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**The Mobility and Fate of Phosphorus Following  
Municipal Biosolids Application to Forest Soils**

by

**Mark Alan Grey**

**A dissertation submitted in partial fulfillment  
of the requirements for the degree of**

**Doctor of Philosophy**

**University of Washington**

**1999**

**College of Forest Resources**

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## Doctoral Dissertation

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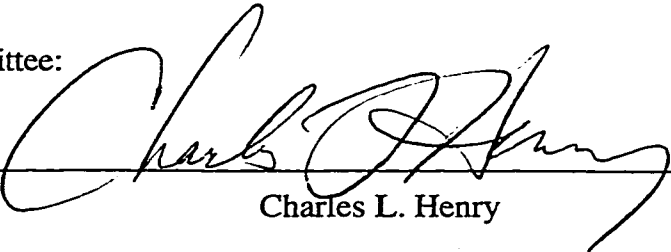
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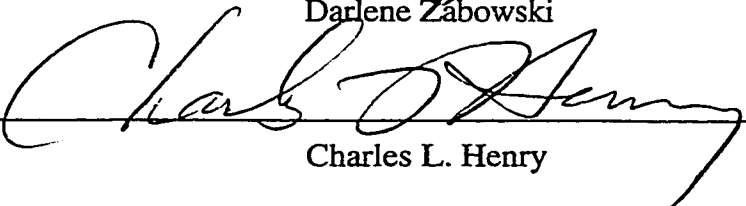
Chair of Supervisory Committee:

  
\_\_\_\_\_  
Charles L. Henry

Reading Committee:

  
\_\_\_\_\_  
Robert B. Harrison

  
\_\_\_\_\_  
Darlene Zabowski

  
\_\_\_\_\_  
Charles L. Henry

Date:

6/8/99

University of Washington

Abstract

THE MOBILITY AND FATE OF PHOSPHORUS FOLLOWING  
MUNICIPAL BIOSOLIDS APPLICATION TO FOREST SOILS

By Mark Alan Grey

Chairperson of the Supervisory Committee:  
Assistant Professor Charles L. Henry  
College of Forest Resources

Municipal biosolids are typically not used on the steepest of forested slopes in the Pacific Northwest. The primary issue in using biosolids on steep slopes is movement of constituents in biosolids to surface waters during runoff events. There is a particular concern with biosolids phosphorus (P), as this nutrient limits productivity of most fresh surface water systems in western Washington. Application rates are based on the release of nitrogen from biosolids, without consideration of the cumulative effect of repeated applications on soil P levels. This dissertation examines P mobility following biosolids application to forested slopes on two scales: whole watershed and small plot. It also examines the vertical mobility and fate of P following biosolids fertilization to two different forest soils that received heavy experimental and lesser application rates using surface application to the forest floor or direct soil incorporation. A small creek draining a 21 ha watershed was monitored for P forms before and after biosolids application to 40% of the watershed. Direct runoff from biosolids into surface water did not occur. Elevated surface water discharge generally did not change the concentration of any P form, with no effect from biosolids. Soil water interflow was suspected as a conduit for direct runoff of P from biosolids to surface waters during heavy rainfall events. Sampling interflow showed that phosphate concentrations decline with horizon depth and, when detected, phosphate concentrations decrease with increasing discharge regardless of biosolids application. A sequential P fractionation approach was used to identify operationally defined P fractions

following biosolids application to acidic forest soils representing two contrasting soil types. There is P retention in the soil following surface application of biosolids; no statistically significant differences in mean P fraction concentrations between treated and control soils were noted below 15 cm. The dominant mechanism for retention of surface applied biosolids P was adsorption to Aluminum (Al) and Fe oxides and amorphous Al silicates and Al humates where volcanic ash was present. P availability was significantly increased in all biosolids treated soils examined between 0-15 cm using application rates between 105 and 470 Mg ha<sup>-1</sup> (2-10 Mg P ha<sup>-1</sup>).

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## CHAPTER I

### INTRODUCTION

Research has clearly shown that applying biosolids to forested sites in the Pacific Northwest (PNW) increases the growth of Douglas-fir, especially on low site index stands (Henry et al., 1993). The reason for such a dramatic growth response is the fertilizing effect of biosolids, namely its capacity to supply nitrogen (N) and other plant essential macro and micro nutrients. Because of this evidence there is interest in using biosolids to fertilize steeply sloped areas in managed forests as well as in site reclamation and ecological restoration efforts. Much of the interest is derived from the Mountains to Sound Greenway program. The Greenway program focuses on land acquisition as well as forest restoration and steep slope stability efforts in the forested, mountainous corridor between Seattle and Snoqualmie Pass, Washington. Biosolids are being used to fertilize managed stands within the Greenway and composted biosolids are a key component of road decommissioning and steep slope stabilization projects.

