

AN ABSTRACT OF THE THESIS OF

Jeffery B. Choate for the degree of Master of Science in Soil Science presented on June 20, 2003.

Title: Phosphorus Availability in Biosolids-Amended Soils.

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Dan M. Sullivan

Quantifying labile phosphorus (P) pools in biosolids is needed to manage biosolids for both agronomic and environmental purposes. Phosphorus indices originated in an effort to protect surface water quality from non-point agricultural P inputs. The objectives of this research were to: (1) evaluate soil test components of the western Oregon P index in field and laboratory experiments; (2) evaluate soil test methods for assessing labile P; (3) determine the relative availability of fertilizer and biosolids P; and (4) evaluate the P sorption index [PSI; defined as the molar ratio of $P/(Al+Fe)*100$ as determined by acid ammonium oxalate extraction] as an indicator of water-soluble P in biosolids and as an indicator of labile P in soil following biosolids application. Soil samples were collected from 18 western Oregon field sites with a history of biosolids application and analyzed for labile P via oxalate extraction (P_{ox}), anion exchange resin (AER) extraction, Bray 1

extraction, and dilute salt extraction (0.01 M CaCl₂). In comparison to untreated buffer areas, biosolids application at field sites increased mean P_{ox}, AER-P, Bray P, and CaCl₂-P by 163, 151, 163 and 128%, respectively in the 0-5 cm depth. Thirty biosolids samples were collected from 22 municipal wastewater treatment facilities and analyzed by oxalate extraction, dilute salt extraction, and total acid digestion. At PSI values less than 65 to 85%, soluble P in biosolids was less than 175 mg kg⁻¹. At PSI values of 85 to 212%, soluble P ranged from 25 to 6065 mg kg⁻¹. Laboratory incubations used selected soils amended with selected biosolids at rates of 0, 300, 600 and 900 mg P per kg soil. Relative P availability for six biosolids sources, as measured by AER extraction, was 12 to 54% in comparison with P from triple superphosphate fertilizer and increased linearly with biosolids PSI values between 44 and 168% ($r^2=0.99$, $p<0.0001$). Phosphorus indices must make use of some form of direct soil P measurement, and the western Oregon P index could be improved with separate weighting factors for biosolids and fertilizer P amendments. Biosolids PSI is a useful index for assessment of water-soluble P in biosolids and short-term P availability following biosolids addition to soil.

Phosphorus Availability in Biosolids-Amended Soils

by
Jeffery B. Choate

A THESIS

Submitted to
Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Presented June 20, 2003
Commencement June 2004

Master of Science thesis of Jeffery B. Choate presented on June 20, 2003.

APPROVED:

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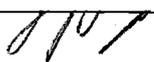
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ACKNOWLEDGEMENTS

Although this list could never be comprehensive, it represents just a few of the people that have helped me get to this point...

Art & Janet Choate, my parents

Court & Dawn Boice & family, and all the folks I've met at Paradise Lodge over the past eight years

Ron & Bobbie Kipp, just two of those folks from Paradise Lodge, and a big reason why I still enjoy returning to the Rogue River

Faculty, staff and volunteers at the Extension offices of Lane and Douglas Counties

Ross Penhallegon, the person responsible for getting me started in Extension

John Hart, a committee member, one of those folks I met at "Paradise Bar," and a major influence on my decision to enroll in Soil Science at OSU

Dan Sullivan, an outstanding major professor whose guidance, patience and sense of humor have been tremendous assets throughout this process

Tim Righetti, minor professor and supplier for all my GPS needs

Stephen Schoenholtz, GCR

The folks at CAL, Will, Sandy, Ellen, Andy & Yan Ping, for the myriad samples processed and a great wealth of information

Neil Christensen, for helpful suggestions on numerous facets of this research

John Baham, for both advice and laboratory materials

ACKNOWLEDGEMENTS (Continued)

Joan Sandeno, for many helpful hints, a friendly personality in the lab next door,
and even a bit of sewing

Elizabeth Sulzman, for whom it was a pleasure to host the first season of "Soil
Jeopardy"

Nan Scott, whose assistance with statistics and software was extraordinarily helpful

Jayne Smith & Tracy Mitzel, whose assistance to an office-illiterate person such as
myself was more helpful than they could possibly imagine

My officemates; particularly Jess and Daniel, whose departures have provided the
impetus to get this little project done

Mike Halbleib, whose flight plan always led to the nearest Subway

All the faculty, staff and students of the Crop & Soil Science Department

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PHOSPHORUS AVAILABILITY IN BIOSOLIDS-AMENDED SOILS

INTRODUCTION

Biosolids, the residual solids remaining after wastewater treatment, often are applied to agricultural lands as a means of utilization. As with other organic amendments, biosolids application rates are typically determined according to the nitrogen (N) content of the biosolids and the N requirement of the crop to which the biosolids will be applied. Such N-based management generally results in the over-application of P relative to crop needs (Maguire et al., 2000a; Penn and Sims, 2002). Phosphorus is generally the limiting element controlling eutrophication of surface water systems (Pierzynski et al., 2000; Sharpley et al., 1999), so understanding the fate of biosolids P in the environment following land application is essential to protecting surface water quality. Wastewater treatment processes and biosolids dewatering methods currently in use by municipalities produce biosolids with a range of chemical and physical characteristics. The availability of P following land application of biosolids is related to biosolids chemistry.

Soil P often is recognized as being divided among several pools, including soluble, labile and non-labile P. Soluble P refers to P that is soluble in water; labile P is that which is readily available to replace P lost from the soil solution through plant uptake, leaching, precipitation or immobilization; and non-labile P includes the P in soil minerals and organic matter which must be dissolved or mineralized in

order to be released into the soil solution (Havlin et al., 1999). Particulate P (labile and non-labile pools) is the predominant form in which P is lost from agricultural fields via soil erosion (Lemunyon and Gilbert, 1993; Sharpley et al., 1999).

However, for soils with high labile P concentrations, soluble P loss in the absence of erosion can be significant as well (Elliott et al., 2002a; Mozaffari and Sims, 1994).

Phosphorus indices are field-scale screening tools used by conservation planners (e.g., NRCS staff) to assess the risk of offsite P movement from agricultural fields. This task is accomplished via site-specific, line-item accounting of the factors controlling P mobility in the environment (Lemunyon and Gilbert, 1993). The western Oregon P index uses the Bray 1 soil P test as a means of assessing the risk of soluble P loss from the soil (USDA-NRCS, 2001). This test has both advantages and disadvantages with regard to its use in the western Oregon P index. Currently, the western Oregon P index weights organic amendments and commercial fertilizers equally with regard to their potential effect on the amount of P available for offsite movement. Commercial fertilizers must be formulated with readily available forms of P, defined as citrate-soluble P (Meister, 2000), whereas the majority of P in biosolids and other organic amendments generally slowly becomes available over time (Pierzynski et al., 2000). Consequently, more information is needed on the relative P availability of organic byproducts such as manures and biosolids.

A potential measure of biosolids P availability is the P sorption index [PSI; defined as the molar ratio of $P/(Al+Fe)*100$ as measured by acid ammonium oxalate extraction]. The threat of soluble P loss following application of biosolids to soils with low P sorption capacities is correlated with the PSI of the biosolids (Elliott et al., 2002a), although these authors note that soils of even moderate sorption capacity may mitigate differences among biosolids.

The objectives of this research were to: (1) evaluate soil test components of the western Oregon P index in field and laboratory experiments; (2) evaluate soil test methods for assessing labile P; (3) determine the relative availability of fertilizer and biosolids P; and (4) evaluate the PSI as an indicator of water-soluble P in biosolids and as an indicator of labile P in soil following biosolids application.

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LITERATURE REVIEW

Introduction

Phosphorus is both a primary macronutrient needed in relatively large quantities by plants—concentrations of about 0.2% of plant shoot dry matter being needed for adequate growth (Hue et al., 2000; Marschner, 1995)—and a major component of manures, biosolids and many synthetic fertilizers. Complicating agricultural P management is the fact that nonpoint-source inputs of P into aquatic ecosystems, primarily associated with agricultural runoff, often have the potential to result in degraded surface water quality (Pote et al., 1999; Sturgul and Bundy, 2002). Despite these facts, much is not understood about the nature and behavior of P in soils, especially with regard to organic soil P (Havlin et al., 1999).

Eutrophication is defined as, “the natural aging of lakes and streams,” and can result in impaired surface water quality due to algal blooms and the subsequent decomposition of algae (Sharpley et al., 1999, p. 1; Sturgul and Bundy, 2002, p. 1). Eutrophication of surface water bodies is often limited by aqueous P concentrations (Pierzynski et al., 2000; Sharpley et al., 1999), and agricultural land has been identified by the USEPA as a major contributor of P to aquatic ecosystems (Sturgul and Bundy, 2002). Great care should be taken to avoid losses of P to aquatic ecosystems, because even small losses of P can have serious consequences (Pote et al., 1999). The eutrophication threshold for most surface water bodies is

approximately 0.02 mg kg^{-1} ; in comparison, soil solution P concentrations in agricultural soils average an order of magnitude greater, typically ranging from about 0.2 to 0.3 mg kg^{-1} (Sharpley et al., 1999), with 0.2 mg kg^{-1} being adequate for most crops (Gardiner and Christensen, 1990). Sufficient soil solution P levels for most agricultural crops generally require supplemental P to be applied (Higgs et al., 2000).

Movement of P from terrestrial to aquatic ecosystems is generally associated with erosion of particulate-bound P rather than leaching of dissolved P. Under certain circumstances, native soil P levels may be sufficient to elevate stream P levels via eroded sediments (Abrams and Jarrell, 1995). The significance of these facts is that information other than soil test P alone, such as soil hydrology, topography, etc., is necessary to evaluate the risk of offsite P movement (Indiati and Sharpley, 1998; Pote et al., 1999; Sims et al., 2000). Phosphorus indices were designed as field-scale screening tools used by conservation planners to assess the risk of offsite P movement from agricultural fields. This task is accomplished via line-item accounting of the factors controlling P mobility in the environment (Lemunyon and Gilbert, 1993).

Although erosion accounts for the majority of offsite P movement from terrestrial to aquatic environments, leaching studies have shown that high levels of labile P in soil can result in significant P leaching (Elliott et al., 2002a; Mozaffari and Sims, 1994). Phosphorus leaching has been shown to occur in areas with coarse soils and high water tables, although lower water tables and soils with

higher clay contents generally result in P being bound before significant leaching can occur (Mozaffari and Sims, 1994). Subsurface drainage also can facilitate offsite P movement, as can macropore flow, especially in no-till situations (Sharpley et al., 1999). However, soils high in amorphous Al and Fe have been shown to readily bind P (Abrams and Jarrell, 1995; Elliott et al., 2002a; Frossard et al., 1995). In particular, Andisols often contain large amounts of allophane, an amorphous Al material which readily binds P. Many commonly used chemical extractants, such as Bray 1 and Mehlich 3, can overestimate available P in some soils as a result of the liberation of P bound by these amorphous Al and Fe constituents (Basta et al., 2000; Myers et al., 1997; Nair, 1996; Qian and Schoenau, 2002; van Raij, 1998). For this reason, Basta et al. (2000) concluded that water extracts were superior to chemical extractants in predicting plant response to P fertilizer when using water treatment residuals (WTRs) as a soil substitute.

The key to avoiding the problems associated with P-induced eutrophication is balancing P inputs into the soil with plant needs (Sharpley et al., 1999; Sturgul and Bundy, 2002), and the key to accomplishing this task is through management practices based upon soil test results which accurately reflect P availability. Anion exchange resins hold promise for this task, and consideration of parameters such as the P sorption index and single point P sorption isotherms may be useful in improving agricultural P management as well.

Soil P Availability

Soils typically range in total P content between about 50 and 3000 mg kg⁻¹ predominantly as orthophosphate (Brady and Weil, 2002; Frossard et al., 1995; Havlin et al., 1999; Pierzynski et al., 2000). Knowledge of a soil's total P content, however, is of limited use in determining the ability of that soil to supply plants with P, as available P seldom exceeds approximately 0.01% of the total P concentration at any given time (Brady and Weil, 2002; Havlin et al., 1999). This introduces the question, "What is 'available' P?"

In the simplest of terms, available P is synonymous with solution P, as plants satisfy their P needs from the pool of P in the soil solution (Indiati and Sharpley, 1998). However, due to the high rate of turnover in solution P—approximately 10-20 times per day (Higgs et al., 2000; Marschner, 1995)—estimates of available P often include labile forms of P that are likely to buffer solution P (Morel et al., 2000; Sturgul and Bundy, 2002). This type of estimate is exemplified by the Association of American Plant Food Control Officials' (AAPFCO) definition of available fertilizer phosphate: "Available phosphate is the sum of the water-soluble and the citrate-soluble phosphates" (Meister, 2000, p. B 20). A recent reevaluation of the Association of Official Analytical Chemists' (AOAC) method for bioavailable P determination verifies that citrate-insoluble P provides an accurate determination of short-term plant-unavailable P (Sikora and Mullins, 1995). This assessment, along with others (Morel et al., 2000), indicates the importance of time as a factor in P availability estimates. Desorption and

dissolution of particulate-bound and mineral P play a significant role in determining the availability of P to crop plants over the course of an entire growing season. If available P is synonymous with solution P, then P availability is intimately related with P solubility, and any test that is to measure soil P availability must somehow account for this relationship.

Chemistry of Soil and Soil Amendment P

Forms of soil P

Approximately 30-65% of soil P is present in organic compounds (Frossard et al., 1995). Of the organic P compounds occurring in soil, only about 50% have been characterized (Havlin et al., 1999). Those include inositol phosphates (up to 50% of the identifiable organic P components), other sugar phosphates, phospholipids, nucleic acids, and phosphonates (Frossard et al., 1995; Havlin et al., 1999). Current knowledge of organic P dynamics in the soil remains limited (Frossard et al., 2000).

Inorganic soil P is commonly subdivided into two broad categories with Ca-bound P compounds tending to dominate in high-pH soils and amorphous Al- and Fe-bound P compounds generally dominating in low-pH soils (Brady and Weil, 2002; Frossard et al., 1995; Frossard et al., 2000; Havlin et al., 1999; Pierzynski et al., 2000). While Al-P and Fe-P compounds tend not to occur in soils in well-crystallized forms, hydroxyapatite is generally the end product of Ca-P compounds

in soils (Frossard et al., 1995). These authors also note that organic acids prevent the formation of intermediates in the formation of hydroxyapatite, perhaps explaining the generally higher available P concentrations associated with calcareous soils amended with organic amendments relative to mineral fertilizers.

pH effects on soil P

When P speciation is plotted as a function of soil pH, H_2PO_4^- is shown to be the dominant P form over the range of pH values from approximately 3 to 7, and HPO_4^{2-} is the dominant form over the pH range from approximately 7 to 11; a near-equal mixture of these two P species occurs at neutrality (Havlin et al., 1999; Ludwick, 1998). Both of these P species are readily plant available, and the range of pH values from 3 to 11 is inclusive of agronomically relevant pH values. Optimum agronomic P availability generally occurs at pH values between approximately 6.5 and 7.5 (Brady and Weil, 2002; Havlin et al., 1999; Ludwick, 1998; Rodriguez et al., 1996). Phosphorus availability over the range of pH values from 3 to 11, however, is not constant and depends less on the dominant P species than on the lability of sorbed and mineral-bound P (Brady and Weil, 2002; Havlin et al., 1999; Pierzynski et al., 2000). Additionally, sorption-desorption reactions are reported to be superior to precipitation-dissolution reactions in their ability to predict P uptake and release between the soil and solution (Frossard et al., 1995). In a study of 24 acidic, southwest Oregon soils, Al-bound and Fe-bound P—as determined by chemical fractionation with 0.5 N NH_4F and 0.1 N NaOH ,

respectively—correlated well with plant uptake of P as well as with Bray 1 and Olsen soil test P values (Doerge, 1979). In this same study, Ca-P exhibited only moderate correlation with plant growth, and this was limited to alluvial soils relatively enriched in Ca-P. The net effect of P interactions in soils is that Al and Fe oxides exert a dominant control on P sorption capacity, even in calcareous soils, although CaCO_3 will dictate long-term sorption of P in calcareous soils (Frossard et al., 1995). Additionally, organic anions can compete for binding sites on oxide surfaces and can chelate metals, thus rendering them unavailable to bind P (Frossard et al., 1995; Frossard et al., 2000). This latter point is particularly relevant with regard to soluble P loss from soils, as organic soil amendments may be more prone to soluble P loss as a result of competition between P and organic anions for binding sites in soil.

Redox effects on soil P

Increased soluble P accompanying soil reduction often has been attributed to solubilization of Fe hydroxides (Vadas and Sims, 1998). These authors found that soil reduction resulted in increased soluble P in unamended, agricultural soils and decreased soluble P in agricultural soils amended with poultry litter; subsoils and wooded soils were unaffected.

Forms of soil amendment P

Commercial P-containing fertilizers are commonly composed of inorganic calcium and ammonium phosphates (Ludwick, 1998). Much of the P contained in manures is present in inorganic forms as well, although the distribution of P between organic and inorganic forms is highly dependent upon manure type (Sharpley, 2000). Similarly, the distribution of biosolids P between organic and inorganic forms is highly dependent upon processing method (Dentel et al., 2001; Elliott et al., 2002a; Jenkins and Horwath, 2001). Most of the inorganic P in biosolids has been reported to be associated with Al and Fe, although alkaline-stabilized biosolids are an exception with P being predominantly associated with Ca and Mg (Elliott et al., 2002a; Jenkins and Horwath, 2001; Soon and Bates, 1982; Wen et al., 1997). Dentel et al. (2001) reported a linear relationship between the amount of total P and total orthophosphate in biosolids, and this held for biosolids derived from a wide variety of treatment processes. Similarly, oxalate-extractable P is reported to be highly correlated with total P in biosolids (Elliott et al., 2002a; van der Zee and Riemsdijk, 1988). Total Al and Fe concentrations for biosolids produced by a variety of treatment processes have been reported to vary from about 2 to 78 g kg⁻¹ and 2 to 85 g kg⁻¹, respectively. P content in these biosolids ranged from 2.2 to 4.5% (Elliott et al., 2002a; Kyle and McClintock, 1995).

Behavior of amendment P in soils

Interactions among the various forms of P in soils are numerous and complex. Many factors that affect P solubility, and thus availability, have been characterized for inorganic P. Factors such as pH, the amount and type(s) of clay present, and soil organic matter content work in conjunction to dramatically influence soil P availability (Brady and Weil, 2002; Indiaty and Sharpley, 1997; Sharpley and Sisak, 1997; Sharpley and Smith, 1995). For example, acidic soils that received applications of poultry manure showed an increase in P solubility, apparently as a result of chelation of P-sorbing Fe and Al by organic matter. In comparison, P solubility was unaffected in calcareous and non-calcareous, non-acidic soils receiving poultry manure, as the P was maintained in metastable and poorly crystalline forms (Toor and Bahl, 1999).

In contrast to inorganic soil P, the study of the complex biological interactions that dictate the behavior of organic P present in many soil amendments remains in its infancy (Brady and Weil, 2002). As mentioned previously, only about 50% of the organic compounds occurring in soils have been characterized (Havlin et al., 1999). As such, information regarding potential differences in the availability of P from sources such as fertilizers and manures is limited (Sharpley and Sisak, 1997), although efforts have been made to characterize the long-term behavior of soil P derived from various manure sources (Sharpley and Smith, 1995). In studies monitoring the availability of P from poultry litter and KH_2PO_4 , the lower availability of P from poultry litter was largely attributed to the increased

Ca content of manure-treated soils (Robinson and Sharpley, 1996; Sharpley and Sisak, 1997). The availability of such Ca-bound P may be overestimated by acidic chemical extractants such as Bray 1 (Sharpley and Smith, 1995). Higgs et al. (2000) cite information from long-term experiments at Rothamsted which show P derived from farmyard manure to behave similarly to P derived from superphosphates with regard to its effects on soil test P.

Regardless of the P source (organic or inorganic), only about 10-25% of the P added to a soil will be available for plant uptake in the first year following application; the remainder will be added to soil P reserves (Brady and Weil, 2002; Higgs et al., 2000; Indiati and Sharpley, 1998; Robinson and Sharpley, 1996). The distribution of added P in any given situation is dependent upon soil type and the rate of P addition (Kovar and Barber, 1988). The reactions associated with the reallocation of P following fertilizer or manure application to soils can occur in as little as a few hours (Sturgul and Bundy, 2002). In a sequential extraction of biosolids-amended soils, extractable P forms were affected by both the biosolids source and soil properties, especially the soil's P retention capacity (Anjos et al., 2001).

