages and slower in the later stages. Also the greater k_d values in the inorganic fertilized soils indicate the rate of P release was much faster than in maximum rate biosolids amended soils, which has been reported by Steffens (1994).

The parabolic diffusion model was best fitted with the kinetic P desorption data for both soils after 480 min of equilibration. The linear relationship between the cumulative fraction desorbed and $t^{1/2}$ indicates that the slower continued desorption of P in soils with longer time periods is a diffusion controlled process in both P amendment treatments. It is reasonable that diffusion would become more important as the concentration of sorbed P decreases at later stages of the experiment. This shift to a diffusion-controlled process with decreasing P concentration has been reported by other researchers (Evans and Jurinak, 1976; Bahl, 1990).

The variability among replicates was not large enough to detect with XANES, so it was reasonable to combine all of the replicates into one composite desorption spectrum per treatment. It was evident that the fraction remaining post-desorption had a spectrum characteristics of crystalline (apatite-type) calcium phosphate present in the inorganically-fertilized soil, but not in the maximum biosolids amended soil. Overall, the observations from P XANES are consistent with a previous sequential chemical extraction study (Chapter 3), which demonstrated much higher apatite content in the inorganic soil.

4.5. Conclusions

The results of this study demonstrate that the mobility and availability of P in soil is controlled by desorption process with P desorption higher in inorganic fertilizer amended soil compared to maximum biosolids amended soil. Low soil:solution ratio increased the P desorption, and P desorption was less at high pH (7.5). Cumulative P desorption as well as P desorption rate with time was higher in the inorganic fertilizer amended soil compared to the maximum biosolids amended soil. Parameters obtained from modeling the kinetic data showed that initial desorption rate of P was faster and probably controlled by chemical reaction whereas the desorption rate was diffusion controlled at the later stages. Phosphorus K-edge XANES results showed that there was excellent repeatability in spectra of replicates, and that the residual post-desorption for the inorganically-fertilized soil was crystalline calcium phosphates, whereas in the biosolids the spectra resembled poorly-crystalline calcium phosphates and other poorly ordered sorption products.

5. GENERAL DISCUSSION AND CONCLUSIONS

Land application of biosolids based on crop N requirements has been shown to supply excess P relative to crop requirement (Kelling et al., 1977; Kick et al., 1981). These studies in this dissertation and past work confirm that total soil P is higher in biosolids amended soils but available P (percentages of labile fraction of P and total desorbable P) is higher in inorganic fertilizer amended soils.

The results presented in this dissertation from sequential extractions demonstrated that proportion of total P comprised of labile P was higher in inorganic fertilizer amended soils, though the total amount of labile P was higher in biosolids amended soils. Total extractable P also increased with increasing rate of biosolids application. The largest amount of total P (10945 mg P kg⁻¹) and the smallest percentages of labile P (27%) were observed in maximum biosolids amended soil. NaOH-extracted Fe and Al-bound P were higher in all biosolids amended soils and HCl-extracted Ca-bound P was much higher in only maximum biosolids amended soil. It is suggested that soil components associated with P retention (Al, Fe, Ca) decrease the available P in biosolids amended soils because these soil components react with P in biosolids (Coker and Carlton-Smith, 1986; Kashem et al., 2003).

Phosphorus sorption is also an important factor for low P availability in soils. In the studied soils, the results from desorption studies indicated that release of desorbable P was greater from inorganic fertilizer amended soils than the biosolids amended soil. Amount of desorbed P decreased with increasing soil:solution ratio, and with high pH (7.5). The desorption studies also showed that the total desorbable P with time and desorption rate were higher in inorganic fertilizer amended soils, which is consistent with the presence of more available P. Desorption rate was observed to be faster at initial stages and slower at later stages, which might indicate a rapid release of weakly bound phosphate sorption complexes followed by a slower dissolution of amorphous phosphates and/or more crystalline phosphate compounds in soils at later stages.