Pure biosolids without composting are typically not applied to steep slopes due to concerns about direct runoff of biosolids or constituents in biosolids to receiving waters. Applying biosolids to steep, forested sites has prompted many questions such as the effect of biosolids application on water quality downstream of an application site. Specifically, potential phosphorus (P) losses from treated watersheds are a concern due to widespread evidence showing that non-point sources of P entering surface waters often cause eutrophication (Schindler, 1977).

Water quality in forest streams may be degraded in several ways and by many different sources, such as natural erosional processes as well as resource extraction, i.e.

logging and mining, road building, and other human activities. If biosolids are applied to a site without regard for proximity to streams or drainage channels, it may adversely affect stream water chemistry and stream productivity by increasing the concentration of nutrient elements, most likely P or N, or by increasing biological oxygen demand. These negative effects may harm living organisms within the stream and could trigger changes in stream biological community structure and function.

Phosphorus mobility following fertilization with organic wastes has been well documented in agricultural settings. It regularly occurs and factors such as total P loading, rainfall intensity, soil characteristics, and cropping strategies are cited as important variables influencing P mobility (Khaleel et al., 1980). Unfortunately, while some of these relationships may also hold for forested ecosystems in the PNW, their overall importance in forested settings has not been established. In forested ecosystems, nutrient export can be accelerated by heavy rainfall. Heavy and prolonged rainfall induces widespread transport of ions through the soil and mobilizes particulate matter in runoff waters. Biosolids add high concentrations of nutrient elements to the forest floor in both soluble and particulate forms. This introduction of potentially mobile constituents may, therefore, change the amount and pattern of export for many different elements including P and N.

Thus, an important consideration in assessing the potential effect of biosolids on receiving water quality is establishing the relationship between biosolids application and vertical and lateral mobility of P. These pathways are poorly understood for biosolids applications, as the primary focus in forest applications is typically nitrogen management and protection of ground water quality by maximizing applied nitrogen. Research has clearly shown that soil water interflow through micro and macro pores is a pathway for surface water flow generation and ion movement from soil water to surface waters (Wilson

et al., 1991; Jardine et al., 1990; Luxmoore et al., 1990). Interflow is defined as rainfall that infiltrates into the soil and moves laterally through the upper soil horizons until intercepted by a stream channel or until it returns to the surface at some point downslope from its point of infiltration (SSSA, 1997).

The vertical mobility and fate of P applied in biosolids to Douglas-fir forests has never been fully documented. This is especially important considering that Douglas-fir plantations receive repeated biosolids applications throughout stand development, and application rates are based primarily on nitrogen demand and utilization within the site. The most useful guidance comes from studies done following heavy experimental biosolids application to glacially derived outwash soils at Pack Forest, Washington. Reikerk (1978) found limited influence of surface applied or incorporated biosolids on soil solution total P concentrations directly below the zone of application and no differences between control and treated soils below the A horizon (approximately 10 cm). Phosphate adsorption onto iron oxides was suggested as the primary retention mechanism limiting mobility. Working in similar glacial outwash soils, Harrison et al., (1994) showed that soil total P concentrations in biosolids treated soils were not significantly different than controls below 25 cm; specific P forms in either biosolids-treated or control soils were not determined.

This dissertation examines the mobility and fate of P following biosolids application to Douglas-fir forests. Emphasis was placed on measuring the mobility of P under heavy rainfall conditions which are conducive to widespread surface and subsurface runoff within forested watersheds in the PNW. The movement of P was measured using experiments conducted on two different spatial scales: a whole watershed and small plots. The watershed study documented the influence of changing stream discharge conditions on the mobility of P before and after a single biosolids application. The plot-scale investigation

sought to measure the movement of phosphate in soil water interflow and identify the extent of vertical P mobility following a single biosolids application. Finally, field soil sampling was used to identify predominant P retention mechanisms and the vertical mobility and fate of P added to two different forest soils that had received biosolids at rates ranging between 105 and 470 Mg ha<sup>-1</sup> (2-10 Mg P ha<sup>-1</sup>).