Also regardless of P source, a linear relationship has been reported to exist between the amount of P added to soil and available soil P, suggesting that the cumulative P application rate may be a more dominant factor in determining available soil P than is the source of the P (Cooperband et al., 2002; Wen et al., 1997). However, manure-derived P has been found to move deeper into the soil

than does fertilizer P at similar loading rates (Eghball et al., 1996; Higgs et al., 2000). It was hypothesized that this was due to movement of P in organic forms or perhaps that organic acids may have prevented the formation of Ca-P compounds. Eghball et al. (1996) also noted that soil P movement correlated poorly with P sorption maxima. This suggests that the ultimate ability of a soil for long-term P sorption may be less of a factor than is the source of P when considering short-term soil P movement.

Management of Soil Amendments

The practice of applying P-containing, organic, soil amendments, such as manures and biosolids is of particular concern regarding P additions to the soil. Application rates of these materials are commonly based upon crop nitrogen requirements (Bary et al., 2000; Maguire et al., 2000b; Penn and Sims, 2002; Robinson and Sharpley, 1996; Sullivan, 1998). In most instances, agronomic P application rates are largely ignored. These practices often result in the over-application of P (Maguire et al., 2000b; Robinson and Sharpley, 1996; Sharpley and Moyer, 2000; Sharpley and Smith, 1995). As a result, areas receiving large inputs of manure over long periods of time commonly experience an increased loss of bioavailable P (Brady and Weil, 2002; Paulter and Sims, 2000; Sharpley and Smith, 1995). A 25-year study of the effects of surplus P (beyond crop removal rates) on soil test P levels indicated that an annual P surplus of 34 kg ha^{-1} would result in an increase of approximately 50 mg kg^{-1} in Bray 1-P after 25 years

(Barber, 1979). A single biosolids application to tall fescue at a rate of 9 Mg ha^{-1} (dry weight basis) would result in a P surplus of approximately 146 kg ha^{-1} (Sullivan, 1998). Nitrogen-based management of manures can result in soil test P reaching excessive levels in 3-5 years (Sharpley et al., 1999). In contrast, short-term P availability has been shown to be substantially higher for additions of KH_2PO_4 or $10\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ than from manures or biosolids (Elliott et al., 2002a; Robinson and Sharpley, 1996; Sharpley and Sisak, 1997). However, soils treated with poultry litter leachate have been reported to contain a relatively high amount of labile P which may increase the potential for long-term bioavailable P loss in runoff relative to that of mineral fertilizers (Robinson and Sharpley, 1996). Taken together, these facts suggest that manure application rates should be based upon field trials rather than on mineral P fertilizer requirements (Robinson and Sharpley, 1996; Sharpley and Sisak, 1997).

Practices are gradually shifting from N-based application rates to P-based application rates, and some authors believe this shift to be inevitable for biosolids and manures (Brandt et al., 2002). In contrast, Elliott et al. (2002a) conclude that the P sorption capacity of most soils is likely to be high enough not to warrant P-based management. A result of the shift toward P-based management is the desire for a better understanding of the differences among various organic soil amendments such as biosolids and manures. Brandt et al. (2002) found that the average water-extractable P for 42 biosolids derived from various treatment processes was significantly lower than that for 13 dairy and poultry manures and

two fertilizers, suggesting that, all other factors being equal, biosolids represent a lower environmental risk for P loss following application than do manures and fertilizers. This difference was attributed to higher Al and Fe levels in the biosolids, as both Al and Fe often are added during the biosolids treatment process for dissolved P removal, dewatering and/or odor control. Similar results have also been reported by others (Elliott et al., 2002a; Penn and Sims, 2002; Soon and Bates, 1982). Several authors note, however, that labile P levels in biosolids associated with wastewater treatment facilities using biological P removal (BPR) were higher than for other biosolids treatment processes, and this is likely due to the lack of Al and Fe added during BPR (Brandt et al., 2002; Dentel et al., 2001; Elliott et al., 2002a; Jenkins and Horwath, 2001; Penn and Sims, 2002). Thus not all organic amendments should be treated as identical with respect to P availability, and neither should all biosolids (Dentel et al., 2001). Water-extractable P in manure and compost may provide a good estimate of the potential for P to be leached from these materials following land application (Sharpley and Moyer, 2000), and this relationship would likely be true for other organic soil amendments such as biosolids as well.

Testing Methods for Soil Phosphorus

Comparison of “new” methods

Numerous tests exist to measure available soil P, suggesting a general lack of consensus regarding the “best” methodology (van Raij, 1998). This author identifies nine standard soil P tests in common use around the world, along with four non-standard methods. Of these non-standard methods, only extraction with ion-exchange resins was identified as a potential replacement for the standard tests in common use today (van Raij, 1998). In tests to estimate the errors associated with two of these non-standard P analyses—*anion exchange resins* and *iron oxide-impregnated filter paper strips*—only *anion exchange resins* exhibited minimal or negligible errors associated with the dissolution of particulate P and the analysis of turbid water (Uusitalo and Yli-Halla, 1999). *Iron oxide strips* tend to collect soil on their surfaces during extraction and are mechanically unstable during very long-term extractions (Freese et al., 1995; Uusitalo and Yli-Halla, 1999).

While *anion exchange resins* have been shown to be superior to *iron oxide-impregnated filter paper strips*, use of the latter has been quite prominent in the literature over the past few years (Uusitalo and Yli-Halla, 1999). One study, using *ryegrass* as an indicator of plant-available P, determined that *iron oxide-impregnated filter paper* was superior to other methods tested, including the standard *Bray 1* and *Olsen* methods (Velthof et al., 1998). This test was designed to isolate P in a similar way as plant roots without chemically reacting with bound

soil P (Myers et al., 1997). Regardless, iron oxide-impregnated filter paper strips are difficult to prepare, and a standardized method of their employment has yet to be established (Myers et al., 1997; Uusitalo and Yli-Halla, 1999).

Soil P pools

Some soil P tests are used in an attempt to define pools of soil P. For example, iron oxide-impregnated filter paper strips often are associated with available P, P_i (Myers et al., 1997; van Raij, 1998). Similarly, chemical fractionation sequences are used regularly to characterize pools of soil P (Chang et al., 1983; Robinson and Sharpley, 1996; Sui et al., 1999). While association of P_i with available P is theoretically justifiable (van Raij, 1998), P pools isolated by chemical extractants are often operationally defined (Abrams and Jarrell, 1992; Freese et al., 1995). Numerous soils varying in such characteristics as texture and parent materials exhibited reduced P solubility when extractant pH was raised above 4.00, while increasing the solvent:soil ratio resulted in increased P solubility (Simonis, 1996). Furthermore, the standard treatment of drying and sieving samples prior to analysis in a batch extraction affects the distribution of P among the various operationally defined pools (Abrams and Jarrell, 1992). As such, comparisons of soil P test results from differing sources must take into account the details of the methods of analysis employed, such as extractant pH, soil:solution ratios and extraction time. Additionally, Frossard et al. (2000) contend that differentiating between available and nonavailable pools of inorganic P is not

possible due to the existence of a continuum of P among such pools. The amount of sorbed P in soil is controlled by soil solution P concentrations, and the latter is ultimately controlled by the K_{sp} of the least soluble P mineral present, thus creating a continuum among these three P forms (Frossard et al., 2000; Morel et al., 2000).

Buffering of soil solution P: implications for soil P testing

The existence of numerous tests for soil P availability is likely a result of the confounding ability of chemically-sorbed and mineral-bound P to replenish the short-term plant-available P as the latter is utilized by actively growing plants. During the growing season, plants deplete the pool of soil solution P in a relatively short period of time; therefore, the P available to be taken up by plants is comprised not only of that in the soil solution but also that which will replenish and buffer the soil solution over time (Morel et al., 2000; Nair, 1996). In that sense, soluble P represents the short-term available P, while determinations of long-term availability must take into account transformations between numerous organic and inorganic P fractions and soil solution P. This buffering action by solid-phase P on the aqueous P concentration must be kept in mind when choosing from among the different techniques available for estimating plant-available P in the soil (Nair, 1996).

Goals of phosphorus soil testing

In order to accurately diagnose the need for P additions to soils, testing methods must be established which accurately estimate the availability of soil P to plants over the course of an entire growing season. A prerequisite of any such test is that it must avoid chemical transformations of P in the sample being analyzed; this could lead to inconsistent or inaccurate determinations. Anion exchange resins have shown promise in these regards through their ability to act as a P sink, thus stimulating desorption and dissolution of P from the solid phase into the soil solution (Abrams and Jarrell, 1992; van Raij, 1998). In this way, anion exchange resins simulate the actions of plant roots by adsorbing P without chemically interacting with solid-phase P in the soil.

The purpose of a soil test is an important consideration when choosing from the many available soil P tests; soil P tests designed for agronomic use fundamentally differ from those designed for environmental purposes. The former utilize composite samples taken from the surface to depths of 15 to 30 cm (Guertal et al., 1991; Mahler and Tindall, 1997), whereas the latter typically utilize composite samples taken from the surface to depths of only 1 to 5 cm (Maguire et al., 2000a; Mahler and Tindall, 1997). The interpretation of agronomic soil P tests is often qualitative, based upon regional calibration with crop response, while environmental soil P test interpretations often involve a quantitative correlation with P concentrations in surface or runoff water (Pote et al., 1999; Sturgul and Bundy, 2002).

Regardless of the intended purpose of a particular soil P test, inferences based upon documented correlations between different soil P test procedures may be possible. For example, anion exchange resin-extractable P (AER-P) has been shown to be significantly correlated with Bray 1-extractable P, with coefficient of determination (r^2) values of 0.91 and 0.80 for 0 to 5 cm and 0 to 30 cm sampling depths, respectively (Moore, 2001). Similarly, work by Barber (1979) reveals a nearly 1:1 relationship between Bray 1-P and AER-P ($y = 0.96x$, $r^2 = 0.94$, $p = 0.0002$). Significant correlations have also been reported for both water soluble and iron oxide P with Mehlich 1 P test values for biosolids-amended soils (Maguire et al., 2000a). Such correlations could allow a soil P test performed for one purpose to be used as a proxy for another test if the nature of the correlation were known (Paulter and Sims, 2000; Sims et al., 2000). Pote et al. (1999) found significant linear relationships between several common soil P test methods (including Bray 1, water extractable P, and the P sorption index) and the associated dissolved reactive P in runoff. Further research may be able to document such correlations in such a way as to determine if any broad empirical relationships exist.

Anion exchange resins

As with any procedure, the use of anion exchange resins (AERs) has both advantages (some of which have been listed above) and disadvantages. In a review by van Raij (1998), the following determinations regarding AERs were made. In

numerous comparisons of various soil P determinations, AERs consistently exhibited higher r^2 values than any of the other tests. Additionally, AERs show applicability over a broad range of soil types, including acid and alkaline soils, which is not the case for most of the extraction methods commonly used for soil P (Qian and Schoenau, 2002; Skogley et al., 1990; van Raij, 1998). Furthermore, AERs demonstrated a sensitivity to changing P concentrations with changes in soil pH which were either not expressed by other methods (Bray 1, Mehlich 1), or were inaccurately reflected (Olsen). The major drawback of AERs for routine testing procedures is the time necessary for equilibration between resin-bound, particulate and solution P, a factor which is not likely to be reduced significantly (van Raij, 1998).

Phosphorus extraction via AERs has been shown to proceed rapidly at first and more slowly as the reaction proceeds, asymptotically approaching a maximum value (Amer et al., 1955). Using ^{32}P equilibration, these authors showed that the rate of P extraction with AERs depended on the rate of P release from soil. The time necessary to allow for equilibrium during the extraction is a critical consideration for quantitative comparisons of results among laboratories. Extraction times as low as 16 hours have been used for routine analyses (Pierzynski, 2000; Qian and Schoenau, 2002), although times ranging from 100 to 300 hours may be necessary to approach equilibrium (Bache and Ireland, 1980). A similar type of extraction using ferrihydrite-filled dialysis membranes detected no adsorption maximum after 500 hours (Freese et al., 1995).

In contrast to the essentially infinite sink of iron oxide-impregnated filter papers, AERs behave as dynamic exchangers of soil P (Cooperband and Logan, 1994). A potential method to avoid this aspect may be to use a considerable excess of the resin (Qian and Schoenau, 2002), an option that was not feasible in the study by Cooperband et al. who were using AERs for in situ studies of soil P. The competitive exchange nature of AERs is particularly important with high concentrations of anions other than orthophosphate, as competition among them for binding sites on the resin can occur (Cooperband and Logan, 1994).

Inclusion of a cation sink has been suggested in addition to the anion sink when extracting soil P, as the former will stimulate continued dissolution of soluble and sparingly-soluble P compounds beyond that which would occur in the presence of only an anion sink (van Raij, 1998). Robinson et al. (1996) found that the size of the cation sink strongly influenced the dissolution of phosphate rock materials.

The complementary anion used with AERs is also a factor affecting P transfer from soil to resin (Bache and Ireland, 1980; Freese et al., 1995). The former authors found that the HCO_3^- form of AER is more efficient than the Cl^- form at extracting P from an acid soil, though results were similar for a calcareous soil. Furthermore, these authors show that the HCO_3^- form of AER is capable of extracting a constant proportion of isotopically-exchangeable P from various soils, whereas the Cl^- form is not. Additionally, the use of resins in the HCO_3^- form has resulted in P determinations that were nearly independent of resin type or soil-water ratio (Sibbesen, 1978). Bache et al. (1980) determined that such

complementary anion effects result from the increasing concentration of previously resin-bound anions in the extraction solution which then limits further desorption of resin-bound anions and thus the amount of P bound by the resin. The HCO_3^- form of AER is able to overcome this effect, because the bicarbonate anion hydrolyzes once in solution thus maintaining a low aqueous HCO_3^- concentration (Bache and Ireland, 1980).

The P sorption index

Also referred to as the degree of P saturation (Maguire et al., 2000a; Paulter and Sims, 2000) and P sorption saturation (Kleinman et al., 2003; Sibbesen and Sharpley, 1997), the P sorption index (PSI) is defined here as the molar ratio of $\text{P}/(\text{Al}+\text{Fe}) \times 100$ as measured by acid ammonium oxalate extraction (Elliott et al., 2002a). Some authors include an empirical correlation coefficient, α , in the denominator that relates soil PSI to Langmuir sorption isotherms (Maguire et al., 2000a; Paulter and Sims, 2000). The P sorption index has the potential to provide information about the magnitude and direction of changes between soluble and particulate P in soil (Indiati and Sharpley, 1998). The general trend is for soils with a higher PSI value to be more likely to contribute P to nearby surface waters (or shallow groundwater) than soils with lower PSI values (Penn and Sims, 2002). The reliability of fertilizer requirement determinations may be improved if the PSI were taken into consideration (Indiati and Sharpley, 1997). Oxalate P is reported to be representative of sorbed soil P (Maguire et al., 2000a), and the oxalate extraction is

associated with amorphous Al and Fe, both of which are attributed to a high P sorption capacity in soil (McKeague and Day, 1966; Paulter and Sims, 2000; Ross and Wang, 1993; van der Zee and Riemsdijk, 1988). Thus the PSI provides an estimate of the net soil P sorption capacity. This is similar to other more time consuming tests such as P sorption isotherms (see heading for *P sorption isotherms* below).

The PSI of biosolids may be useful in predicting whether or not P will be released following application to soils with a low P sorption capacity (Dentel et al., 2001; Elliott et al., 2002a). Elliott et al. (2002a) found a general qualitative correlation between biosolids PSI and labile (water- or KCl-extractable) P, although this trend did not hold true in all cases. However, these authors note that a soil of even modest sorptive capacity, which characterizes most U.S. soils, can mitigate the differences among biosolids; a combination of the biosolids PSI and soil P sorption capacity will ultimately dictate the threat of P leaching from biosolids-amended soils. Additionally, a linear relationship between biosolids PSI (determined from total elemental analysis rather than oxalate extraction) and Bray 1 P for biosolids-amended soil and soil+sand mixtures has been reported (Jenkins and Horwath, 2001). These authors also report that a biosolids PSI value of 100 represents the threshold above which leachable P can be expected to be significant. While such a PSI threshold may be theoretically justifiable (a PSI value of 100 represents a stoichiometric balance between P and Al+Fe), some authors have reported a more conservative estimate based upon split-line models. When various

measurements of labile P are plotted as a function of the PSI, split-line models can be used to identify a change point below which P lability remains consistently low and above which P lability increases markedly with increasing PSI (Maguire et al., 2000a, b; McDowell and Sharpley, 2001).

Fair correlations for both water soluble and iron oxide P with the PSI of biosolids-amended soils have been reported, with r^2 values of 0.60 and 0.55, respectively (Maguire et al., 2000a). The soil PSI may not change dramatically following land application of biosolids, because P, Al and Fe concentrations increase simultaneously following biosolids application (Maguire et al., 2000a; Penn and Sims, 2002).

P sorption isotherms

Phosphorus sorption isotherms are developed by equilibrating a known amount of soil with varying amounts of added P in solution and measuring the change in solution P after a period of time (Fox and Kamprath, 1970). More recent work has explored the use of a single P-containing solution to characterize the P sorption capacity of soils. Paulter et al. (2000) reported that such a single-point P sorption isotherm was highly correlated with soil P sorption capacities for 41 soils. Additionally, Pote et al. (1999) reported such measurements to be highly correlated with dissolved P in runoff. Indeed, single-point P sorption isotherms have been recognized as a possible alternative to the more labor-intensive multiple-point isotherms for characterizing the P sorption capacity soils (Mozaffari and Sims,

1994). These authors also noted that the single-point P sorption isotherm was highly correlated with soil clay content.

Land Management Options

Agricultural P management is not limited simply to the choice of whether or not to apply P-containing fertilizers and amendments. Water treatment residuals have been successfully used to reduce dissolved P in agricultural runoff due to their high levels of amorphous Al and/or Fe oxides (Basta et al., 2000; Dayton and Basta, 2001; Elliott et al., 2002b). Tillage also has the ability to mitigate environmental risks associated with land application of P-containing soil amendments (Pierzynski et al., 2000). In no-till situations such as permanent pastures P tends to accumulate at the surface, as it is essentially mined from the soil by plants and deposited at the surface in plant debris (Guertal et al., 1991). Phosphorus applied with fertilizers and amendments is also concentrated at the surface and only slowly moves into the soil.

Summary

The prevalence of numerous tests for available soil P indicates a lack of consensus on methodology. By taking into consideration the chemistry of soil P, as characterized by the chemical forms, interactions among forms, and the factors which control those interactions, tests for soil P have the potential to more

accurately estimate the amount of P available to plants over an entire growing season. In particular, anion exchange resins hold promise as a result of their ability to simulate the actions of plant roots in soil by acting as a sink to adsorb P from the soil solution without reacting with solid-phase P directly. Finally, consideration of parameters such as the P sorption index and single-point P sorption isotherms could potentially improve recommendations for additions of P to soils, including both organic and inorganic amendments. "There is no merit, some unnecessary cost, and possible environmental risk in maintaining soils significantly above an appropriate critical level of soil P for a crop or rotation as assessed by soil analysis" (Higgs et al., 2000, p. 86), a sentiment echoed by others (Hue et al., 2000; Paulter and Sims, 2000).

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PHOSPHORUS AVAILABILITY IN BIOSOLIDS-AMENDED SOIL

Abstract

Phosphorus (P) indices originated in an effort to protect surface water quality from non-point, agricultural P inputs. However, P availability varies among agricultural soil amendments. Objectives of this study were to: (1) evaluate soil test components of the western Oregon P index in field and laboratory experiments; (2) evaluate soil test methods for assessing labile P; and (3) determine the relative availability of fertilizer and biosolids P. Samples were collected from 18 western Oregon field sites with a history of biosolids application and analyzed for labile P via oxalate extraction (P_{ox}), anion exchange resin (AER) extraction, Bray 1 extraction, and dilute salt extraction (0.01 M $CaCl_2$). In comparison to untreated buffer areas, biosolids application at field sites increased mean P_{ox} , AER-P, Bray P and $CaCl_2$ -P by 163, 151, 163 and 128%, respectively in the 0-5 cm depth. Neither the accounting of cumulative P loading rates or the soil P sorption index [PSI; defined as the molar ratio of $P/(Al+Fe)*100$ as measured by oxalate extraction] were well-correlated with changes in soil test P following biosolids application. Five soils were amended with either one of two biosolids or triple superphosphate fertilizer in laboratory incubations at rates of 0, 300, 600 and 900 mg P per kg soil. The availability of fertilizer-derived P in incubations was approximately twice that of biosolids P as measured by AER extraction. Phosphorus indices must make use

of some form of direct soil P measurement, and the western Oregon P index could be improved with separate weighting factors for biosolids and fertilizer P amendments.