The XANES spectroscopy was successful in identifying different minerals present in soil samples. The results from the XANES spectroscopy showed that the total amount of P was much larger in biosolids soils and that much of the total P was present as dicalcium phosphate minerals. In contrast, most of the P in inorganic fertilized soils was present as labile and sorbed

forms with some apatite-type calcium phosphate. The XANES results from the desorption studies were consistent with apatite-type Ca-P minerals remaining after desorption in the inorganically fertilized soils.

Overall, the results in this dissertation indicate that speciation of inorganic fertilizer and biosolids amended soils is quite different and the potential for release of P to environment from biosolids amended soils is less than expected based upon their total P levels (i.e. the majority of P being present in less labile fractions). However, absolute value of P is also important. The results also suggest that while sequential chemical extractions do remove distinct forms of P, the actual minerals present may be quite different in inorganic vs. biosolids amended soils. This makes extending chemical extractants to providing a useful measure of environmental risk quite difficult. However, the knowledge from this thesis will help us to understand the fate of biosolids P in soils, knowledge of P speciation, and release kinetics for further research work.

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APPENDIX A

P = Plots
T = Treatments

Treatments

T-1 = Control
 336-224-112 kg ha⁻¹ yr⁻¹ N-P-K

T-2 = 16.8 Mg ha⁻¹ biosolids and
 112 kg K ha⁻¹ yr⁻¹

T-3 = 33.6 Mg ha⁻¹ biosolids and
 112 kg K ha⁻¹ yr⁻¹

T-4 = 67.2 Mg ha⁻¹ biosolids and
 112 kg K ha⁻¹ yr⁻¹

P-01 T-2	P-02 T-3	P-03 T-1	P-04 T-4
P-05 T-1	P-06 T-2	P-07 T-4	P-08 T-3
P-09 T-2	P-10 T-3	P-11 T-1	P-12 T-4
P-13 T-3	P-14 T-2	P-15 T-4	P-16 T-1

Figure. A 1 Plots diagram of the field site.

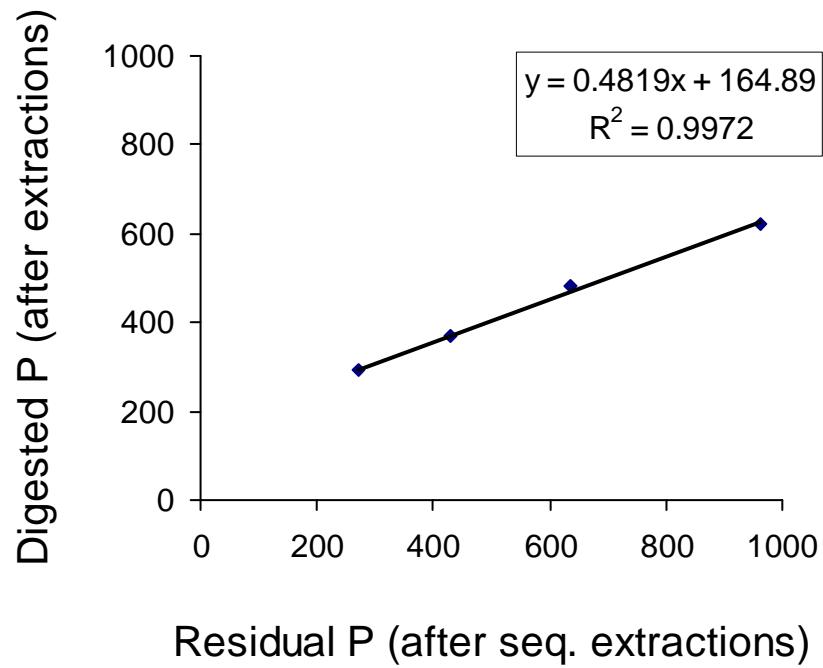


Figure. A 2 Correlation between the residual phosphorus (mg P kg^{-1}) determined after sequential extractions and digestion.