## CHAPTER II

## STUDY OBJECTIVES AND HYPOTHESES TESTED

The objective of this research was to examine the mobility and fate of P following biosolids application to Douglas-fir forests. The mobile nature of nitrogen (N) following biosolids application to PNW forests has been demonstrated repeatedly. For this reason, N was also included in this work for contrast with P, which is thought to be strongly retained in acidic, PNW forest soils. Three distinct studies are included in this work, as described in Chapter IV: Runoff of Phosphorus and Nitrogen from a Steep, Forested Watershed Fertilized with Biosolids; Chapter V: Mobility and Fate of Phosphorus following Biosolids Application to a Forested Slope; Chapter VI: Vertical Mobility and Fate of Phosphorus Applied to Two Forest Soils.

### 2.1 Objectives

Watershed and plot scale studies were performed to establish the mobility of P and N following a single application of biosolids to steep slope areas (Chapters IV and V, respectively). Field soil sampling and subsequent laboratory chemical analyses established the vertical mobility and fate of P in soils receiving surface applications of biosolids at a cumulative loading of 105 Mg ha<sup>-1</sup> (~2 Mg P ha<sup>-1</sup>), or heavy experimental biosolids applications ranging between 190 and 470 Mg ha<sup>-1</sup> (~4-10 Mg P ha<sup>-1</sup>) (Chapter VI). The study objectives were to:

1. Establish if surface water runoff or lateral soil-water flow (interflow) are pathways of P and N movement from a biosolids application site located on steep terrain.

2. Determine if runoff events can induce movement of P and N in biosolids via either surface runoff or soil interflow on slopes greater than 30%.
3. Examine the pattern of P mobility vertically in the soil profile following one-time (15 Mg ha<sup>-1</sup>), repeated (105 Mg ha<sup>-1</sup>), and heavy (>190 Mg ha<sup>-1</sup>) biosolids applications.
4. Establish the dominant forms of P in biosolids and in several Puget Sound forest soils by fractionation.
5. Identify the primary mechanisms responsible for retention of P by forest soils under contrasting biosolids application methods and rates.

## 2.2 Basis for examining P mobility on a watershed and plot scale

Intuitively, the critical time to assess whether or not constituents in biosolids will move from a particular site is during periods of prolonged rainfall, preferably when soil moisture is elevated due to frequent rain. Such conditions are ideal for producing high rates of surface water discharge. High discharge events can release some elements from the soil and dislodge organic debris and move them into runoff water. Biosolids contains high concentrations of P and N in both soluble and particulate form while runoff waters are relatively low in comparison. If P and N movement from biosolids treated areas occurs, then stream water concentrations could change and changes may be related to discharge.

In many instances, interflow through forest soil is a major contributor to surface water runoff and storm flow generation. Water contacting a biosolids application site may move to surface waters via this pathway, especially on sloping terrain and where impermeable layers exist in the soil that encourage interflow. However, the vertical and

lateral mobility of phosphate-P in interflow following biosolids application is restricted by the affinity of the phosphate ion for mineral sorption, precipitation reactions with metal cations, and by biotic uptake. Thus, it was expected that phosphate-P concentrations would decline with depth of soil horizon sampling and with increasing interflow discharge.

### 2.3 Hypotheses tested

Anaerobically digested biosolids contains a relatively high concentration of water soluble P, which can be as high as 0.5% on a dry weight basis (data contained herein). Biosolids contains an additional 1 to 2.5% P that is less soluble and less likely to move far from the zone of application. In contrast, soil total P concentrations in the Puget Sound region are typically less than 0.2% (Compton and Cole, 1998; Harrison et al., 1994; Cole and Rapp, 1981). It is believed that most forest soils in the Puget Sound region have a large capacity to retain P in both inorganic and organic forms (Johnson et al. 1986). A number of different mechanisms can act at any one time to limit the vertical movement of P released from biosolids near the forest floor. Thus, the effect of biosolids in elevating the concentration of soil P fractions should decline significantly with depth of soil sampling. This pattern should hold true for both single and repeated biosolids applications. The hypotheses tested were:

Hypothesis 1. The concentration of soil P fractions will be significantly increased by a single biosolids application to a Tokul series soil. (Chapter V)

Hypothesis 2. The concentration of phosphorus in the soil following biosolids application at a P loading rate of 2 Mg ha<sup>-1</sup> will decline significantly with depth below the forest floor. (Chapter VI)