Introduction

Biosolids, the residual solids remaining after wastewater treatment, are often applied to agricultural lands as a fertilizer and soil amendment. The rate of such biosolids applications is generally determined by biosolids nitrogen (N) concentration and the N demand of the crop to which the biosolids will be applied. This practice of N-based biosolids management results in the over-application of phosphorus (P) relative to crop needs (Maguire et al., 2000a; Penn and Sims, 2002). Phosphorus is generally the limiting element controlling eutrophication of surface water systems (Pierzynski et al., 2000; Sharpley et al., 1999), so understanding the fate of biosolids P in the environment following land application is essential to protecting surface water quality.

Soil P is often recognized as being divided among several pools, including soluble, labile and non-labile P. Soluble P refers to P that is soluble in water; labile P is that which is readily available to replace P lost from the soil solution through plant uptake, leaching, precipitation or immobilization; and non-labile P includes the P in soil minerals and organic matter which must be dissolved or mineralized in order to be released into the soil solution (Havlin et al., 1999). These pools of soil P do not exist as distinct entities; rather a continuum among such pools of soil P

exists (Frossard et al., 2000). For example, due to the low aqueous solubility of P, much of the soluble P in soil exists as labile P at any given time. Particulate P (labile and non-labile pools) is the predominant form in which P is lost from agricultural fields via soil erosion (Lemunyon and Gilbert, 1993; Sharpley et al., 1999). However, for soils with high labile P concentrations, soluble P loss in the absence of erosion can be significant as well (Elliott et al., 2002a; Mozaffari and Sims, 1994).

Phosphorus indices are field-scale screening tools used by conservation planners (e.g., NRCS staff) to assess the risk of offsite P movement from agricultural fields. This task is accomplished via site-specific, line-item accounting of the factors controlling P mobility in the environment (Lemunyon and Gilbert, 1993). The western Oregon P index uses the Bray 1 test as a means of assessing the risk of soluble P loss from the soil (USDA-NRCS, 2001). This test has both advantages and disadvantages with regard to its use in the western Oregon P index.

The primary advantage of using the Bray 1 extraction as a measure of soil test P (STP) for the western Oregon P index is that this test is routinely used for agronomic purposes; thus STP results are generally readily available for many soils. However, the fact that this test is used for agronomic purposes also presents a potential disadvantage. Soil tests designed with the purpose of assessing the risk of soluble P loss in surface runoff generally utilize samples taken to a depth of only 5 cm, whereas soil tests used for agronomic purposes generally utilize samples taken to a depth of 15 to 30 cm (Maguire et al., 2000a; Mahler and Tindall, 1997).

These deeper sampling depths are inclusive of the surface soil, but such samples have a relatively low sensitivity to changes in STP occurring near the surface.

A possible alternative to the use of the Bray 1 extraction in the western Oregon P index is an accounting of cumulative P loading rates. The amount of heavy metals that can be applied to land in the form of biosolids is currently regulated according to cumulative loading rates (Sullivan, 1998). Given that both heavy metals and P are relatively immobile in soils, a similar cumulative loading limit for P may be suitable as well. Furthermore, a linear relationship has been reported to exist between the amount of P added to soil and available soil P, suggesting that the cumulative P application rate may be a more dominant factor in determining available soil P than is the source of the P (Cooperband et al., 2002; Wen et al., 1997).

Another theoretically justifiable alternative to the Bray 1 extraction for use in the western Oregon P index is the soil P sorption index [PSI; defined as the molar ratio of $P/(Al+Fe)*100$ as measured by acid ammonium oxalate extraction]. Both Al and Fe are present in soils mainly as poorly crystallized, amorphous forms which have the ability to readily bind P (Frossard et al., 1995). The acid ammonium oxalate extractant is particularly effective at measuring these amorphous materials and thus provides a measure of both the amount of bound P and the P sorption capacity of the soil (Maguire et al., 2000a; McKeague and Day, 1966; Paulter and Sims, 2000; Ross and Wang, 1993; van der Zee and Riemsdijk,

1988). Soils with high PSI values (near 100%) have a high amount of sorbed P relative to their P sorption capacities.

In addition to STP, the western Oregon P index also accounts for the form in which P is added to soils (organic amendments versus commercial fertilizers). Currently, the western Oregon P index weights both P sources equally with regard to their potential effect on the amount of P available for offsite movement. However, commercial fertilizers must be formulated with readily available forms of P, defined as citrate-soluble P (Meister, 2000), whereas the majority of P in biosolids and other organic amendments generally slowly becomes available over time (Pierzynski et al., 2000). Consequently, more information is needed on the relative P availability of organic byproducts such as manures and biosolids.

The management of field sites used for land application of biosolids differs from field to field with regard to application rates, application frequency and frequency of cultivation in addition to numerous other factors. Characteristics such as soil type can vary considerably among sites as well. Such variability among sites makes the comparison of results difficult from a survey-based study. Both laboratory incubations and long-term research plots offer the possibility to study such factors in a controlled fashion.

The objectives of this study were to: (1) evaluate the impact of biosolids applications on STP and the corresponding environmental risk as assessed by the current western Oregon P Index and other potential regulatory schemes; (2) evaluate soil test methods for assessing labile P; and (3) determine the effects of

soil and P source on STP when the factors of P application rate, time since application, and incorporation are controlled in a laboratory incubation.

Materials and Methods

Field site characterization

Site selection

The field sites sampled for this study were chosen from biosolids application sites associated with eight cooperating municipalities located in and around the Willamette Valley region of western Oregon. Site selection was based upon several criteria. All soils must have received one or more biosolids applications, and these applications must have included well-defined buffer areas (e.g., areas adjacent to roads, buildings or wells having received no biosolids). These buffer areas must be of the same soil series as those in the application areas, as delineated in the local soil survey, and any fertilizers applied must have been applied uniformly to both areas. Additionally, records allowing the determination of cumulative biosolids P loading for each site must be available.

Soil sampling

Soils were sampled during the summer of 2001. Soil cores were taken to two depths, 0-5 cm and 0-30 cm, with a 2.22 cm (7/8 in) inner diameter soil probe (Model 401.01, AMS, Inc., American Falls, ID) outfitted with a slide hammer

accessory for 0-30 cm samples. Separate composite samples were taken for each depth in both biosolids application areas and adjacent buffer areas and consisted of approximately 20 to 30 cores (0-5 cm sampling depth) or 6 to 8 cores (0-30 cm sampling depth) with a total composite sample volume of approximately 600 cm³.

The fields sampled ranged in size from approximately 5 ha to 120 ha with an average field size of about 20 ha. However, due to soil variability within these fields, areas sampled were considerably smaller. Buffer areas varied in size from approximately 15 m (50 ft) in width near public roads to 60 m (200 ft) wide near buildings and wells.

Bulk soil samples were collected from the top 30 cm of buffer areas for use in laboratory incubations. Biosolids were collected for use in laboratory incubations from cooperating municipal wastewater treatment facilities at the end of the treatment process in a form representative of that which is land applied. Incubation procedures are described below under "Laboratory incubations."

Soil sample preparation

All soil samples were oven-dried for 24 h at 65°C and crushed with a rolling pin to pass a 2 mm (No. 10) sieve. A suite of analyses were then performed, including: acid ammonium oxalate extraction, anion exchange resin extraction, Bray 1 extraction, dilute salt extraction, total Al, Fe and P, total C, pH and particle size analysis (% sand, silt and clay).

All extractions were performed on a reciprocating shaker (Model 6000, Eberbach Corp., Ann Arbor, MI) at a speed of approximately 120 cycles min^{-1} . With the exception of the acid ammonium oxalate extraction, all extractions were performed with a 1:10 soil:extractant ratio.

Acid ammonium oxalate extraction

The extractant was prepared by mixing 0.2 M ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, and 0.2 M oxalic acid, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, in proportions resulting in a solution pH of 3.0 (Ross and Wang, 1993). Ten milliliters of this extractant was added to either 0.25 g of soil or 0.13 g of biosolids in a 50 mL HDPE centrifuge tube and shaken for 4 h. Samples were centrifuged at 510 x g and the supernatant was analyzed for Al, Fe and P via ICP-AES (Optima 3000 DV, PerkinElmer, Wellesley, MA). Samples remained in an enclosed, opaque box during the 4 h extraction to exclude light that could otherwise react with the extractant.

Anion exchange resin extraction

Anion exchange resin sheets (204-U-386, Ionics, Watertown, MA), with a capacity of approximately 0.02 $\text{cmol}_e \text{ cm}^{-2}$ (Cooperband and Logan, 1994), were cut into 1 cm^2 squares and saturated with 1 M NaHCO_3 through 3 successive 10 min intervals with fresh NaHCO_3 . Squares were then rinsed with deionized water,

and 1 square was used with 20 mL of deionized water in a 60 mL HDPE screw-cap bottle to extract 2 g of soil. Samples were shaken for 16 h. Resin squares were then rinsed with deionized water, transferred to clean 60 mL bottles and extracted with 1 M HCl for 4 h on a reciprocating shaker. The HCl extracts were analyzed for P colorimetrically via the Murphy-Riley molybdenum blue method (Pierzynski, 2000) on a spectrophotometer (Model 8453, Hewlett-Packard, Palo Alto, CA) integrating absorbance from 840 to 880 nm. Pierzynski (2000) calls for multiple extractions of the resins with HCl prior to analysis, but previous work in our laboratory showed that over 99% of bound P was recovered during the first extraction (Moore, 2001). Resin squares were reused multiple times by recharging with NaHCO₃ between uses as described previously.

Bray 1 extraction

Two grams of soil were extracted with 20 mL of the Bray 1 extracting solution (Pierzynski, 2000) in 50 mL HDPE centrifuge tubes for 60 s on a reciprocating shaker. The soil extract was then filtered through Whatman No. 42 filter paper and analyzed for P colorimetrically as described previously.

Dilute salt extraction

Two grams of either soil or biosolids were extracted with 20 mL of 0.01 M CaCl₂ in a 60 mL HDPE screw-top bottle for 1 h on a reciprocating shaker. The

extract was filtered through Whatman No. 42 filter paper. Biosolids extracts were analyzed colorimetrically as described previously. Due to low aqueous P concentrations, soil extracts were analyzed on an Alpkem autoanalyzer (Model 550, Perstorp Analytical, Perstorp, Sweden) with a detection limit of approximately 0.01 mg L^{-1} , roughly one order of magnitude lower than the spectrophotometer. For comparison, biosolids extracts were also analyzed via ICP-AES.

Total acid digestion

Total Al, Fe and P in biosolids and soils were determined using a modified version of EPA Method 3051 (USEPA, 1994). The modification consisted of utilizing 2 mL of concentrated HNO_3 and 2 mL of 30% H_2O_2 rather than 10 mL of HNO_3 for digestion. Preliminary analyses showed low P recovery with the standard EPA Method 3051. Biosolids P recovery increased by approximately 40% with the modified extraction solution. All other parameters are as stated in the original method. Digests were analyzed for Al, Ca, Fe, Mg, Mn and P via ICP-AES.

Total C

Samples weighing 0.3 g (soils) or 0.2 g (biosolids) were analyzed for total C. Total C was measured with a LECO C-144 carbon analyzer (LECO Corporation, St. Joseph, MI).

pH

The pH of soils and biosolids were determined using 0.01 M CaCl₂ in a 2:1 liquid:sample ratio. Forty milliliters of 0.01 M CaCl₂ was added to 20 g samples of either soil or biosolids and stirred thoroughly. After 15 minutes, samples were stirred a second time and allowed to stand an additional 15 minutes, after which the pH was measured with a digital ion analyzer (Model 501, Thermo Orion, Beverly, MA) by inserting the electrode into the supernatant.

Physical characterizations

Soil texture was determined by sedimentation using hydrometer readings at 45 s and 8 h (Brady and Weil, 2002). A drop of amyl alcohol was used to control foaming. Biosolids total solids were determined from the difference between fresh and dry weights (65°C drying temperature).

Laboratory incubations

Materials

Incubations were performed using selected soils from the field characterization portion of this study and biosolids from a related study (Chapter 3). Five soils were chosen to represent the range of P sorption capacities and soil types exhibited at field sites. Phosphorus sorption capacity was gauged by the P

sorption index (PSI), defined as the molar ratio of $P/(Al+Fe)*100$ as determined by acid ammonium oxalate extraction. The PSI values ranged from 0.4 to 11.3% for selected soils (Table 2.1).

Table 2.1. P sorption characteristics of soils sampled at 18 western and two eastern Oregon sites.

Site	$P_{ox}\dagger$ mmol kg ⁻¹	$Al_{ox}\dagger$ mmol kg ⁻¹	$Fe_{ox}\dagger$ mmol kg ⁻¹	$(Al_{ox} + Fe_{ox})$ mmol kg ⁻¹	PSI \dagger %
1	19	83	105	188	10.3
2‡	4	43	71	114	3.3
3	9	39	104	142	6.3
4‡	6	47	100	148	4.4
5	11	204	84	287	3.7
6	15	267	79	346	4.3
7	25	70	110	180	13.6
8	15	86	88	174	8.6
9‡	14	46	80	125	11.3
10	10	63	162	225	4.4
11	8	96	163	260	3.0
12‡	1	113	172	285	0.4
13	6	71	160	231	2.7
14	1	73	108	181	0.7
15‡	25	876	84	960	2.6
16	6	354	87	440	1.4
17	18	213	95	309	5.9
18	27	61	115	176	15.4
19	27	86	134	221	12.2
20	7	137	105	242	3.1

† Abbreviations: P_{ox} = oxalate-extractable P; Al_{ox} = oxalate-extractable Al; Fe_{ox} = oxalate-extractable Fe; PSI = P sorption index [defined as the molar ratio of $P/(Al+Fe)$ as measured by oxalate extraction].

‡ These soils were used in laboratory incubations.

Amendments included two biosolids and a fertilizer control, triple superphosphate ($10 \text{ Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$; 0-45-0, Voluntary Purchasing Groups, Inc. Bonham, TX). The biosolids were selected to be representative of the majority of land-applied biosolids in western Oregon. Selection was based upon chemical characterization of these biosolids as described above. In particular, biosolids were chosen that exhibited intermediate PSI values. A group of 27 biosolids from across the Pacific Northwest ranged in PSI value from 44 to 213% with a mean of 111% and a median of 109% (Chapter 3). The biosolids selected for use in laboratory incubations, designated by source facility as Eugene and Rock Creek, had PSI values of 91% and 119%, respectively (Table 2.2).

Both Eugene and Rock Creek biosolids are anaerobically digested. Following anaerobic digestion, Eugene biosolids are further stabilized by lagoon storage, whereas Rock Creek biosolids are dewatered shortly after removal from the digester. Eugene biosolids are subsequently dried on drying beds prior to land application, while Rock Creek biosolids are dewatered with a belt press. Samples were collected during the summer of 2001 from Eugene drying beds and from Rock Creek following the dewatering process. Samples were oven-dried at 65°C and were then ground with a mechanical grinder to pass a 2 mm (No. 10) sieve.

Experimental design

The experimental design was a 5 x 4 x 3 soil x rate x amendment factorial. The five soil samples consisted of a 0-30 cm composite sample from Concord,

Table 2.2. Chemical characterization data for biosolids used in laboratory incubations.

Facility	Treatment Process	total P mg kg ⁻¹	P _{ox} † mg kg ⁻¹	P _{ox} mmol kg ⁻¹	Al _{ox} † mmol kg ⁻¹	Fe _{ox} † mmol kg ⁻¹	PSI† %	CaCl ₂ -P† mg kg ⁻¹	total C %	pH
Eugene	lagoon, drying bed	27826	25750	831	510	191	118.7	1040	30.3	6.9
Rock Creek	anaerobic, dewatered	25974	23538	760	627	205	91.3	1186	30.3	6.7

† Abbreviations: P_{ox} = oxalate-extractable P; Al_{ox} = oxalate-extractable Al; Fe_{ox} = oxalate-extractable Fe; PSI = P sorption index [defined as the molar ratio of P/(Al+Fe) as measured by oxalate extraction]; CaCl₂-P = dilute salt-extractable P.

Table 2.3. Site characterization data for 18 western and two eastern Oregon sites (0-30 cm sampling depth, non-application buffer areas).

Site	Soil Series	Soil Taxonomic Class	Textural Class	Sand %	Clay %	Organic C %	pH†	Present Crop	Last Cultivation
1	Woodburn	Fine-silty, mixed, superactive, mesic Aquultic Argixerolls	silt loam	15	25	1.9	4.4	hay	none
2	Concord	Fine, smectitic, mesic Typic Endoaqualfs	silty clay loam	3	30	0.8	4.3	pasture/hay	none
3‡	Deschutes	Coarse-loamy, mixed, superactive, mesic Vitritorrandic Haploxerolls	sandy loam	70	7	1.5	5.3	pasture/hay	none
4‡	Deschutes	Coarse-loamy, mixed, superactive, mesic Vitritorrandic Haploxerolls	sandy loam	60	10	1.0	5.6	hay	none
5	Jory	Fine, mixed, active, mesic Xeric Palehumults	silty clay loam	20	28	3.9	4.7	pasture/hay	none
6	Jory	Fine, mixed, active, mesic Xeric Palehumults	sandy clay loam	18	32	3.1	4.4	hay	none
7	Woodburn	Fine-silty, mixed, superactive, mesic Aquultic Argixerolls	silt loam	5	28	1.9	4.6	fescue (seed)	none
8	Santiam	Fine, mixed, superactive, mesic Aquultic Haploxeralfs	silty clay loam	7	28	2.3	4.5	annual ryegrass	2000
9	Dayton	Fine, smectitic, mesic Vertic Albaqualfs	silt loam	5	20	2.1	4.4	annual ryegrass	2000
10	Bashaw	Very-fine, smectitic, mesic Xeric Endoaquerts	silty clay	7	40	3.2	4.6	annual ryegrass	2000
11	Natroy	Very-fine, smectitic, mesic Xeric Endoaquerts	clay loam	27	33	2.5	4.7	pasture	none
12	Natroy	Very-fine, smectitic, mesic Xeric Endoaquerts	clay	20	42	1.8	4.8	fescue (seed)	none
13	Natroy	Very-fine, smectitic, mesic Xeric Endoaquerts	silty clay	10	48	2.8	4.4	fescue (seed)	2000
14	Bashaw	Very-fine, smectitic, mesic Xeric Endoaquerts	clay	15	47	4.3	5.2	pasture	none
15	Jimbo	Coarse-loamy, mixed, superactive, mesic Andic Dystrudepts	loam	52	8	6.5	5.0	pasture	none
16	Bull Run	Medial, amorphic, mesic Eutric Fulvudands	clay loam	25	28	5.4	5.0	hay	none
17	Nekia	Fine, mixed, active, mesic Xeric Haplohumults	silt loam	15	23	1.7	5.1	annual ryegrass	2000
18	Amity	Fine-silty, mixed, superactive, mesic Argiaquic Xeric Argialbolls	silt loam	25	25	4.6	5.4	fescue (seed)	none
19	Willamette	Fine-silty, mixed, superactive, mesic Pachic Ultic Argixerolls	silty clay loam	5	28	1.8	4.5	fescue (seed)	none
20	Nekia	Fine, mixed, active, mesic Xeric Haplohumults	clay loam	27	28	2.5	5.1	pasture	none

† Soil pH was determined using 0.01 M CaCl₂ in a 2:1 liquid:sample ratio.

‡ Fields 3 and 4 are located in central Oregon, whereas the other 18 sites presented here are located in western Oregon. Data from fields 3 and 4 are presented in Appendix A but are not discussed in text or included in figures.

Dayton, Deschutes, Jimbo and Natroy series. Table 2.3 contains chemical analyses and textural classes for these soils, which correspond to sites 2, 9, 4, 15 and 12, respectively from the field characterization portion of this study. Table 2.1 contains P sorption characteristics for these soils. Biosolids and triple superphosphate fertilizer were each applied at 4 rates of P application (0, 300, 600 and 900 mg P per kg soil) with treatments replicated three times.

Laboratory incubations

Incubations were initiated by adding dried, ground biosolids or fertilizer to 200 g of air-dried soil in Ziploc bags. Samples were thoroughly mixed and moisture was added to achieve a gravimetric moisture content of 200 g kg⁻¹. Samples were mixed again to evenly distribute the water and break up any aggregates that formed as a result of the addition of water to the amended soil. Ziploc bags were arranged one layer deep in plastic storage containers and placed in an incubation chamber held at 25°C for 28 d. Bags remained open at the top to assure aerobic conditions during the incubation, though the tops were folded over to avoid significant moisture loss. After 28 d, 2 g samples were analyzed for P via anion exchange resin extraction as described previously.