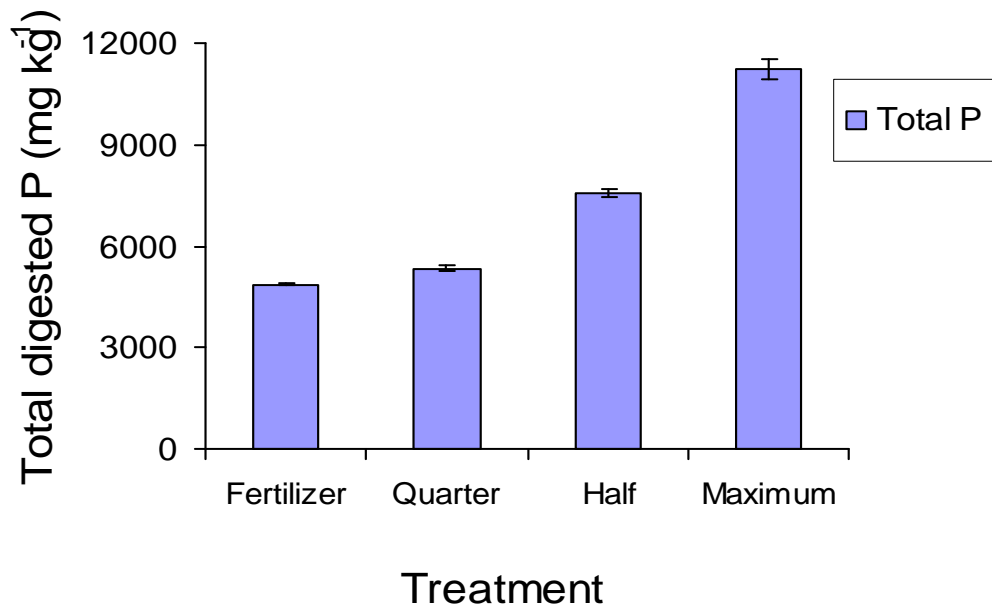


Figure. A 3 Mean total digested phosphorus of four different treatments with standard error.

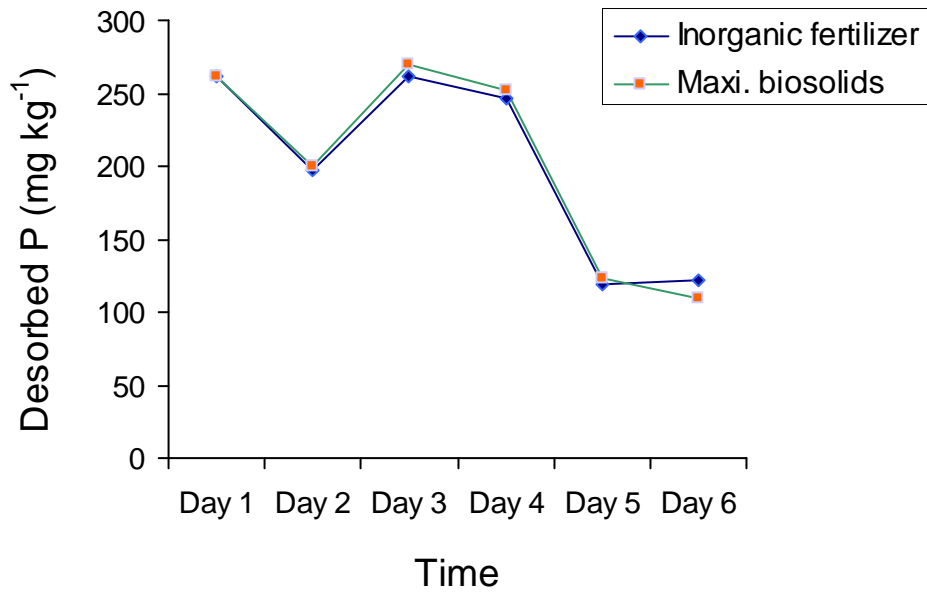


Figure. A 4 Phosphorus desorption with time for inorganic fertilizer and maximum biosolids amended soils.