Transport of phosphate downward to ground water or streams through the soil profile via percolating rainwater is the primary pathway for P movement from surface applied biosolids. With repeated biosolids applications, an increase in available P should occur in the forest floor with the equilibrium phosphate concentration in the soil solution increased as well. Given an overall increase in P availability, it is expected that phosphate adsorption will be a dominant mechanism for the retention of P following repeated biosolids applications. Phosphate adsorption is concentration dependent, and as soil solution P concentrations increase adsorbed P should increase as well. Soil inorganic and organic phosphorus can be generally separated into “operationally defined” labile, moderately labile, and non-labile fractions using progressively stronger chemical extractants. This separation highlights important differences in P accumulation or decline among fractions and identifies dominant retention mechanisms for P applied via fertilization. The hypotheses tested were:

Hypothesis 3. Biosolids application at a P loading rate of 2 Mg ha<sup>-1</sup> will significantly increase the concentration of sorbed P fractions in the top 15 cm of mineral soil. (Chapter VI)

Hypothesis 4. Biosolids application at a P loading rate of 2 Mg ha<sup>-1</sup> will significantly increase soil P availability in the top 15 cm of mineral soil. (Chapter VI)

## CHAPTER III

### LITERATURE REVIEW

This literature review examines research into the mobility and fate of phosphorus (P) following biosolids application to forest soils and it examines some of the factors affecting its retention and release. The first section places the application of biosolids P in the context of existing P pools and fluxes in a typical Douglas-fir forest in the Pacific Northwest (PNW). This is followed by a discussion of the predominant inorganic and organic forms of P found in biosolids. Research into the mobility of biosolids P and measurement of its effect on water quality is reviewed along with a discussion of the potential pathways for transfer of soluble and particulate P from the soil to surface and ground waters. Finally, the key processes controlling P release and retention are reviewed, and research into the fate and forms of biosolids P in forest soils discussed.

#### 3.1 Introduction

Biosolids are the nutrient-rich organic residuals from primary and secondary treatment of wastewater. The effect of municipal biosolids application on the mobility and fate of phosphorus (P) in forest soils has been scarcely examined. Most of the research conducted in forestry focuses on suitability of application techniques, tree growth response, nitrogen management, trace metal mobility and fate, and effects on wildlife (Henry et al., 1994). Few peer-reviewed studies exist in the literature describing the quality of water leaving forested biosolids application sites, either via surface runoff or via subsurface flow pathways (Loch et al., 1995; Kimmins et al., 1991; Univ. of Washington, 1986). In addition, there is little information on the P forms, concentrations, and vertical mobility following single or repeated applications to forest stands, despite its widespread use in Pacific Northwest (PNW) forestry for more than 20 years.

There are several published reports on P runoff and mobility from agricultural soils amended with municipal biosolids or animal manures. Direct comparisons of runoff quality between agricultural and forest ecosystems are limited in utility, as these ecosystems differ dramatically with respect to soil properties, soil management, and vegetative cover. In addition, there is tremendous variability in nutrient forms depending on organic fertilizer source. Runoff processes and specific mechanisms affecting the release and retention of P following agricultural fertilization with biosolids are useful, however, in understanding the fate of biosolids P in forest soils.

### 3.2 Biosolids contribution to P pools and fluxes in Douglas-fir forests

Application rates for biosolids fertilization vary among soil types and stand ages in the PNW, but recent dry weight rates generally range between 11-18 Mg ha<sup>-1</sup>. These rates are based on Douglas-fir nitrogen (N) uptake and understory demands, soil N storage, and mineralization, volatilization, and denitrification transformation rates. Using N demand as the basis for fertilizing a Douglas-fir stand, a single application of biosolids can add from 300 to 450 kg ha<sup>-1</sup> of P assuming a concentration of 3.0 % total P and varying with the application rate, biosolids source, and P concentration. This is a relatively small amount compared to total soil pools (Figure 3-1). However, the amount of water soluble P applied in one application exceeds that required for tree and understory uptake assuming a water soluble P concentration of 0.5% in biosolids. Assuming stand harvest age at 50, a site could receive up to seven biosolids applications. This equals approximately 70% of the total mineral soil pool at the time of the first application using values in Figure 3.1. In some cases the P added to a site from biosolids is more than 100% greater than literature values for O horizon accumulation in PNW Douglas-fir forest soils, (Cole and Rapp, 1981; Compton, 1994).