An incubation period of 28 d was chosen based upon the results of preliminary incubations. Preliminary incubation results showed that anion exchange resin-extractable P rapidly decreased for several days following the addition of biosolids and began to stabilize after approximately 5 d (Appendix 2).

An incubation period of 28 d was chosen to assure sufficient time for equilibration of P between soils and amendments.

Results and Discussion

Field site characterization

The field sites sampled for this study were chosen to represent the range of soils and cropping systems currently used for biosolids application in western Oregon. Most sites were planted to pasture grasses, hay or grass seed crops and were tilled infrequently (Table 2.3). Soils used for biosolids application reflected considerable taxonomic diversity. The sites sampled include soils from six soil orders (Table 2.3). Although 20 field sites were sampled for this study, two of these, sites 3 and 4, were located in central Oregon; data for these sites are included in tables and appendices but have been excluded from all figures and will not be discussed here.

Cumulative P application rates at the sites in this study varied widely, ranging from 149 to 1548 kg P ha⁻¹. The number of biosolids applications at these sites ranges from 1 to 8 with the average amount of P per application ranging from 43 to 443 kg P ha⁻¹ (Table 2.4). Biosolids treatment processes employed at treatment plants were responsible for the P application rates observed. Application rates for biosolids were based upon biosolids N content and the N

Table 2.4. Biosolids application history for 18 western and two eastern Oregon sites.

Site	Facility	Biosolids Treatment Process	No. of Biosolids Applications	Average P	Cumulative	Biosolids Application History	Last Biosolids Application	Sampling Date
				Application	P loading			
				kg P ha ⁻¹	kg P ha ⁻¹			
1	Albany	anaerobic, liquid	2	74	149	1998-1999	1999	8/24/01
2	Albany	anaerobic, liquid	4	79	317	1997-2000	Oct. 2000	8/24/01
3†	Bend	anaerobic, drying bed	6	242	1453	1996-2001	Feb. 2001	8/30/01
4†	Bend	anaerobic, drying bed	5	310	1548	1996-1998, 2000-2001	Mar. 2001	8/30/01
5	Clackamas	anaerobic, liquid	8	66	524	1993-1997, 1999-2001	Jan. 2001	10/31/01
6	Clackamas	anaerobic, liquid	3	52	155	1999-2001	Mar. 2001	10/31/01
7	CWS	anaerobic, dewatered	3	391	1173	1998-2000	Oct. 2000	8/28/01
8	CWS	anaerobic, dewatered	3	443	1330	1998-2000	Jul. 2000	8/28/01
9	CWS	anaerobic, dewatered	3	412	1235	1998-2000	Jul. 2000	8/28/01
10	Eugene	lagoon, drying bed	3	384	1153	1995-1996, 1999	Jul. 1999	10/2/01
11†	Eugene	lagoon, drying bed	2	136	272	1988, 1995	Jul. 1995	10/4/01
12†	Eugene	lagoon, drying bed	4	74	296	1982, 1984-1985, 1994	Oct. 1994	10/4/01
13	Eugene	lagoon, drying bed	1	219	219	1994	Sep. 1994	10/4/01
14	Eugene	lagoon, drying bed	1	166	166	1992	Sep. 1992	10/8/01
15	Gresham	anaerobic, dewatered	3	137	410	1997-1999	Nov. 1999	10/24/01
16	Gresham	anaerobic, dewatered	4	135	539	1991, 1995, 1999-2000	Sep. 2000	10/24/01
17	Salem	anaerobic, liquid	2	108	217	1998-1999	1999	10/17/01
18	Salem	anaerobic, liquid	3	96	289	1996, 1998, 2000	2000	10/17/01
19	Salem	anaerobic, liquid	2	210	420	1995, 1997	1997	10/17/01
20	Stayton	anaerobic, dewatered, lime-stabilized	5	43	216	1997-2001	2001	10/15/01

† These sites have received a combination of liquid biosolids and biosolids from drying beds. Bend sites received liquid biosolids from 1996-1998; Eugene sites received liquid biosolids prior to 1992. In all cases, the majority of P applied was in the form of biosolids from drying beds.

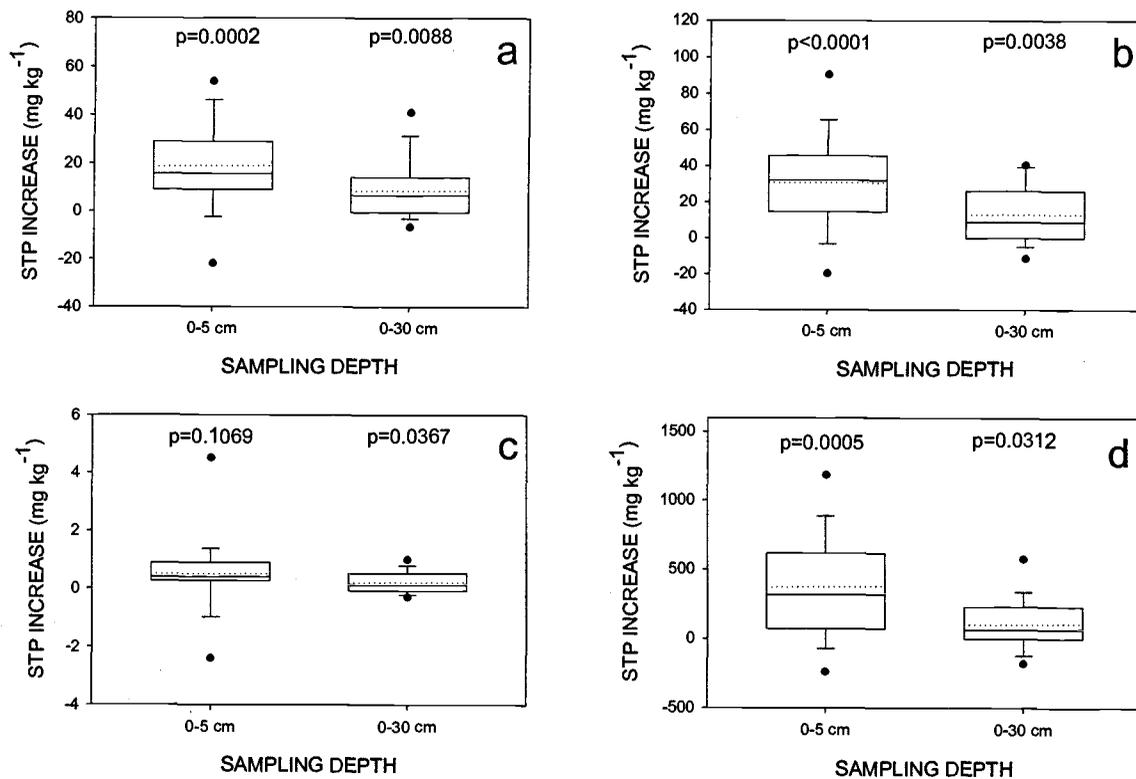


Figure 2.1. Increase in soil test P (STP) associated with biosolids applications at 18 western Oregon sites as measured by four soil P tests: (a) anion exchange resin-extractable P; (b) Bray 1-extractable P; (c) 0.01 M CaCl₂-extractable P; (d) acid ammonium oxalate-extractable P. Boxes delineate the middle 50 % of the data with a solid inner line marking the median and a dashed inner line marking the mean. Whiskers extend to the 5th and 95th percentiles, and dots signify outliers beyond the 5th and 95th percentiles.

needs of the crop to which these biosolids were applied. Typically, 30% of organic N and 50% of ammonium-N in biosolids is estimated to be plant-available during the first year following biosolids application (Maguire et al., 2000a; Penn and Sims, 2002; Sullivan, 1998). Therefore, treatment processes that produced biosolids with higher plant-available N concentrations (e.g., liquid, Table 2.4) had lower P application rates, while biosolids treatment processes that produced biosolids with relatively low plant-available N concentrations (e.g., drying bed, Table 2.4) resulted in relatively high P application rates.

The application of biosolids increased mean soil test P (STP) for both the 0-5 and 0-30 cm sampling depths (Figure 2.1). The mean increase in STP detected by anion exchange resin (AER) extraction was 19 mg kg^{-1} for the 0-5 cm sampling depth and 8 mg kg^{-1} for the 0-30 cm sampling depth. Similarly, the Bray 1 extraction detected a mean increase in STP of 31 and 13 mg kg^{-1} ; dilute salt-extractable P ($\text{CaCl}_2\text{-P}$) increased by 0.5 and 0.2 mg kg^{-1} ; and acid ammonium oxalate-extractable P (P_{ox}) increased by 370 and 99 mg kg^{-1} for the 0-5 and 0-30 cm sampling depths, respectively. Similar increases in STP following long-term additions of P-containing soil amendments to agricultural fields have been summarized previously (Sharpley and Rekolainen, 1997).

Each of the soil P tests used in this study detects a similar mean percent increase in STP across study sites (Figure 2.2). For the 0-5 cm sampling depth, increases in mean STP of 151, 163, 128 and 163% were measured for AER-P, Bray

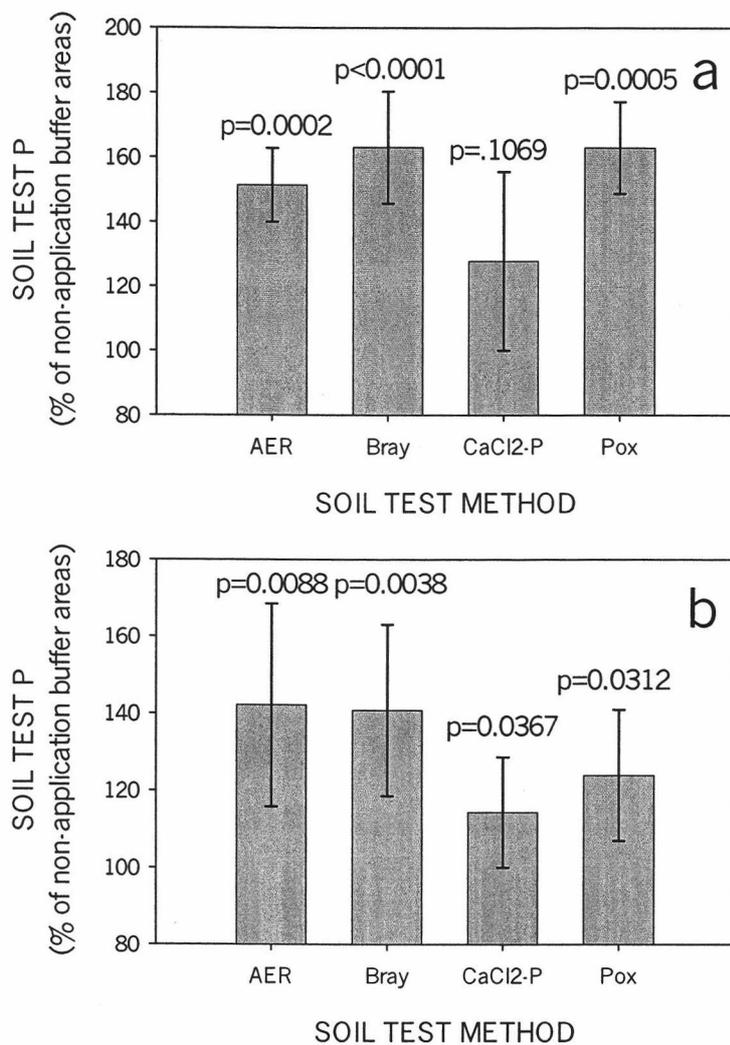


Figure 2.2. Average soil test P (STP) associated with biosolids applications at 18 western Oregon sites as measured by four soil P tests for: (a) 0-5 cm sampling depth; and (b) 0-30 cm sampling depth. Soil P tests include anion exchange resin extraction (AER), Bray 1 extraction (Bray), dilute salt extraction (CaCl₂-P), and acid ammonium oxalate extraction (P_{ox}). Results for individual sites were calculated as follows: $(STP_{\text{biosolids application area}})/(STP_{\text{non-application buffer area}})*100$. Error bars indicate the standard error of the mean across all sites.

P, CaCl₂-P and P_{ox}, respectively. Similarly, increases in mean STP of 142, 141, 114 and 124% were measured by these tests for the 0-30 cm sampling depth.

Although all of these soil P tests detected similar changes in STP, the variability

across sites was not consistent among tests or sampling depths. Dilute salt-extractable P exhibited a relatively large standard error of 28% for the 0-5 cm sampling depth as compared to standard errors of 11 to 17% for the other soil P tests (Figure 2.2). For the 0-30 cm sampling depth, however, both AER-P and Bray P exhibited relatively high variability, whereas CaCl_2 -P exhibited the lowest variability among soil P tests for this sampling depth (Figure 2.2).

Each of the soil P tests used in this study measures the various pools of soil P to different degrees. Dilute salt-extractable P measures water soluble P; AER-P includes both water soluble P and labile P; both Bray P and P_{ox} include water soluble and labile P but differ in the extent to which non-labile forms of soil P are measured. P_{ox} is considered to be particularly effective at solubilizing P bound by amorphous Al and Fe (McKeague and Day, 1966; Ross and Wang, 1993). Considering the fact that these soil P tests measure different pools of soil P, the similar degree to which these tests detect changes in STP associated with biosolids applications suggests that each of the pools of P is increased proportionally following land application of biosolids.

Current P loading rates associated with biosolids applications in western Oregon are not increasing STP values at excessive rates. The average cumulative P loading rate for the sites in this study was 504 kg ha^{-1} , with sites receiving an average of three biosolids applications. The average increase in Bray P at these sites was 2.2 mg kg^{-1} per 100 kg ha^{-1} of biosolids P added. Of the 18 western

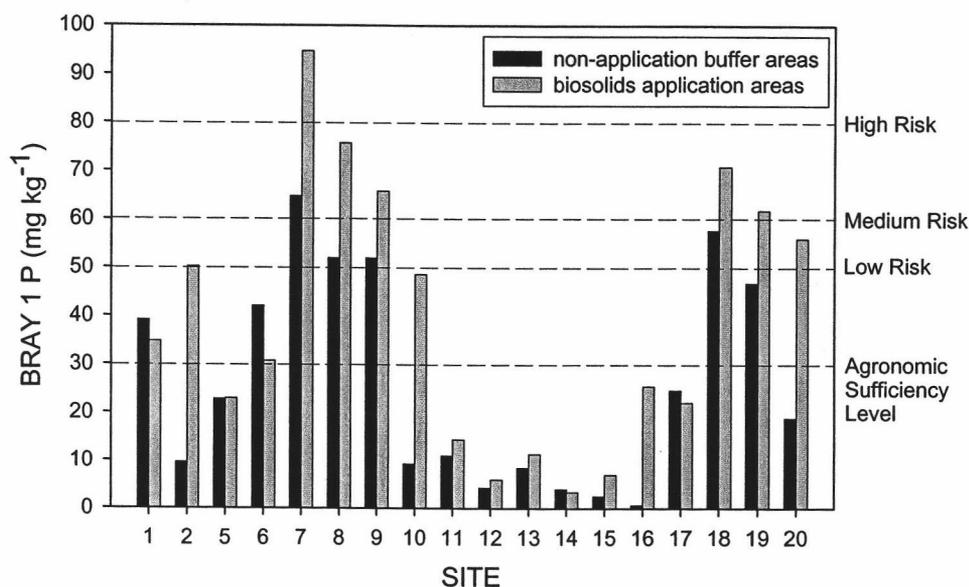


Figure 2.3. Bray 1 soil test P results (0-30 cm sampling depth) for 18 western Oregon sites. Western Oregon P index risk categories are demarcated by dashed lines [USDA-NRCS, 2001], as is a generalized agronomic sufficiency level corresponding with Oregon State University recommendations [Marx et al., 1998].

Oregon sites in this study, 11 sites tested below a generalized agronomic sufficiency level (ASL) in non-application buffer areas at the 30 cm sampling depth, and 10 sites test at or below this ASL in application areas as well (Figure 2.3). This ASL is the approximate Bray P value below which most crops in western Oregon respond to P fertilization and above which P fertilization is generally uneconomical. The ASL value used here corresponds with the middle of the “medium” Bray P category as characterized in Oregon State University soil test guidelines (Marx et al., 1998). Relative risk categories associated with the western Oregon P index are also shown in Figure 2.3. Only five field sites tested above the medium risk category in application areas, and four of these fields also tested above

the low risk category in buffer areas (Figure 2.3). Only one out of 18 field sites exhibited a disparity of more than one risk category between application and buffer areas (Site 19, Figure 2.3).

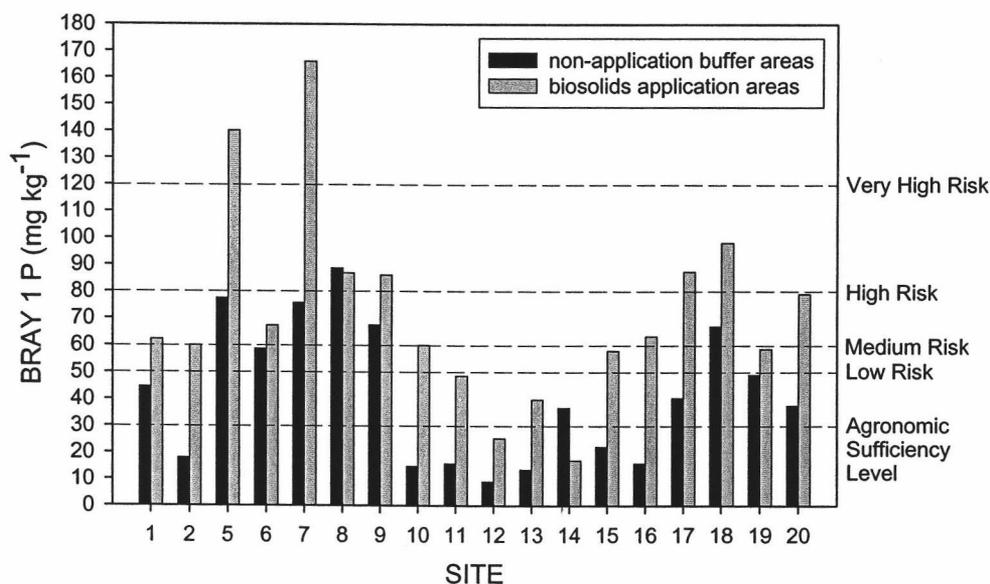


Figure 2.4. Bray 1 soil test P results (0-5 cm sampling depth) for 18 western Oregon sites. Western Oregon P index risk categories are demarcated by dashed lines [USDA-NRCS, 2001], as is a generalized agronomic sufficiency level corresponding with Oregon State University guidelines [Marx et al., 1998].

Soil test P values associated with a sampling depth of 0-5 cm are expected to be higher than those associated with a sampling depth of 0-30 cm. This is due to the removal of P by plant roots and subsequent deposition of P-containing plant materials at the soil surface. Thus, because P is relatively immobile in the soil, P concentrations are higher near the soil surface (Guertal et al., 1991). Indeed, this is the case for every field site in this study for both biosolids application areas and non-application buffer areas alike (Figures 2.3 and 2.4). The majority of P losses

from agricultural fields are due to soil erosion (Lemunyon and Gilbert, 1993; Sharpley et al., 1999), and this trend explains, in part, why environmental soil P tests examine only the top 5 cm of soil where the risk of P loss is greatest. Additionally, runoff water interacts with only the surface soil, so dissolved P lost in runoff originates in the surface of the soil profile.

The fact that biosolids have been added in application areas and withheld from buffer areas does not fully explain the magnitude of differences in Bray P between application and buffer areas for individual sites in this study (0-5 cm sampling depth, Figure 2.4). Consideration of whether these sites have been cultivated and how much time has passed since the last biosolids application may offer additional insights. Sites 7-9 all consist of similar soils and have all received similar amounts of biosolids from the same municipality (Table 2.4), yet only site 7 exhibits a large disparity between Bray P in buffer areas and application areas (Figure 2.4). This may be due to the fact that sites 8 and 9 were tilled between the most recent biosolids application and the date of sampling, whereas site 7 was not (Tables 2.3 and 2.4). In contrast to this trend, however, is the fact that both sites 10 and 17 were tilled between the time of the last biosolids application and the date of sampling (Tables 2.3 and 2.4), yet both of these sites exhibit a large disparity in Bray P values between buffer and application areas (Figure 2.4). Site 5 exhibited a difference of 63 mg kg^{-1} between Bray P in buffer areas and applications areas (Figure 2.4). Application of biosolids occurred at site 5 approximately eight

months prior to sampling with no tillage between application and soil sampling (Tables 2.3 and 2.4).

The effects of tillage and time since biosolids application may be impossible to deduce from any survey-based study such as that presented here. Most of the sites in this study received infrequent tillage. However, detailed records of tillage frequency for these sites generally were not maintained by municipalities. A long-term research plot dedicated to clarifying the effects of these factors on STP following land application of biosolids offers a possible solution.

Based upon trends of increasing STP associated with the application of biosolids, a natural assumption may be that the total amount of P added to a soil might provide a useful predictor of the corresponding change in STP. The amount of heavy metals that can be land applied in the form of biosolids is currently limited by cumulative loading rates (Sullivan, 1998), so a similar approach may be suitable for P as well. Furthermore, a linear relationship has been reported to exist between the amount of P added to soil and available soil P, suggesting that the cumulative P application rate may be a more dominant factor in determining available soil P than is the source of the P (Cooperband et al., 2002; Wen et al., 1997). However, plotting AER-P as a function of cumulative P loading rates for the sites in the present study reveals a poor correlation at best (Figure 2.5). Similar results were obtained for the other soil P tests employed in this study as well. The bimodal trend exhibited in Figure 2.5 is simply the result of a lack of intermediate

cumulative P loading rates. More relevant than this bimodal distribution is the fact that cumulative P loading rates do not appear to explain STP increases. The coefficients of determination (r^2) for linear regression of the 0-5 cm and 0-30 cm data are 0.11 and 0.04, respectively. Furthermore, the slope of the linear regression for the 0-5 cm data is negative. Clearly, knowledge of cumulative P loading rates is insufficient information upon which to base predictions of STP changes associated with biosolids applications.

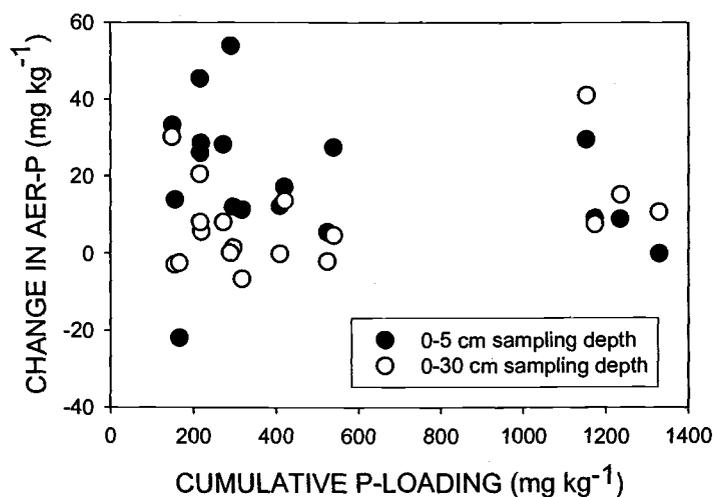


Figure 2.5. Change in anion exchange resin-extractable P (AER-P) associated with biosolids applications at 18 western Oregon sites plotted as a function of cumulative P loading.

The soil P sorption index [PSI; defined as the molar ratio $P/(Al+Fe)$ as measured by acid ammonium oxalate extraction] has been suggested as a means of determining environmental limits for soil P (Maguire and Sims, 2002b). In a column leaching study, these authors used a split line model to identify a change point degree of P saturation (DPS) value of 56%; below this DPS value, leachable

P concentrations remained low, while above this DPS value, leachate P concentrations increased rapidly for five Delaware soils (Maguire and Sims, 2002a). These authors defined the DPS as the molar ratio of $P/[0.5*(Al+Fe)]*100$ which differs from the PSI by a factor of 2 ($DPS = 2*PSI$). Thus a DPS value of 56% corresponds to a PSI value of 28%. However, the soils sampled in the present study exhibited PSI values of only 0.4 to 17.0% (Table 2.1) and exhibited no such trend as that described above for the Delaware soils with regard to a change point (Figure 2.6). Linear regression of the data for the 0-5 and 0-30 cm sampling depths resulted in r^2 values of 0.10 and 0.004, respectively. Although Figure 2.6 displays only AER-P as a function of soil PSI, similar results were obtained for the other soil P tests used in this study as well. Elliott et al. (2002) noted that soils of even moderate P sorption capacity may mitigate differences in P availability among biosolids amendments. It seems likely that the P sorption capacity of the soils used in the present study was too great to allow a significant relationship between AER-P and PSI to be observed.

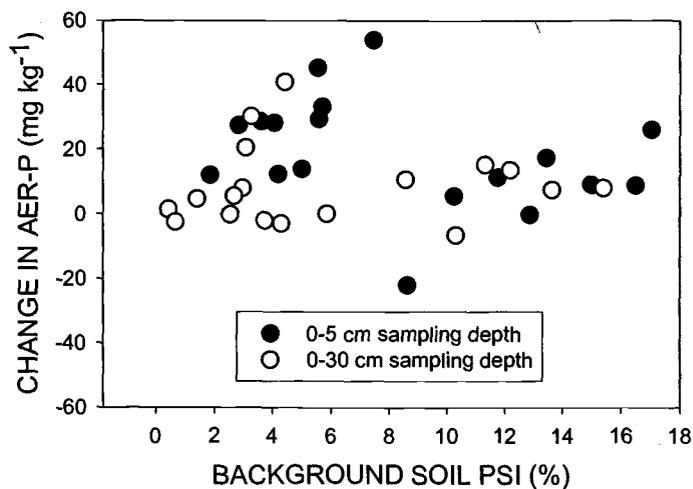


Figure 2.6. Change in anion exchange resin-extractable P (AER-P) associated with biosolids applications at 18 western Oregon sites plotted as a function of the background soil P sorption index (PSI). Background PSIs were determined for samples from buffer areas to which biosolids have never been applied.

Labile P determination

The western Oregon P index uses the Bray 1 extraction as a means of assessing the relative risk of dissolved P loss in runoff, so the second objective of this study was to evaluate the ability of various soil P tests, including the Bray 1 extraction, to measure labile P. Linear regression analysis of CaCl₂-P on AER-P, Bray P and P_{ox} for the 5 cm sampling depth (Figure 2.7) results in coefficients of determination (r^2) of 0.59, 0.18 and 0.18, respectively. Linear regression analysis of these same comparisons for the 30 cm sampling depth (Figure 2.8) yield r^2 values of 0.83, 0.70 and 0.35, respectively. Two trends are immediately apparent: 1) correlations associated with the 30 cm sampling depth are stronger than those

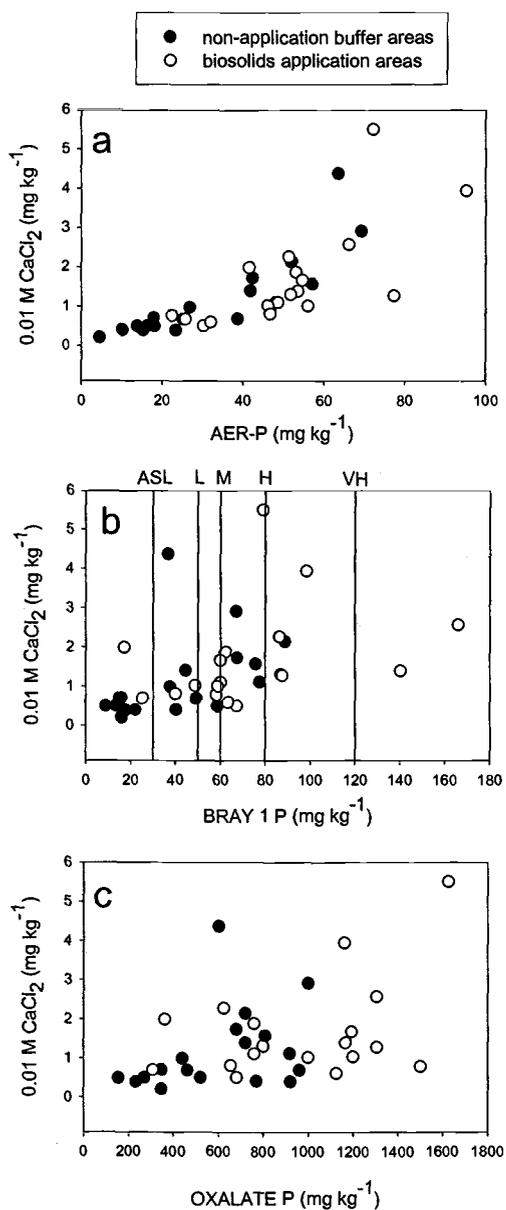


Figure 2.7. Comparison of dilute salt-extractable P (CaCl₂-P) with: (a) anion exchange resin-extractable P (AER-P); (b) Bray 1-extractable P; and (c) acid ammonium oxalate-extractable P for soils sampled at 18 western Oregon sites (0-5 cm sampling depth). Delineations in graph (b) include western Oregon P index risk categories (L=low; M=medium; H=high; VH=very high; USDA-NRCS, 2001) and a generalized agronomic sufficiency level (ASL) corresponding with Oregon State University guidelines [Marx et al., 1998].

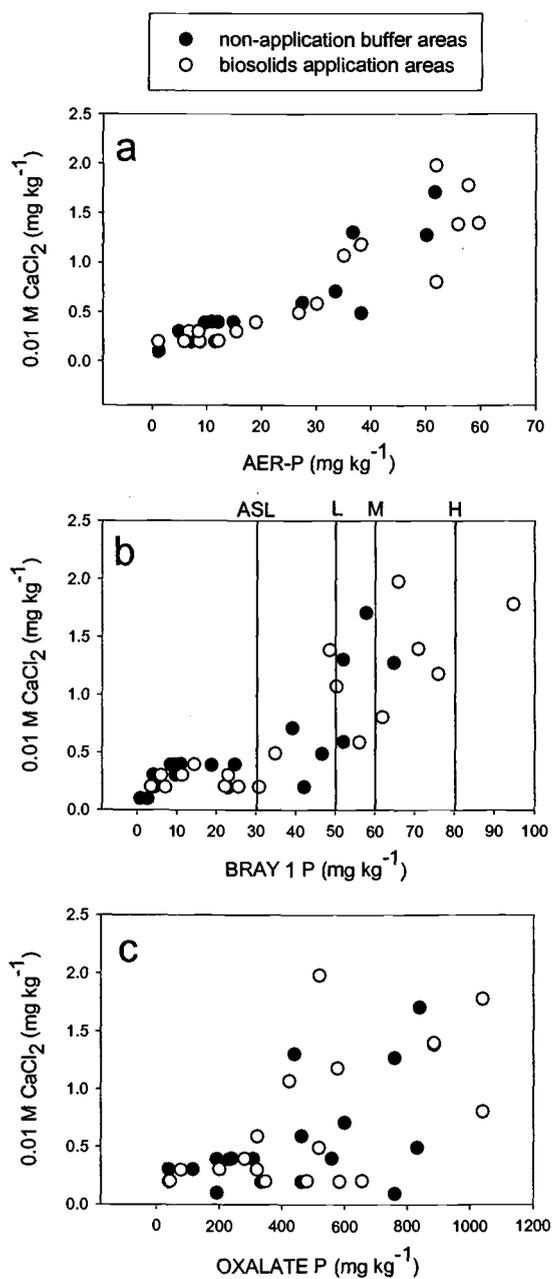


Figure 2.8. Comparison of dilute salt-extractable P (CaCl₂-P) with: (a) anion exchange resin-extractable P (AER-P); (b) Bray 1-extractable P; and (c) acid ammonium oxalate extractable P for soils sampled at 18 western Oregon sites (0-30 cm sampling depth). Delineations in graph (b) include western Oregon P index risk categories (L=low; M=medium; H=high; VH=very high; USDA-NRCS, 2001) and a generalized agronomic sufficiency level (ASL) corresponding with Oregon State University guidelines [Marx et al., 1998].

associated with the 5 cm sampling depth for all comparisons; and 2) the correlation of dilute salt-extractable P with AER-P is stronger than other comparisons for both sampling depths.

The increased variability associated with the shallow sampling depth is likely the result of elevated P and organic matter contents near the soil surface which serve to increase STP values. The effect of higher STP values can be seen in Figures 2.7 and 2.8, where the spread of data increases dramatically at the point where $\text{CaCl}_2\text{-P}$ levels begin to increase. Additionally, obtaining shallow samples to a consistent depth was more difficult than for deeper samples.

The stronger correlation between $\text{CaCl}_2\text{-P}$ and AER-P relative to the other comparisons in Figures 2.7 and 2.8 can be accounted for by taking into consideration the various pools of soil P that these tests measure. The more soil P a test measures in addition to water soluble P, the less likely that test is to correlate well with a direct measure of water soluble P. Anion exchange resin-extractable P includes one additional soil P pool, labile P, in addition to water soluble P, whereas both Bray P and P_{ox} include two additional soil P pools, labile P and non-labile P. At both sampling depths, AER-P exhibited a better correlation with $\text{CaCl}_2\text{-P}$ than did either Bray P or P_{ox} . Furthermore, P_{ox} extracts greater amounts of P from the non-labile pool of soil P in the form of P bound by amorphous Al and Fe, and it shows a weaker correlation with $\text{CaCl}_2\text{-P}$ than does Bray P at the 30 cm sampling depth. This latter relationship would hold true for the 5 cm sampling depth if not

for two outliers that exert a strong influence on the regression analysis. When these outliers are excluded, the r^2 value increases from 0.18 to 0.36.

The stronger correlation between $\text{CaCl}_2\text{-P}$ and AER-P relative to that between $\text{CaCl}_2\text{-P}$ and Bray P indicates that AER-P would offer an improved assessment of the risk of dissolved P loss following land application of biosolids as compared to Bray P. The use of Bray P for agronomic purposes is deeply entrenched and provides readily available data for use in the western Oregon P index. Therefore, replacement of Bray P with AER-P in the western Oregon P index would require additional soil P testing beyond what is already done for agronomic purposes. This requirement for additional testing is likely to present a major obstacle to replacement of Bray P as the measure of STP used in the western Oregon P index.

Laboratory incubations

Laboratory incubations allowed for the control of factors such as P application rate, time since application, and incorporation of amendments that were unable to be controlled in the field characterization portion of this study. Such a controlled environment provided a direct examination of the effects of soil, P source and rate of P application on STP.

An analysis of variance of the AER-P results for laboratory incubations reveals a significant interaction among the three main effects: soil, amendment and rate (Table 2.5; means in Table 2.6). However, the mean squares (MS) for the main

effects are perhaps more relevant than is this three-way interaction. The MS associated with the rate of P addition is approximately twice that of the next largest MS value, and since P was the entity being measured, such a relatively large MS value associated with the rate of P addition is to be expected. The next largest MS

Table 2.5. Analysis of variance for soils, P application rates and amendments (biosolids or triple superphosphate fertilizer) in laboratory incubations.

Source	Degrees of freedom	Sum of squares	Mean square	F-statistic†
Total	179	1685081		
Replications	2	409	204	0.61
Soil (S)	4	281562	70391	211.44
Amendment (A)‡	2	242557	121279	364.31
Rate (R)	3	764542	254847	765.53
S x A	8	59262	7408	22.25
S x R	12	95273	7939	23.85
A x R	6	156896	26149	78.55
S x A x R	24	45298	1887	5.67
Error	118	39283	333	

† $P < 0.0001$ for all results.

‡ Amendment = biosolids or triple superphosphate.

value is associated with the amendments themselves (biosolids or fertilizer) and is nearly twice that of the lowest MS value which is associated with soil. Aside from the obvious and expected effect of P application rate, the amendments exerted a greater influence on the resulting STP than did soils in this incubation experiment.

The availability of P derived from triple superphosphate (TSP) fertilizer over the course of the incubation was roughly twice that of biosolids P (Table 2.6). While some variation is exhibited across soils and rates of P addition, the average

Table 2.6. Effect of biosolids and triple superphosphate (TSP) application on anion exchange resin-extractable P (AER-P) in laboratory incubations.

Amendment	Rate	Soil					Average
		Jimbo (15)	Natroy (12)	Deschutes (4)	Dayton (9)	Concord (2)	
mg kg ⁻¹							
Eugene biosolids	0	1(0)†	6(1.1)	11(0.7)	37(0.4)	2(0.1)	11(0.5)
Eugene biosolids	300	8(0.7)	50(1.9)	40(1.9)	72(3.2)	54(3.3)	45(2.2)
Eugene biosolids	600	27(6)	95(7.5)	53(1)	105(5.1)	88(4.5)	74(4.8)
Eugene biosolids	900	45(8.8)	138(4.7)	80(4.9)	178(4.7)	136(29)	115(10)
Rock Cr. Biosolids	0	1(0.1)	6(1.1)	11(0.7)	37(0.4)	2(0.1)	11(0.5)
Rock Cr. Biosolids	300	16(1.4)	68(3.9)	44(1.8)	93(2.3)	65(4.6)	57(2.8)
Rock Cr. Biosolids	600	52(6.8)	130(21)	74(2.8)	174(13)	101(1.8)	106(9)
Rock Cr. Biosolids	900	78(12)	152(5.1)	123(12)	206(4.9)	181(39)	148(15)
TSP	0	1(0.1)	6(1.1)	11(0.7)	37(0.4)	2(0.1)	11(0.5)
TSP	300	17(2.3)	88(4.5)	82(11)	161(2.7)	95(3.8)	89(4.9)
TSP	600	45(8.1)	236(19)	190(10)	297(6.7)	218(1.7)	197(9.3)
TSP	900	59(9.5)	351(5.7)	306(41)	404(12)	333(13)	291(16)
Average	0	1(0.1)	6(1.1)	11(0.7)	37(0.4)	2(0.1)	11(0.5)
Average	300	14(1.5)	69(3.4)	55(4.9)	109(2.7)	71(3.9)	63(3.3)
Average	600	41(7)	154(16)	106(4.7)	192(8.2)	136(2.6)	126(7.7)
Average	900	61(10)	214(5.2)	170(19)	263(7.3)	217(27)	185(14)
% of TSP‡							
Eugene biosolids	300	41(7.3)	54(4.1)	40(7)	28(2.6)	56(4.2)	44(5)
Eugene biosolids	600	60(18)	39(4.7)	23(1.5)	26(2.1)	40(2.1)	38(5.6)
Eugene biosolids	900	76(20)	38(1.5)	23(3.6)	38(1.8)	40(8.8)	43(7.1)
Rock Cr. Biosolids	300	90(16)	76(6.6)	47(8)	45(2.1)	68(5.6)	65(7.6)
Rock Cr. Biosolids	600	117(27)	54(10)	35(2.6)	52(5.2)	46(0.9)	61(9.1)
Rock Cr. Biosolids	900	133(30)	42(1.7)	38(6.7)	46(2)	54(12)	63(11)
Average	300	65(11)	65(5.3)	44(7.5)	36(2.4)	62(4.9)	54(6.3)
Average	600	89(22)	46(7.4)	29(2.1)	39(3.6)	43(1.5)	49(7.4)
Average	900	104(25)	40(1.6)	31(5.2)	42(1.9)	47(10)	53(8.8)

† SE of mean (n=3)

‡ Determined as follows: $(STP_{(rate\ x)} - STP_{(rate\ 0)}) / [STP_{(TSP, rate\ x)} - STP_{(TSP, rate\ 0)}] * 100$

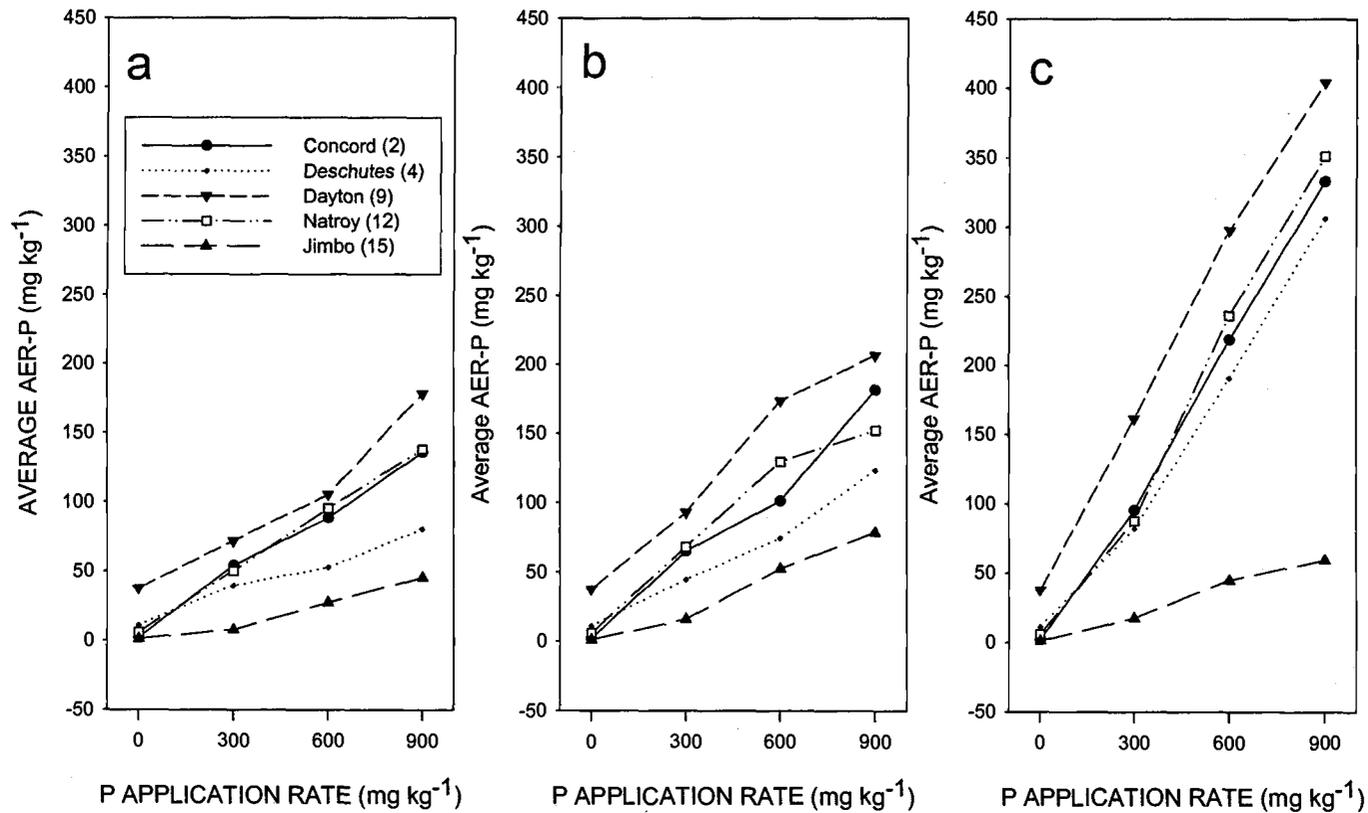


Figure 2.9. Soil anion exchange resin-extractable P (AER-P) for laboratory incubations plotted as a function of P application rate for: (a) Eugene biosolids; (b) Rock Creek biosolids; and (c) triple superphosphate fertilizer. Linear regression analysis results for this data are presented in Table 7. Numbers in parentheses following soil names correspond to sites in Table 2.

availability of biosolids P across all comparisons is 52% (SE: 13%) of that for TSP-derived P. This finding is of particular significance with regard to the western Oregon P index which currently weights P inputs from fertilizer and organic sources equally. Consequently, the current western Oregon P index overestimates the short-term, relative risk posed by biosolids P as compared to fertilizer P. However, results for longer-term (e.g., months or years) equilibration of amended soils may differ.