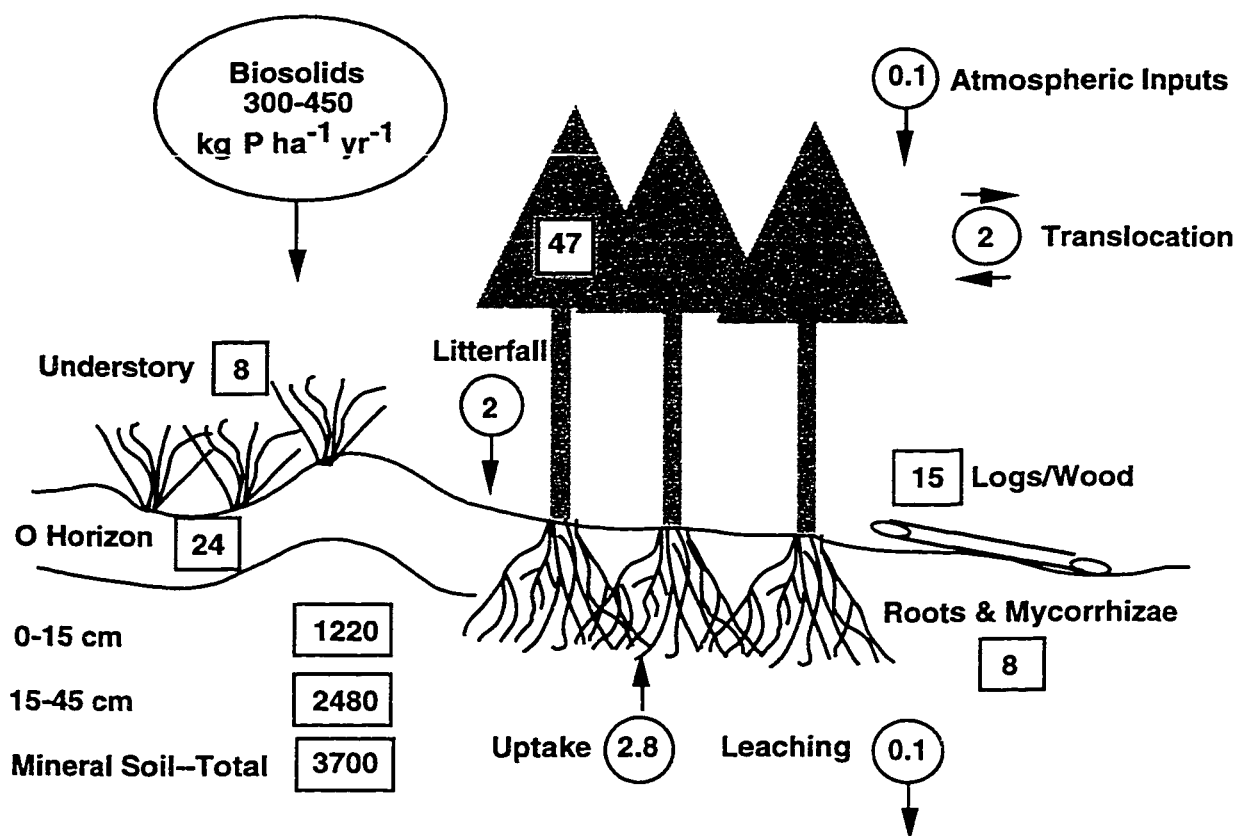


Figure 3.1. Biosolids P addition relative to 50-yr old Douglas-fir P pools and fluxes. Figure developed from data in Compton (1994) and Cole and Rapp (1981). Pools (kg ha<sup>-1</sup>) are shown in boxes, while fluxes (kg ha<sup>-1</sup> yr<sup>-1</sup>) are shown in circles.

Site history and tree species can have a marked effect on P pools and fluxes among pools irrespective of fertilizer addition. For example, Compton (1994) examined P dynamics in Douglas-fir and red alder stands and reported wide differences in total P pools between red alder and Douglas-fir, 1680 and 2440 kg ha<sup>-1</sup>, respectively. Above ground P pools were similar between stands yet pool amounts below ground differed dramatically. There was three times more total P in the red alder O horizon than in Douglas fir, but soil under the influence of Douglas fir had a 27% larger mineral soil P pool as well as a tenfold difference in the amount of P available for plant uptake (4 kg ha<sup>-1</sup> in red alder versus 44 kg

ha<sup>-1</sup> in Douglas-fir). Despite this wide difference in P availability, P uptake for red alder is nearly double that of Douglas-fir. The author hypothesized that perhaps red alder secretes chelating agents which act on the adsorbed P<sub>i</sub> fraction of the soil, depleting this pool and ultimately increasing the pool amounts of P<sub>o</sub> through increased litterfall and recalcitrance of the C forms in litter.