An exception to the trend of higher P availability for biosolids relative to TSP occurred with the Jimbo soil which had similar STP values across amendments (Figure 2.9). A likely explanation is that the Jimbo soil has andic properties (Table 2.3) and a P sorption capacity—as measured by $(Al_{ox}+Fe_{ox})$ —from 3 to 8 times higher than the other soils (Table 2.1). Such a high P sorption capacity appears to mitigate the effects of the varying P availabilities among amendments. This finding is consistent with that of Elliott et al. (2002), who noted that soils of even moderate P sorption capacity can mitigate differences in P availability among biosolids.

While the very high P sorption capacity of the Jimbo soil may explain the similar AER-P of biosolids and TSP when added to this particular soil, the soil PSI and its components did not exhibit any such predictive utility across soils. None of the components of the PSI (Table 2.1), either alone or in combination, consistently predicted relative STP results following the addition of P to soil, regardless of the form in which the P was added (biosolids or fertilizer). Linear regression analysis

Table 2.7. Linear regression analysis for anion exchange resin-extractable P as a function of P application rate ($y = a*x$; data presented in Figure 2.9).

Soil†	Amendment	Slope	r^2 ‡
Jimbo (15)	Eugene biosolids	0.05	0.75
Jimbo (15)	TSP§	0.07	0.84
Deschutes (4)	Eugene biosolids	0.07	0.95
Jimbo (15)	Rock Creek biosolids	0.09	0.85
Deschutes (4)	Rock Creek biosolids	0.12	0.94
Concord (2)	Eugene biosolids	0.15	0.82
Natroy (12)	Eugene biosolids	0.15	0.99
Dayton (9)	Eugene biosolids	0.15	0.92
Natroy (12)	Rock Creek biosolids	0.17	0.88
Concord (2)	Rock Creek biosolids	0.19	0.81
Dayton (9)	Rock Creek biosolids	0.20	0.95
Deschutes (4)	TSP	0.33	0.90
Concord (2)	TSP	0.37	0.99
Natroy (12)	TSP	0.39	0.96
Dayton (9)	TSP	0.41	0.99

† Numbers in parentheses correspond to sites in Table 3.

‡ All p-values <0.0001 except for Jimbo soil with Eugene biosolids, for which $p = 0.0002$.

§ TSP = triple superphosphate fertilizer.

was used to compare STP results across treatments (Table 2.7). Prior to such analysis, background STP results for each of the soils—corresponding to the zero P application rate—were subtracted from all results to normalize the regression analyses to a y-intercept of zero. Thus treatments can be compared directly via the slopes of their respective regression lines. For each of the soil amendments individually, STP results across soils generally increase in the same manner: Jimbo (low STP), Deschutes, Concord, Natroy, Dayton (high STP). The only exception to this trend is that STP results for Rock Creek biosolids added to the Concord and

Natroly soils are reversed (Table 2.7). Neither soil Al_{ox} , Fe_{ox} , $(Al_{ox}+Fe_{ox})$ or PSI accurately predicted these trends.

Summary and Conclusions

The acid ammonium oxalate extraction, anion exchange resin extraction, Bray 1 extraction, and dilute salt extraction detected similar changes in soil test P associated with land application of biosolids. Each of these tests measures the different pools of soil P to differing degrees, thus such a finding suggests that biosolids P is redistributed among the various pools of soil P following biosolids application in proportions similar to those occurring in the soil prior to biosolids application. The effects of tillage and the time elapsed between biosolids application and soil sampling are confounded by the various site management practices encountered in this survey-based study. Neither cumulative P loading rates or the soil P sorption index (PSI) correlated with changes in soil P availability associated with biosolids applications. The narrow range of PSI values exhibited by soils in this study was too low to adequately evaluate the effect of PSI on soil P availability. Any regulatory scheme used to limit excessive P loss resulting from the land application of biosolids must make use of some form of direct soil P measurement.

The correlation between soluble P and soil test P diminishes with the ability of the soil test to measure additional pools of soil P beyond soluble P. In a comparison of the correlation between several soil P tests and dilute salt-extractable

P, anion exchange resin extraction exhibited the highest correlation, followed by the Bray 1 extraction and finally the acid ammonium oxalate extraction. As such, anion exchange resin extraction would provide an improved measure of the risk of soluble P loss following land application of biosolids relative to Bray P. However, the deeply entrenched use of Bray P for agronomic purposes represents a major obstacle to its replacement in the western Oregon P index.

The controlled environment of laboratory incubations demonstrated that the availability of P derived from triple superphosphate fertilizer is approximately twice that of biosolids-derived P following a 28 d incubation period. This provided justification for the use of separate weighting factors for biosolids and fertilizer P sources in the western Oregon P index which currently weights these P sources equally with regard to their relative risk of enhancing offsite movement of dissolved P. However, results for longer-term (e.g., months or years) equilibration of amended soils may differ.

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BIOSOLIDS PHOSPHORUS AVAILABILITY

Abstract

Quantifying labile phosphorus (P) pools in biosolids is needed to manage biosolids for both agronomic and environmental purposes, a task which may be suited to the P sorption index (PSI). The PSI is defined as the molar ratio of $P/(Al+Fe)*100$ as determined by acid ammonium oxalate extraction. The objective of this study was to evaluate the PSI as: (1) an indicator of water-soluble P in biosolids; and (2) an indicator of labile P in soil following biosolids application. Thirty biosolids samples were collected from 22 municipal wastewater treatment facilities and analyzed via oxalate extraction, dilute salt extraction (0.01 M $CaCl_2$), and total acid digestion. At PSI values less than 65 to 85%, soluble P in biosolids was less than 175 mg kg^{-1} . At PSI values of 85 to 212%, soluble P ranged from 25 to 6065 mg kg^{-1} . Similar results were obtained for soluble P as determined by both colorimetric and ICP-AES analysis. Biosolids PSI values determined by total acid digestion provided a satisfactory proxy for those obtained via oxalate extraction. Woodburn silt loam soil from two field locations was amended with biosolids or triple superphosphate fertilizer at P rates of 0, 300, 600 and 900 mg kg^{-1} and analyzed for anion exchange resin-extractable P following a 28 d incubation. Relative P availability for six biosolids sources was 12 to 54% in comparison with P fertilizer and increased linearly with biosolids PSI values between 44 and 168%

($r^2=0.99$, $p<0.0001$). Biosolids PSI is a useful index for assessment of water-soluble P in biosolids and short-term P availability following biosolids addition to soil.

Introduction

Municipal wastewater treatment residuals, also known as biosolids, are often applied to agricultural land as a means of utilization. As with other organic soil amendments, biosolids application rates are typically determined according to the nitrogen (N) content of the biosolids and the N requirement of the crop to which the biosolids will be applied. Such N-based management generally results in the over-application of P (Maguire et al., 2000a; Penn and Sims, 2002). Wastewater treatment processes and biosolids dewatering methods currently in use by municipalities produce biosolids with a range of chemical and physical characteristics. The availability of P following land application of biosolids is related to biosolids chemistry.

A potential measure of biosolids P availability is the P sorption index [PSI; defined as the molar ratio of $P/(Al+Fe)*100$ as measured by acid ammonium oxalate extraction]. The threat of soluble P loss following application of biosolids to soils with low P sorption capacities is correlated with the PSI of the biosolids (Elliott et al., 2002a), although these authors note that soils of even moderate sorption capacity may mitigate differences among biosolids.

Phosphorus indices are field-scale screening tools used by conservation planners (e.g., Natural Resource Conservation Service staff) to assess the relative risk of offsite P movement from agricultural fields. This task is accomplished via site-specific, line-item accounting of the factors controlling P mobility in the environment (Lemunyon and Gilbert, 1993). The western Oregon P index does not currently distinguish among P sources in its assessment of the potential risk of offsite P movement (USDA-NRCS, 2001). However, previous work demonstrates that differences in P availability exist between biosolids and commercial P fertilizers (Chapter 2; Elliott et al., 2002).

The objectives of this study were to evaluate the PSI as: (1) an indicator of water soluble P in biosolids; and (2) an indicator of labile P in soil following biosolids application.

Materials and Methods

Biosolids P availability

Two sets of biosolids were utilized in this study (Table 3.1). One set was collected from Oregon agencies cooperating in the current study and consisted of 13 samples collected during the summer of 2001. The other set remained after a previous regional nitrogen study and consisted of 17 biosolids samples collected in 1998 and 1999 (Cogger et al., 2003; Gilmour et al., 2003). Samples obtained for the current study were selected to represent a wide range of treatment processes and

Table 3.1. Characterization data for 30 biosolids.

Sample ID	Year Collected	Facility	Facility Abbreviation	Treatment Process	Process Category	Total Solids	P _{ox}	Al _{ox}	Fe _{ox}	PSI	P _{ox}	CaCl ₂ -P†	CaCl ₂ -P‡	LECO C	pH
						%	mmol kg ⁻¹	mmol kg ⁻¹	mmol kg ⁻¹	%	g kg ⁻¹	mg kg ⁻¹	mg kg ⁻¹	%	
1	2001	Albany	Al	anaerobic, dewatered	cake	14	632	516	179	91	16.7	25	108	34	6.9
2§	2001	Bend	Be	anaerobic, drying bed	drying bed	91	767	379	78	168	25.5	1167	947	33	7.0
3	2001	Clackamas, Kellogg	Ke	anaerobic, liquid	liquid	3	885	544	157	126	27.6	1964	1990	34	7.1
4	2001	Clackamas, Tri-Cities	TC	anaerobic, liquid	liquid	2	1046	519	143	158	33.5	4312	5030	33	7.0
5§	2001	Durham w/ alum	D+	anaerobic, dewatered, alum added	cake	23	1016	1038	303	76	33.0	248	355	29	7.0
6§	2001	Rock Creek w/ alum	R+	anaerobic, dewatered, alum added	cake	25	998	1309	256	64	32.2	25	72	30	6.8
7	2001	Durham w/o alum	D-	anaerobic, dewatered	cake	22	961	838	231	90	28.7	476	419	35	6.8
8§	2001	Rock Creek w/o alum	R-	anaerobic, dewatered	cake	24	760	627	205	91	26.0	723	1186	30	6.7
9	2001	Eugene	Eu	lagoon, drying bed	lagoon	18	831	510	191	119	27.8	716	1040	30	6.9
10	2001	Gresham	Gr	anaerobic, dewatered	cake	16	829	457	123	143	27.1	1410	1102	30	7.0
11	2001	Portland	P1	anaerobic, 1*/2* mix, dewatered	cake	16	767	339	231	134	21.3	1258	1034	29	6.9
12	2001	Salem	Sa	anaerobic, liquid	liquid	2	817	266	119	212	23.5	6065	5638	33	7.0
13	2001	Stayton	Y1	anaerobic, dewatered, lime-stabilized	lime	24	283	131	20	186	15.6	BDL¶	271	28	12.4
14	1998	Stayton	Y2	anaerobic, dewatered, lime-stabilized	lime	42	120	81	17	123	9.1	BDL	149	25	12.3
15	1998	Chelan	Ch	anaerobic, drying bed	drying bed	96	605	584	128	85	21.7	314	329	32	6.0
16	1998	Entiat	En	oxidation ditch, clarifier, air-dried	drying bed	69	708	547	105	109	23.2	878	790	30	6.8
17	1998	USA	U	anaerobic, belt press	cake	17	708	633	209	84	24.2	667	662	27	6.6
18§	1998	Everett	V1	lagoon, dewatered	lagoon	31	240	336	205	44	9.2	BDL	5	27	5.9
19	1998	Tacoma	Ta	aerobic/anaerobic thermophilic, belt press	cake	25	1113	1388	262	67	35.0	46	82	33	6.7
20	1998	Ellensburg	EI	anaerobic, drying bed	drying bed	94	708	221	337	127	22.7	576	480	28	6.5
21	1998	Baltimore	B1	anaerobic, heat dried	heat	97	658	272	766	63	7.6	BDL	58	31	6.3
22	1999	Portland	P2	anaerobic, 1*/2* mix, dewatered	cake	17	594	291	180	126	23.5	3703	1640	30	6.2
23§	1999	Renton	Re	anaerobic, dewatered	cake	19	889	408	278	130	33.1	2124	1246	33	6.2
24	1999	Stayton	Y3	anaerobic, belt press, lime-stabilized	lime	21	191	101	19	159	13.2	BDL	287	31	12.2
25	1999	Everett	V2	lagoon, dewatered	lagoon	30	285	374	243	46	7.9	10	14	29	5.3
26	1999	Bingen	Bi	aerobic, centrifuge, drying bed	drying bed	19	589	507	113	95	20.6	521	597	34	6.3
27	1999	California	Ca	anaerobic, lagoon	lagoon	75	484	194	328	93	7.1	214	200	10	6.8
28	1999	Iona	Io	anaerobic, lagoon	lagoon	31	192	132	185	61	9.1	142	76	22	5.5
29	1999	Milorganite	Mi	anaerobic, heat dried	heat	97	380	226	955	32	3.1	BDL	172	36	5.3
30	1999	Baltimore	B2	anaerobic, heat dried	heat	96	702	288	815	64	8.6	11	116	32	5.8

† 0.01 M CaCl₂-extractable P, determined colorimetrically.

‡ 0.01 M CaCl₂-extractable P, determined via ICP-AES.

§ These biosolids were used in incubations.

¶ Below detection limit (detection limit: 10 mg kg⁻¹).

to represent biosolids generated in the Willamette Valley region of Oregon.

Biosolids sampling procedures were unique to each wastewater treatment facility. However, all samples were collected at the end of the treatment process when biosolids were in the same form as is applied to agricultural fields. All samples were oven-dried at 65°C and ground with a mechanical grinder to pass a 2 mm (No. 10) sieve. A suite of analyses (described below) was then performed, including acid ammonium oxalate extraction, dilute salt extraction, total acid digestion, total C, pH and percent total solids.

Acid ammonium oxalate extraction

The extractant was prepared by mixing 0.2 M ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, and 0.2 M oxalic acid, $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, in proportions resulting in a solution pH of 3.0 (Ross and Wang, 1993). Ten milliliters of this extractant was then added to 0.13 g of biosolids in a 50 mL HDPE centrifuge tube and shaken for 4 h at a speed of approximately 120 cycles min^{-1} . Samples were then centrifuged at 510 x g and the supernatant was analyzed for Al, Fe and P via ICP-AES (Optima 3000 DV, PerkinElmer, Wellesley, MA). Samples remained in an enclosed, opaque box during the 4 h extraction to exclude light that could react with the extractant.

Dilute salt-extractable P

Two grams of biosolids were extracted with 20 mL of 0.01 M CaCl_2 in a 60 mL HDPE screw-top bottle for one hour on a reciprocating shaker at a speed of approximately $120 \text{ cycles min}^{-1}$. Samples were filtered through Whatman No. 42 filter paper. Biosolids extracts were analyzed colorimetrically via the Murphy-Riley molybdenum blue method (Pierzynski, 2000) on a spectrophotometer (Model 8453, Hewlett-Packard, Palo Alto, CA) integrating absorbance from 840-880 nm. For comparison, biosolids extracts also were analyzed via ICP-AES (Optima 3000 DV, PerkinElmer, Wellesley, MA).

Total acid digestion

Total Al, Fe and P in biosolids were determined using a modified version of EPA Method 3051 (USEPA, 1994). The modification consisted of utilizing 2 mL of concentrated HNO_3 and 2 mL of 30% H_2O_2 rather than 10 mL of HNO_3 for digestion. Preliminary analyses showed low P recovery with the standard EPA Method 3051. Biosolids P recovery increased by approximately 40% with the modified extraction solution. All other parameters are as stated in the original method. Digests were analyzed for Al, Ca, Fe, Mg, Mn and P via ICP-AES.

Total C

Biosolids samples weighing 0.2 g were analyzed for total C. Total C was measured with a LECO C-144 carbon analyzer (LECO Corporation, St. Joseph, MI).

pH

Biosolids pH was determined using 0.01 M CaCl₂ in a 2:1 liquid:sample ratio. Forty milliliters of 0.01 M CaCl₂ was added to 20 g samples of biosolids and stirred thoroughly. After 15 minutes, samples were stirred a second time and allowed to stand an additional 15 minutes, after which the pH was measured with a digital ion analyzer (Model 501, Thermo Orion, Beverly, MA) by inserting the electrode into the supernatant.

Physical characterizations

Biosolids total solids were determined from the difference between fresh and dry weights. Biosolids were oven-dried at a temperature of 65°C.

Laboratory incubation

Materials

Laboratory incubations were performed using selected amendments from this study and soils from a related study (Chapter 2). The P sorption index (PSI),

defined as the molar ratio of $P/(Al+Fe)*100$ as determined by acid ammonium oxalate extraction, was used to characterize soil P sorption capacity and ranged from 0.4 to 15.4% for available soils (Chapter 2). Soils used in incubations exhibited PSI values of 10.3 and 13.6%. Amendments included 6 biosolids and a fertilizer control, triple superphosphate [$10 Ca(H_2PO_4)_2 \cdot H_2O$; 0-45-0, Voluntary Purchasing Groups, Inc., Bonham, TX].

Table 3.2. Chemical characterization data for soils used in laboratory incubations.

Site	Soil Series	Soil Taxonomic Class	Soil Texture	Percent Sand %	Percent Clay %	Organic C %	pH	PSI† %
A	Woodburn	Fine-silty, mixed, superactive, mesic Aquultic Argixerolls	silt loam	15	25	2.0	4.4	10.3
B	Woodburn	Fine-silty, mixed, superactive, mesic Aquultic Argixerolls	silt loam	5	28	1.7	4.6	13.6

† P sorption index, defined as the molar ratio of $P/(Al+Fe)*100$ as determined by acid ammonium oxalate extraction.

Experimental design

The experimental design was a 7 x 4 x 2 amendment x rate x soil factorial. Physicochemical characterization data for the two soils, hereafter referred to as soils A and B, are presented in Table 3.2. Biosolids amendments are designated by source facility and in some cases by treatment process as well: Bend, Durham with alum, Everett, Renton, Rock Creek with alum, and Rock Creek without alum (Table 3.1). From approximately May to October, the Durham and Rock Creek facilities use alum, $Al_2(SO_4)_3$, for P removal (w/ alum), whereas alum is not added during the remainder of the year (w/o alum). Amendments included these six

biosolids and triple superphosphate fertilizer each applied at rates of: 0, 300, 600 or 900 mg P per kg soil. Treatments were replicated 3 times.

Sample preparation and analysis

Incubations were initiated by adding dried, ground amendments to 200 g of air-dried soil in a Ziploc™ bag. Samples were thoroughly mixed and moisture added to achieve a gravimetric moisture content of 200 g kg⁻¹. Samples were again mixed to evenly distribute the water and break up any aggregates that formed as a result of the addition of water to the amended soil. Ziploc™ bags were arranged one layer deep in plastic storage containers and placed in an incubation chamber held at 25°C for 28 d. Bags remained open at the top to assure aerobic conditions during the incubation, although the tops were folded over to avoid significant moisture loss. After 28 d, 2 g samples were analyzed for P via anion exchange resin extraction as described below.

An incubation period of 28 d was chosen based upon the results of preliminary incubations. Preliminary incubation results showed that anion exchange resin-extractable P rapidly decreased for several days following the addition of biosolids and began to stabilize after approximately five days (Appendix 2). An incubation period of 28 d was chosen to assure sufficient time for equilibration of P between soils and amendments.

Anion exchange resin extraction

Anion exchange resin sheets (204-U-386, Ionics, Watertown, MA), with a capacity of approximately $0.02 \text{ cmol}_c \text{ cm}^{-2}$ (Cooperband and Logan, 1994), were cut into 1 cm^2 pieces and saturated with 1 M NaHCO_3 through 3 successive 10 min intervals with fresh NaHCO_3 . Resin squares were rinsed with deionized water, and 1 square was used with 20 mL of deionized water in a 60 mL HDPE screw-cap bottle to extract 2 g of soil. Samples were shaken for 16 h on a reciprocating shaker at a speed of approximately $120 \text{ cycles min}^{-1}$. Resins were then rinsed with deionized water, transferred to clean 60 mL bottles and extracted with 1 M HCl for 4 h on a reciprocating shaker at the same speed. The HCl extracts were analyzed for P colorimetrically as described previously. Pierzynski (2000) calls for multiple extractions of the resins with HCl prior to analysis, but previous work in our laboratory showed that over 99% of P adsorbed by the resin was recovered during the first extraction (Moore, 2001). Resin squares were reused multiple times by recharging with NaHCO_3 between uses as described previously.

Results and Discussion

Biosolids P availability

Biosolids sources were selected to include a wide variety of treatment processes and to span a wide range of P sorption index (PSI) values. This study utilized a total of 30 biosolids samples from 22 municipal wastewater treatment

facilities, and PSI values for these biosolids ranged from 32 to 213% (Table 3.1). The combination of treatment processes and dewatering methods varied considerably among facilities (Table 3.1). Biosolids were assigned to one of six general categories that qualitatively describe dominant traits of each treatment process and dewatering method combination. These categories include dewatered cake, drying beds, heat-drying, lagoon storage, lime-stabilization, and liquid. The lagoon classification was given precedence over dewatering methods with which it was associated. Lagoon storage and heat drying produced biosolids with lower soluble P concentrations than other treatment processes, while liquid biosolids far exceeded dewatered biosolids in soluble P content (Figure 3.1). This relatively high P content for liquid biosolids is likely related to soluble P removal from biosolids via the dewatering process.

The western Oregon P index (USDA-NRCS, 2001) currently assesses only the rate of P application, not the source of P, with respect to the relative risk to contribute labile P to surface waters following land application. All organic and inorganic P sources have the same risk in this P index. Given the variability of soluble P contents associated with the numerous biosolids treatment processes and dewatering methods encountered in this study, the western Oregon P index would be improved by accounting for differences in soluble P content among organic P inputs. Such an approach has been utilized in the development of the Pennsylvania

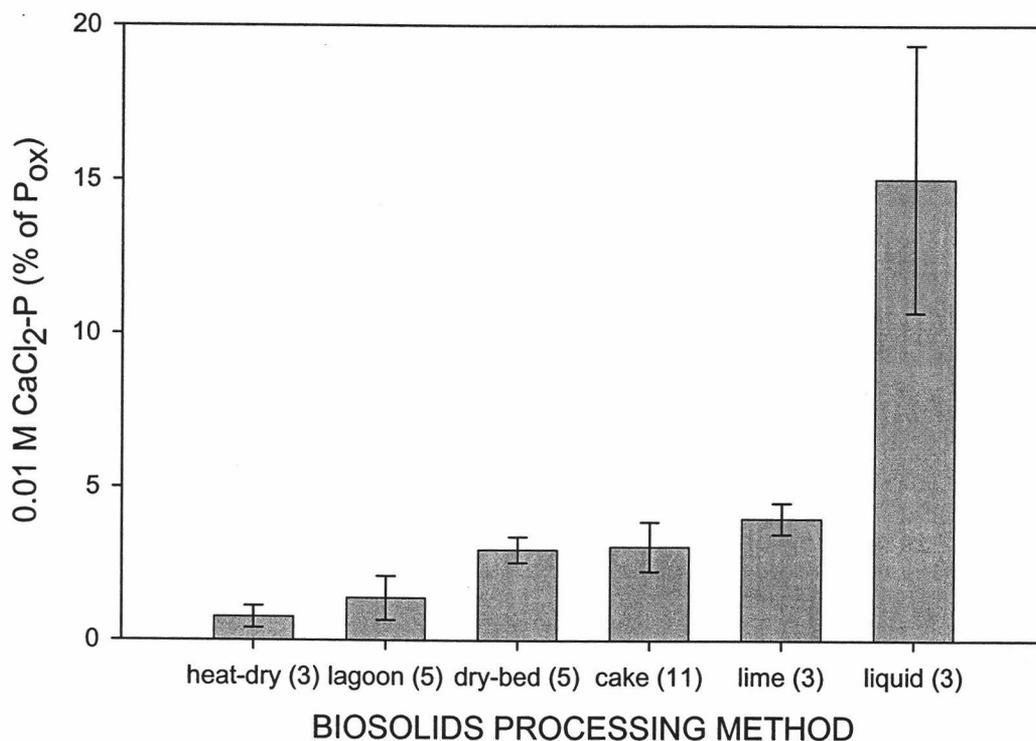


Figure 3.1. Average 0.01 M CaCl₂-P, expressed as a percent of P_{ox}, for six general biosolids processing methods.

P index which currently differentiates among 7 manure types and 6 biosolids treatment processes (Weld and Beegle, 2003). When soluble P is plotted as a function of PSI for biosolids, a change point is exhibited below which soluble P remains nearly constant with increasing PSI and above which soluble P values increase sharply with increasing PSI (Figure 3.2). This change point occurs somewhere in the range of PSI values from 65 to 85% (Figure 3.2). Split-line models have been used to identify the exact PSI value where such a change point

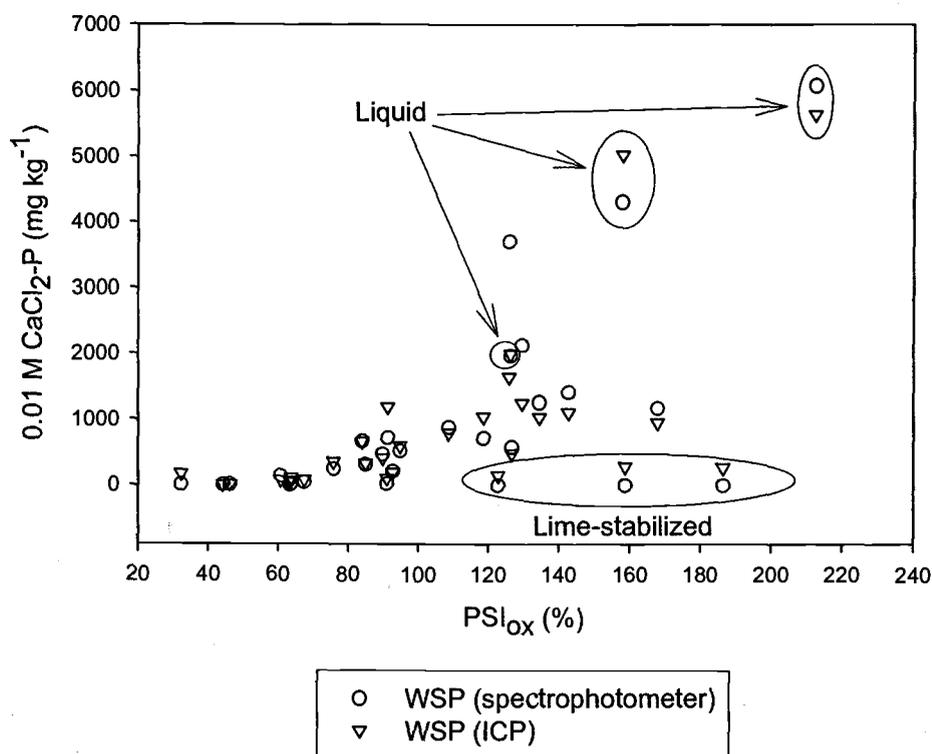


Figure 3.2. Biosolids 0.01 M CaCl₂-P, as determined colorimetrically and via ICP-AES, plotted as a function of the biosolids P sorption index (PSI).

occurs (Maguire and Sims, 2002a). In the current study, however, sparse data corresponding to PSI values in the vicinity of the change point do not justify the use of such a technique. Theoretically, the change point would occur near a PSI value of 100%, as this value represents a stoichiometric balance between P and the sum of Al and Fe (Jenkins and Horwath, 2001). In a study of the leaching of P from biosolids-amended, sandy soils, Elliott et al. (2002) note that no appreciable leaching occurred for biosolids with PSI values less than approximately 110%.

In the plot of soluble P versus PSI discussed above (Figure 3.2), two groups of biosolids are identified: lime-stabilized biosolids and liquid biosolids. Lime-

stabilized biosolids consistently exhibited low soluble P and high PSI values, both of which are a result of the addition of lime during treatment. The calcium content of lime-stabilized biosolids ranged from 11.8 to 15.0%, whereas the calcium content for all other biosolids ranged from 1.1 to 3.3%. Calcium in the lime effectively binds P in insoluble forms while the lime simultaneously dilutes the Al and Fe content of the biosolids. Thus soluble P content is reduced while the PSI is increased. In contrast to lime-stabilized biosolids, liquid biosolids consistently exhibit high soluble P contents in addition to high PSI values (Figure 3.2). The high PSI values associated with liquid biosolids are likely due to the fact that these biosolids are not dewatered. Dewatering often involves the addition of iron-containing salts that would reduce PSI.

Results of colorimetric P determinations have recently been reported to be generally lower than for samples analyzed by ICP-AES (Maguire and Sims, 2002a). In the present study, biosolids soluble P was measured using dilute salt extraction with 0.01 M CaCl_2 and analyzed both colorimetrically and by ICP-AES. Neither test method produced results that were consistently higher or lower than the other, and the disparity between test methods was generally small (Figure 3.2). Conclusions based upon one method of analysis would not differ from those based upon the other method of analysis for most biosolids in this study.

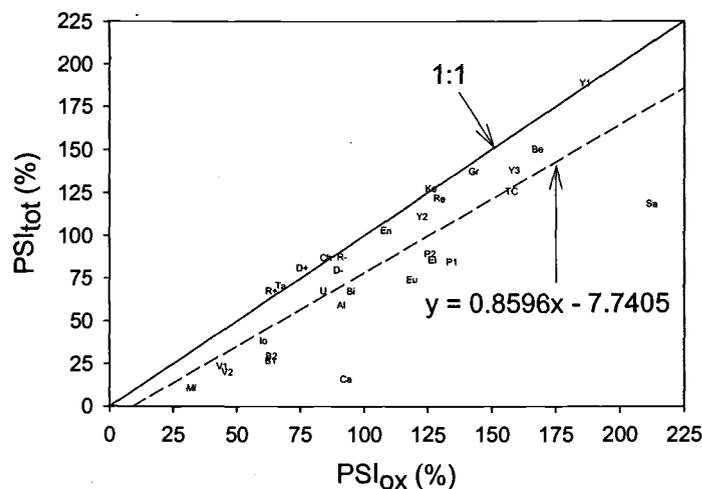


Figure 3.3. Biosolids P sorption index as determined via total acid digestion (PSI_{tot}) plotted as a function of the PSI as determined via acid ammonium oxalate extraction (PSI_{ox}). Symbols correspond to facility abbreviations in Table 3.2.

The acid ammonium oxalate extraction is not a routine analysis for many laboratories, so the utility of the PSI as a predictor of biosolids P availability is contingent upon additional testing beyond that typically performed. However, a PSI based upon biosolids total Al, Fe and P (PSI_{tot}) may provide a suitable proxy for that based upon oxalate Al, Fe and P (PSI_{ox}). A comparison of these two methods of calculating biosolids PSIs reveals that PSI_{ox} values were generally higher than PSI_{tot} (Figure 3.3). Linear regression of PSI_{tot} on PSI_{ox} results in a coefficient of determination (r^2) value of 0.73 ($p < 0.0001$), indicating that the PSI_{tot} provides a reasonable proxy for PSI_{ox} for the biosolids in this study. Two outliers exhibit noticeably higher PSI_{ox} values relative to PSI_{tot} (Figure 3.3). However, these outliers correspond to different treatment processes and appear to be unique

among their respective treatment process categories with regard to their relatively high PSI_{ox} values.

A comparison between total acid digestion and oxalate extraction for the individual components of the PSI provides additional insights beyond comparison of the PSIs alone. Both tests proved equally successful at measuring biosolids P, but the total acid digestion measured higher amounts of both Al and Fe thus resulting in the lower PSI_{tot} values observed in Figure 3.3 (Figure 3.4). Heat-dried biosolids, however, exhibited relatively high P_{ox} and Fe_{ox} values, the combined result of which is similar PSI_{tot} and PSI_{ox} values (B1, B2, Mi; Figure 3.4a,c). In contrast, lagoon-stabilized biosolids exhibited relatively high Al_{tot} values (C2, Eu, V1, V2; Figure 3.4b). Overall, PSI_{tot} provided a satisfactory qualitative assessment of PSI_{ox} for the biosolids in this study.

Laboratory incubation

Laboratory incubations were performed to compare the availability of P derived from biosolids with that of triple superphosphate (TSP) fertilizer. Biosolids used in incubations were chosen to include both a wide variety of treatment processes and to span a wide range of P sorption index values. The six biosolids used in incubations spanned a range of PSI values from 44 to 168% and included biosolids from four distinct treatment processes (Table 3.1). Biosolids P ranged from 12 to 54% as available as the P from TSP across all soils with a mean of 30% and a standard error of 5% (results averaged across rates of P addition,

Table 3.3. Analysis of variance for soils, P application rates and amendments (biosolids or triple superphosphate fertilizer) in laboratory incubations.

Source	Degrees of freedom	Sum of squares	Mean square	F-statistic	P-value
Total	167	940268			
Replications	2	5672	2836	10.46	<0.0001
Soil (S)	1	14376	14376	53.01	<0.0001
Rate (R)	3	330535	110178	406.29	<0.0001
S x R	3	3524	1175	4.33	0.0063
Amendment (A)†	6	328726	54788	202.04	<0.0001
S x A	6	879	146	0.54	0.7767
R x A	18	224578	12477	46.01	<0.0001
S x R x A	18	2147	119	0.44	0.9757
Error	110	29830	271		

† Amendment = biosolids or triple superphosphate fertilizer.

n=3). An analysis of variance of the anion exchange resin-extractable P (AER-P) results for laboratory incubations reveals that the three-way interaction between soils, rates and amendments was not significant [Table 3.3; averaged source data (n=3) presented in Table 3.4]. However, two two-way interactions were significant: soil x rate and rate x amendment (Table 3.3). Two-way tables of means for these interactions are presented in Tables 3.5 and 3.6, respectively.

Anion exchange resin-extractable P increased with P application rate on both soils, although the magnitude of the increase differed between soils (Table 3.5). Given the similarity of the soils used in this study with respect to physicochemical characteristics (Table 3.2), the interaction between P application

Table 3.4. Effect of biosolids and triple superphosphate (TSP) application on anion exchange resin-extractable P (AER-P) in laboratory incubations.

Soil ID	Rate	Bend	Source					TSP	Average
			Rock Creek with alum	Rock Creek without alum	Durham with alum	Everett	Renton		
mg kg ⁻¹									
7	0	34(3)†	34(2.8)	34(2.8)	34(2.8)	34(2.8)	34(2.8)	34(2.8)	34(2.8)
7	300	86(7.3)	54(2.5)	61(2.1)	55(3.7)	49(5.6)	70(6.3)	116(10)	70(5.4)
7	600	143(24)	66(5.4)	88(14)	82(5.3)	51(4.1)	118(17)	265(15)	116(12)
7	900	177(10)	68(5.1)	97(12)	91(8.6)	49(4.9)	170(7.4)	350(10)	143(8.3)
1	0	11(0.4)	11(0.4)	11(0.4)	11(0.4)	11(0.4)	11(0.4)	11(0.4)	11(0.4)
1	300	63(7.3)	30(0.6)	48(5.2)	41(4.5)	28(3)	56(4.8)	97(3.7)	52(4.2)
1	600	120(22)	47(4.9)	63(4.4)	54(3.8)	36(6.2)	89(13)	199(30)	87(12)
1	900	180(16)	62(8.3)	102(5.7)	78(5)	44(6.2)	167(30)	341(25)	139(14)
Avg	0	22(1.6)	22(1.6)	22(1.6)	22(1.6)	22(1.6)	22(1.6)	22(1.6)	22(1.6)
Avg	300	74(7.3)	42(1.5)	55(3.7)	48(4.1)	38(4.3)	63(5.5)	107(7)	61(4.8)
Avg	600	131(23)	56(5.2)	76(9.1)	68(4.6)	44(5.2)	104(15)	232(23)	101(12)
Avg	900	179(13)	65(6.7)	100(8.7)	85(6.8)	46(5.5)	168(19)	346(18)	141(11)
% of TSP‡									
7	300	63(12)	24(5.5)	33(6)	25(6.5)	18(7.9)	44(10)		35(8.1)
7	600	47(11)	14(2.8)	24(6.3)	21(3)	8(2.2)	37(7.7)		25(5.5)
7	900	45(3.7)	11(1.9)	20(3.9)	18(2.9)	5(1.8)	43(2.9)		24(2.8)
1	300	60(9)	22(1.3)	43(6.4)	34(5.5)	19(3.6)	52(6)		38(5.3)
1	600	58(15)	19(4)	28(5)	23(4.1)	13(3.9)	41(9.7)		30(6.9)
1	900	51(6.2)	15(2.8)	27(2.7)	20(2.2)	10(2)	47(9.7)		28(4.3)
Avg	300	62(11)	23(3.4)	38(6.2)	30(6)	19(5.8)	48(8)		36(6.7)
Avg	600	53(13)	16(3.4)	26(5.7)	22(3.5)	10(3.1)	39(8.7)		28(6.2)
Avg	900	48(4.9)	13(2.3)	24(3.3)	19(2.5)	7(1.9)	45(6.3)		26(3.6)

† SE of mean (n=3)

‡ Determined as follows: $(STP_{(rate\ x)} - STP_{(rate\ 0)}) / [STP_{(TSP, rate\ x)} - STP_{(TSP, rate\ 0)}] * 100$

Table 3.5. Two-way table of means for Soil x Rate interaction in laboratory incubations.

Soil	Rate (mg kg ⁻¹)			
	0	300	600	900
	mg kg ⁻¹			
A	34†	155	260	417
B	101	210	348	430

† SE = 4

Table 3.6. Two-way table of means for Rate x Amendment interaction in laboratory incubations.

Rate	Bend	Amendment					
		Rock Creek with alum	Rock Creek without alum	Durham with alum	Everett	Renton	TSP
		mg kg ⁻¹					
0	67†	67	67	67	67	67	67
300	223	143	115	164	128	188	320
600	394	204	131	227	168	311	696
900	536	254	139	299	195	504	1038

† SE = 7

rate and soil type would almost certainly be more pronounced for soils with a greater variability of physicochemical characteristics. Had such soils been used in this incubation, a three-way soil x rate x amendment interaction would likely also have been significant.