### 3.3 Forms of P in biosolids

Biosolids are rich in phosphorus compounds. The concentration of total phosphorus in biosolids generally ranges from 1 to 4% on a dry weight basis (Sommers, 1977; McLaughlin, 1983). The concentration of total P in biosolids can be much greater than 4%, as Sommers (1977) reported a range of 0.1—14.3%. The relative distribution of inorganic to organic P in biosolids appears to be strongly influenced by the biosolids digestion process used. Any form of digestion, because it involves the breakdown of organic material, will tend to decrease the organically bound P component of biosolids (McLaughlin (1983). In general, anaerobically digested biosolids contains primarily inorganic P while aerobically digested and waste activated biosolids contain a greater proportion of organic P.

Some of the inherent difficulties in comparing biosolids P forms and its fate in the soil can be traced to vastly different wastewater input sources, treatment processes such as the use of aluminum (Al) and iron (Fe) flocculants, and the specific wastewater solids digestion methods used. However, the characterization of biosolids phosphorus has been performed using two general techniques: chemical extractions and <sup>31</sup>P nuclear magnetic resonance (<sup>31</sup>P NMR) spectroscopy. The chemical extractions usually involve a series of progressively stronger reagents to remove labile forms of P followed by more resistant P compounds. In addition, some reagents and reagents in combination can be used to

separate P bound to certain metals including Al, calcium (Ca), and Fe. Chemical extractions are most useful to identify pools of P in organic wastes and soils.  $^{31}\text{P}$  NMR spectroscopy is a noninvasive technique for solid phase structure determination. It has been used on untreated solid phase biosolids samples and samples that have undergone prior chemical extraction. The primary emphasis with  $^{31}\text{P}$  NMR has been to characterize specific P species and identify the presence of certain P compounds such as polyphosphates and P mono- and diesters; both mineral and organic P species can be identified depending on sample handling methods.

Hinedi et al., (1989a) characterized four southern Californian biosolids using  $^{31}\text{P}$  NMR and showed that waste-activated and aerobically digested biosolids have a greater proportion of organic P than inorganic P, while the reverse is true for anaerobically digested biosolids. In all the biosolids examined, P diesters and monesters were the primary organic P compounds identified along with several phospholipids including phosphatidylcholine, phosphatidylserine, and phosphatidylethanolamine. Fine and Mingelgrin (1996) found that approximately 70% of total P in waste activated biosolids from Israel was in inorganic form and the dissolution of inorganic phosphate is the predominant source of P in solution in soils amended with waste-activated biosolids. In their study, about 40% of the total biosolids P was in readily soluble mineral forms. They suggested that N transformations such as the pH reducing nitrification process would enhance biosolids P dissolution. Hanotiaux et al., (1981) fractionated P from biosolids from four Belgium treatment plants treating urban and industrial wastewaters. Using a sequential fractionation ( $\text{NH}_4\text{Cl}$ — $\text{NH}_4\text{F}$ — $\text{NaOH}$ — $\text{H}_2\text{SO}_4$ ) procedure, the researchers found that from 15 to 35% of biosolids total P was in organic form and 65 to 85% in inorganic forms. Of the inorganic fraction, most of the P was found to be associated with

Al compounds. Chae and Tabatabai (1981) found that organic P of biosolids in Iowa ranged between 41 and 67% of total P.