Anion exchange resin-extractable P increased with P application rate for all amendments, although the magnitude of increase varied among amendments (Table

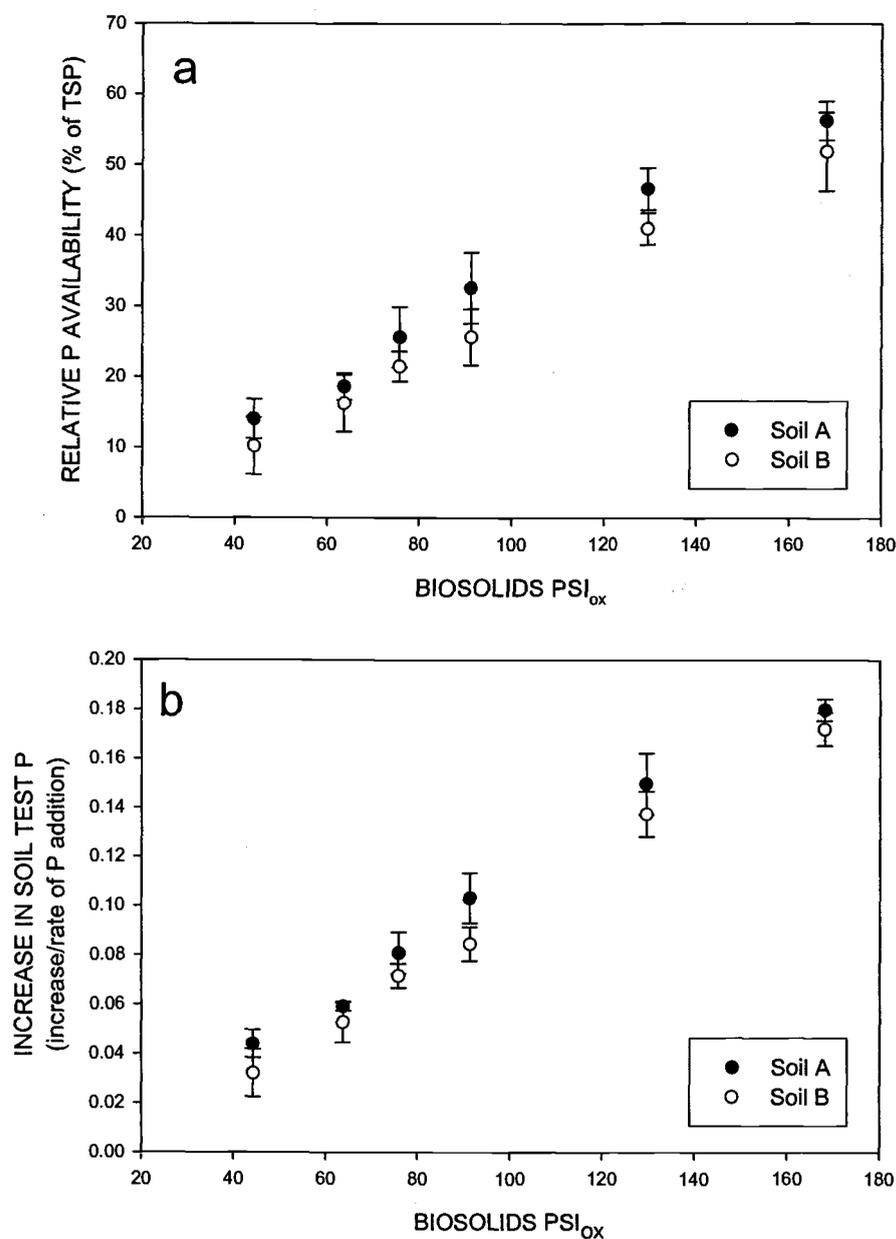


Figure 3.5. Anion exchange resin-extractable P (AER-P) for laboratory incubations plotted as a function of biosolids P sorption index (PSI) with: (a) the AER-P of biosolids-amended soils expressed as a percentage of that for triple superphosphate-amended soils; and (b) AER-P of biosolids-amended soils expressed as the net increase in AER-P per unit addition of P.

3.6). The largest increases in AER-P observed in this incubation experiment were consistently associated with TSP fertilizer across all P application rates (Table 3.6). When AER-P values are expressed as a percentage of those obtained for TSP, the relative availability of biosolids P is directly proportional to and strongly correlated with biosolids PSI (Figure 3.5a; results averaged across all P application rates, $n=3$). Linear regression analysis of these data results in coefficients of determination (r^2) of 0.987 and 0.997 for soils A and B, respectively ($p<0.0001$ for both soils). Thus the biosolids PSI was an excellent predictor of relative P availability for the materials and conditions used in this study. This relationship also was apparent when the increase in STP per unit of P added was plotted as a function of biosolids PSI (Figure 3.5b).

Summary and Conclusions

For the 30 biosolids sampled in this study from 22 municipal wastewater treatment facilities, soluble P, as measured by dilute salt extraction with 0.01 M CaCl_2 , varied significantly among treatment processes. The lowest soluble P contents were associated with lagoon-stored and heat-dried biosolids, and liquid biosolids contained significantly more soluble P than dewatered biosolids. The western Oregon P index could be improved by accounting for such differences in P availability among P sources. When soluble P was plotted as a function of P sorption index (PSI) for the biosolids sampled in this study, a change point occurred in the range of PSI values from 65 to 85%. Similar results were obtained

for soluble P determinations by both colorimetric and ICP-AES analysis.

Determination of the PSI through total acid digestion provided a suitable proxy for that obtained via acid ammonium oxalate extraction ($r^2=0.73$, $p<0.0001$).

Laboratories that currently measure total P via ICP-AES could easily include Al and Fe in analyses and thereby eliminate the need to perform an oxalate extraction for the purpose of calculating PSI values.

Biosolids P availability, as measured by anion exchange resin-extraction, ranged from 12 to 54% of that for triple superphosphate fertilizer following laboratory incubations with selected biosolids and soils. When anion exchange resin P for biosolids-amended soils is expressed as a percentage of that for fertilizer-amended soils, an excellent correlation with biosolids PSI is observed ($r^2=0.99$, $p<0.0001$). Similar results were obtained when the increase in STP per unit of P added was plotted as a function of biosolids PSI. Thus biosolids PSI was a successful predictor of the short-term (28 d), relative availability of biosolids P for the materials and conditions used in this study. Results for longer-term (e.g., months or years) equilibration of amended soils may differ.

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CONCLUSION

The acid ammonium oxalate extraction, anion exchange resin (AER) extraction, Bray 1 extraction, and dilute salt extraction detected similar changes in soil test P associated with land application of biosolids. Each of these tests measures the different pools of soil P to differing degrees, thus such a finding suggests that biosolids P is redistributed among the various pools of soil P following biosolids application in proportions similar to those occurring in the soil prior to biosolids application. Neither cumulative P loading rates nor the soil P sorption index (PSI) correlated with changes in soil P availability associated with biosolids applications. The narrow range of PSI values exhibited by soils in this study was too low to adequately evaluate the effect of PSI on soil P availability. Any regulatory scheme used to limit excessive P loss resulting from the land application of biosolids must make use of some form of direct soil P measurement.

The correlation between soluble P and soil test P diminishes with the ability of the soil test to measure additional pools of soil P beyond soluble P. In a comparison of the correlation between several soil P tests and dilute salt-extractable P, anion exchange resin extraction exhibited the highest correlation, followed by the Bray 1 extraction and finally the acid ammonium oxalate extraction. As such, anion exchange resin extraction would provide an improved measure of the risk of soluble P loss following land application of biosolids relative to Bray P.

For 30 biosolids sampled from 22 municipal wastewater treatment facilities, soluble P, as measured by dilute salt extraction with 0.01 M CaCl_2 , varied

significantly among treatment processes. The lowest soluble P contents were associated with lagoon-stored and heat-dried biosolids, and liquid biosolids contained significantly more soluble P than did dewatered biosolids. The western Oregon P index could be improved by accounting for such differences in P availability among P sources. When soluble P was plotted as a function of PSI for the biosolids sampled in this study, a change point occurred in the range of PSI values from 65 to 85%. Similar results were obtained for soluble P determinations by both colorimetric and ICP-AES analysis. Determination of the PSI through total acid digestion provided a suitable proxy for that obtained by acid ammonium oxalate extraction ($r^2=0.73$, $p<0.0001$).

Biosolids P availability, as measured by AER extraction, ranged from 12 to 54% of that for triple superphosphate fertilizer following 28 d laboratory incubations with selected biosolids and soils. When anion exchange resin P for biosolids-amended soil is expressed as a percentage of that for fertilizer-amended soil, an excellent correlation with biosolids PSI is observed ($r^2=0.99$, $p<0.0001$). Thus biosolids PSI was a successful predictor of the short-term (28 d), relative availability of biosolids P for the materials and conditions used in this study. Results for longer-term (e.g., months or years) equilibration of amended soils may differ.

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APPENDIX

Table 1. Soil characterization data for 0-5 cm sampling depth.

Facility	Biosolids:		no	yes	no	yes	no	yes	no	yes	no	yes	no	yes	no	yes	no	yes	no	yes	no	yes	no	yes			
	Field ID	AER-P																							AER-P	Bray P	Bray P
														mg kg ⁻¹													
														mmol kg ⁻¹										%			
Albany	1	42	53	45	62	1.4	1.9	719	759	2160	2120	6560	6520	23	25	80	79	117	117	11.8	12.6	4.2	4.4	4.3	4.4		
Albany	2	15	49	18	60	0.4	1.1	231	759	1115	1640	4962	6480	7	25	41	61	89	116	5.7	13.9	2.5	3.5	4.0	4.1		
Bend	3	66	68	103	109	9.9	7.5	384	653	1000	1346	5385	5846	12	21	37	50	96	105	9.3	13.7	1.7	2.2	5.6	5.6		
Bend	4	51	62	59	79	4.8	8.2	400	807	1320	1577	6480	5654	13	26	49	58	116	101	7.8	16.3	3.6	5.3	5.6	5.4		
Clackamas	5	48	54	77	140	1.1	1.4	919	1166	5240	5500	5320	4875	30	38	194	204	95	87	10.3	12.9	6.5	6.6	4.4	4.3		
Clackamas	6	16	30	59	67	0.5	0.5	520	679	6920	6560	4400	4000	17	22	256	243	79	72	5.0	7.0	5.5	4.3	4.4	4.5		
CWS	7	57	66	76	166	1.6	2.6	807	1307	1923	2577	5731	5808	26	42	71	96	103	104	15.0	21.2	1.9	2.4	4.6	4.3		
CWS	8	52	52	89	87	2.1	1.3	719	799	2520	2720	4880	4840	23	26	93	101	87	87	12.9	13.8	2.7	2.7	4.3	4.4		
CWS	9	42	51	67	86	1.7	2.3	679	624	1560	1542	4200	4167	22	20	58	57	75	75	16.5	15.3	1.8	1.7	4.3	4.4		
Eugene	10	25	55	15	60	0.7	1.7	461	1191	1962	2423	10808	10000	15	38	73	90	194	179	5.6	14.3	3.5	3.3	4.4	4.6		
Eugene	11	18	46	16	49	0.7	1.0	346	1199	2577	2440	10000	13200	11	39	96	90	179	236	4.1	11.9	5.6	6.9	4.7	4.3		
Eugene	12	14	26	9	25	0.5	0.7	154	307	2000	2423	10577	10500	5	10	74	90	189	188	1.9	3.6	3.2	4.0	5.0	4.3		
Eugene	13	18	47	13	40	0.5	0.8	269	653	1769	2077	9769	10462	9	21	66	77	175	187	3.6	8.0	3.7	3.0	4.5	4.1		
Eugene	14	64	42	37	17	4.4	2.0	599	360	1880	2480	8640	9600	19	12	70	92	155	172	8.6	4.4	11.9	11.4	4.8	4.8		
Gresham	15	10	22	22	58	0.4	0.8	919	1499	16840	17923	4640	4769	30	48	624	664	83	85	4.2	6.5	11.6	11.5	4.8	4.4		
Gresham	16	5	32	16	63	0.2	0.6	346	1124	8385	11833	4577	5125	11	36	311	439	82	92	2.8	6.8	7.9	8.8	4.9	4.6		
Salem	17	23	77	40	87	0.4	1.3	769	1307	6308	6423	5538	6269	25	42	234	238	99	112	7.5	12.1	5.0	7.2	5.8	4.1		
Salem	18	69	95	67	98	2.9	3.9	999	1159	1731	2160	7000	6880	32	37	64	80	125	123	17.0	18.4	2.0	2.1	4.8	4.1		
Salem	19	39	56	49	59	0.7	1.0	961	999	2538	2667	7654	7625	31	32	94	99	137	137	13.4	13.7	2.0	2.2	4.6	4.4		
Stayton	20	27	72	38	79	1.0	5.5	440	1624	4120	5083	5720	3667	14	52	153	188	102	66	5.6	20.7	4.5	6.5	5.3	7.0		

Table 2. Soil characterization data for 0-30 cm sampling depth.

Facility	Field ID	Biosolids:		no Bray P	yes Bray P	no CaCl ₂ -P	yes CaCl ₂ -P	mg kg ⁻¹				mmol kg ⁻¹				%									
		no AER-P	yes AER-P					P _{ox}	P _{ox}	Al _{ox}	Al _{ox}	Fe _{ox}	Fe _{ox}	P _{ox}	P _{ox}	Al _{ox}	Al _{ox}	Fe _{ox}	Fe _{ox}	PSI	PSI	C _{tot}	C _{tot}	pH	pH
Albany	1	33	27	39	35	0.7	0.5	599	520	2240	2000	5840	5520	19	17	83	74	105	99	10.3	9.7	2.0	1.6	4.4	4.5
Albany	2	5	35	10	50	0.3	1.1	115	423	1154	1577	3962	5577	4	14	43	58	71	100	3.3	8.6	1.1	1.9	4.3	4.1
Bend	3	35	41	57	49	3.1	2.2	280	307	1040	1115	5800	5269	9	10	39	41	104	94	6.3	7.3	1.2	1.0	5.3	5.6
Bend	4	10	11	13	14	0.5	0.6	200	269	1280	1308	5600	5231	6	9	47	48	100	94	4.4	6.1	1.0	1.1	5.6	5.6
Clackamas	5	9	7	23	23	0.2	0.3	333	320	5500	5120	4667	4320	11	10	204	190	84	77	3.7	3.9	3.7	3.6	4.7	4.6
Clackamas	6	12	9	42	31	0.2	0.2	461	346	7192	6115	4423	4192	15	11	267	227	79	75	4.3	3.7	3.7	2.8	4.4	4.4
CWS	7	50	58	65	95	1.3	1.8	759	1039	1880	2520	6160	6160	25	34	70	93	110	110	13.6	16.5	1.7	2.1	4.6	4.4
CWS	8	27	38	52	76	0.6	1.2	461	576	2308	2462	4923	4731	15	19	86	91	88	85	8.6	10.6	2.3	2.3	4.5	4.5
CWS	9	37	52	52	66	1.3	2.0	440	520	1240	1440	4440	4720	14	17	46	53	80	85	11.3	12.2	1.4	1.4	4.4	4.5
Eugene	10	15	56	9	49	0.4	1.4	307	884	1692	2115	9038	9846	10	29	63	78	162	176	4.4	11.2	2.5	2.8	4.6	4.8
Eugene	11	11	19	11	14	0.4	0.4	240	280	2600	2000	9120	10080	8	9	96	74	163	180	3.0	3.6	2.7	2.3	4.7	4.6
Eugene	12	7	9	4	6	0.2	0.3	38	77	3038	2192	9615	10000	1	2	113	81	172	179	0.4	1.0	2.3	2.4	4.8	4.6
Eugene	13	10	15	8	11	0.4	0.3	192	200	1923	2160	8923	8600	6	6	71	80	160	154	2.7	2.8	2.9	2.1	4.4	4.1
Eugene	14	9	6	4	3	0.3	0.2	38	42	1962	2083	6038	7708	1	1	73	77	108	138	0.7	0.6	2.1	2.2	5.2	5.3
Gresham	15	1	1	3	7	0.1	0.2	759	583	23640	19167	4680	4708	25	19	876	710	84	84	2.6	2.4	6.9	6.4	5.0	4.8
Gresham	16	1	6	1	25	0.1	0.2	192	480	9538	10720	4846	5240	6	15	354	397	87	94	1.4	3.2	5.3	5.8	5.0	4.9
Salem	17	12	12	25	22	0.4	0.2	560	653	5760	7385	5320	6231	18	21	213	274	95	112	5.9	5.5	3.9	4.2	5.4	4.5
Salem	18	52	60	58	71	1.7	1.4	839	884	1640	1962	6440	5923	27	29	61	73	115	106	15.4	16.0	1.5	1.7	5.1	4.6
Salem	19	38	52	47	62	0.5	0.8	833	1039	2333	2840	7500	8280	27	34	86	105	134	148	12.2	13.2	1.9	2.1	4.5	4.4
Stayton	20	10	30	19	56	0.4	0.6	231	320	3692	4480	5846	3040	7	10	137	166	105	54	3.1	4.7	2.3	3.0	5.1	6.2

Table 3. Biosolids characterization data.

Sample ID	Facility	AER-P	P _{tot}	Al _{tot}	Fe _{tot}	PSI _{tot}	P _{ox}	Al _{ox}	Fe _{ox}	PSI _{ox}	CaCl ₂ -P†	CaCl ₂ -P‡	C _{tot}	pH
		mg kg ⁻¹	mmol kg ⁻¹			%	mmol kg ⁻¹			%	mg kg ⁻¹		%	
1	Albany	13	538	688	215	60	632	516	179	91	25	108	34	6.9
2§	Bend	224	824	444	106	150	767	379	78	168	1167	947	33	7.0
3	Clackamas, Kellogg	320	891	554	146	127	885	544	157	126	1964	1990	34	7.1
4	Clackamas, Tri-Cities	301	1080	669	190	126	1046	519	143	158	4312	5030	33	7.0
5§	Durham with alum	48	1066	1023	290	81	1016	1038	303	76	248	355	29	7.0
6§	Rock Cr. with alum	16	1041	1283	260	67	998	1309	256	64	25	72	30	6.8
7	Durham without alum	223	925	905	250	80	961	838	231	90	476	419	35	6.8
8§	Rock Cr. without alum	207	839	721	236	88	760	627	205	91	723	1186	30	6.7
9	Eugene	223	898	934	275	74	831	510	191	119	716	1040	30	6.9
10	Gresham	251	875	513	124	137	829	457	123	143	1410	1102	30	7.0
11	Portland	159	688	568	245	85	767	339	231	134	1258	1034	29	6.9
12	Salem	463	759	477	164	118	817	266	119	212	6065	5638	33	7.0
13	Stayton	3	505	230	38	189	283	131	20	186	BDL¶	271	28	12.4
14	Stayton1	3	293	218	45	111	120	81	17	123	BDL	149	25	12.3
15	Chelan1	172	702	657	150	87	605	584	128	85	314	329	32	6.0
16	Entiat1	242	750	599	129	103	708	547	105	109	878	790	30	6.8
17	USA1	51	782	855	303	68	708	633	209	84	667	662	27	6.6
18§	Everett1	4	297	881	381	24	240	336	205	44	BDL	5	27	5.9
19	Tacoma1	18	1129	1336	262	71	1113	1388	262	67	46	82	33	6.7
20	Ellensburg1	47	733	463	393	86	708	221	337	127	576	480	28	6.5
21	Baltimore1	6	244	527	387	27	658	272	766	63	BDL	58	31	6.3
22	Portland2	290	759	556	295	89	594	291	180	126	3703	1640	30	6.2
23§	Renton2	392	1068	555	323	122	889	408	278	130	2124	1246	33	6.2
24	Stayton2	3	426	260	48	138	191	101	19	159	BDL	287	31	12.2
25	Everett2	2	255	932	326	20	285	374	243	46	10	14	29	5.3
26	Bingen2	262	664	778	206	68	589	507	113	95	521	597	34	6.3
27	California2	25	228	1076	332	16	484	194	328	93	214	200	10	6.8
28	Iona2	13	292	452	307	39	192	132	185	61	142	76	22	5.5
29	Milorganite2	10	100	297	622	11	380	226	955	32	BDL	172	36	5.3
30	Baltimore2	4	279	523	426	29	702	288	815	64	11	116	32	5.8

† 0.01 M CaCl₂-extractable P, determined colorimetrically.

‡ 0.01 M CaCl₂-extractable P, determined via ICP-AES.

§ These biosolids were used in incubations.

¶ Below detection limit (detection limit: 10 mg kg⁻¹).