Using  $^{31}\text{P}$  NMR, Hinedi et al., (1989b) found that most of the solid phase P in an anaerobically digested biosolids from Los Angeles was a calcium phosphate, while in an alum-treated biosolids from Riverside, the predominant P forms were carbonated apatite, a pyrophosphate, and an aluminum phosphate. Frossard et al., (1994) identified the mineral forms of P in three French biosolids using high resolution solid state  $^{31}\text{P}$  NMR coupled with a modified Hedley sequential extraction. Their work showed that complex P mixtures exist in biosolids, comprising a mixture of octacalcium phosphates and apatites. In an anaerobically digested, dewatered biosolids, they showed the presence of dehydrogenated condensed calcium phosphates such as fluorapatite or tricalcium phosphate. The NaOH and HCl extractable fractions were the largest source of P, with 38% of total biosolids P in the NaOH fraction and 27% in the HCl fraction. In a subsequent study, Frossard et al., (1996a) used an isotopic exchange kinetic method to determine P availability in 12 different urban biosolids and to correlate isotopically exchangeable P with chemical extractants used to estimate immediately versus slowly available P. The results showed that activated biosolids and composted biosolids made from activated biosolids had the highest quantities of exchangeable P (immediately available), while flocculated and heat treated biosolids contained low amounts of rapidly exchangeable P but large amounts of slowly available P.

The scientific literature clearly points out the difference in biosolids P forms as a result of the anaerobic or aerobic treatment process used. Where anaerobically digested biosolids are used, the dominant forms appear to be Ca and Al phosphates of varying solubility. However, where additives are used in the treatment process, such as Fe or Al flocculants, the resulting P forms tend to be associated with metal complexes of these

elements in addition to calcium phosphates. Organic P in anaerobically digested biosolids is a minor component on a mass basis and primarily consists of diesters that are easily hydrolyzed within a month of biosolids application (Hinedi et al., (1988) and monoesters and pyrophosphates that are moderately labile but persist longer in biosolids-amended soil than diesters.

### 3.4 The mobility of phosphorus following forest fertilization with biosolids

In forest fertilization, incorporation of biosolids into the soil is rarely, if ever, performed. Some restoration prescriptions do involve direct incorporation of biosolids compost into disturbed soils or decommissioned road beds, but this is not widely practiced in forests. When biosolids are applied to a young Douglas-fir stand (<20 years-old) the material covers the branches and bole as well as the forest floor; canopy and bole retention is relatively short (usually less than one year) and its movement to the forest floor is accelerated by rainfall. Under thinned, older stands (>35 years-old) almost all biosolids reaches the forest floor directly. The primary means, therefore, for constituents in biosolids to enter water bodies is the movement of rain water once it reaches the forest floor at a biosolids application site.

#### 3.4.1 Water Quality Concerns

The quality of water leaving a biosolids application site is important for several reasons. For forested sites, streams draining application areas may contribute to public drinking water supplies directly through surface water runoff and transfer into storage impoundments. Water moving vertically or laterally through the soil from an application site could potentially enter a ground water aquifer as well. If the water leaving a biosolids application site is high in some nutrients (primarily P or N), it has the potential to cause eutrophication in streams. This is the process by which a body of water becomes nutrient

rich, altering biological productivity and potentially changing the composition of living organisms through a reduction in dissolved oxygen concentration.

Springtime concentrations of inorganic and total P in natural waters exceeding 0.01 and 0.02 mg L<sup>-1</sup>, respectively, have been suggested as levels above which excessive algal growth or eutrophication is accelerated (Vollenwieder, 1968). However, according to U.S. EPA water quality criteria (USEPA, 1986), total P should not exceed 0.05 mg L<sup>-1</sup> in streams entering lakes or reservoirs to control eutrophication, while in flowing waters not discharging directly to lakes or impoundments, the concentration should not exceed 0.1 mg L<sup>-1</sup>. Correll (1998) recently prepared a review of the role of P in contributing to the eutrophication of receiving waters; the review was done in the context of agricultural runoff and its effect on receiving waters. He found that there is no widely accepted answer to the question of what concentration of P in runoff waters is acceptable. He suggested that total P concentrations of 0.1 mg L<sup>-1</sup> in all types of surface waters are unacceptably high and that concentrations as low as 0.02 mg L<sup>-1</sup> may create problems. Edmondson (1977) reported an equilibrium total P concentration of approximately 0.02 mg L<sup>-1</sup> for Lake Washington after recovery from sewage induced eutrophication.

### 3.4.2 Runoff from biosolids application sites and water quality effects

Runoff water quality research following biosolids fertilization has been limited. This is due primarily to lack of concern for water runoff from application sites. Typically, flat to moderately sloping terrain is used for biosolids application and buffers from 10 to 50 meters are used around perennial waterways or wetlands (USEPA 1995; WDOE, 1994). In addition, guidelines in Washington state suggest that biosolids application be restricted to slopes less than 30% (WDOE, 1994). However, the guidelines were first developed when liquid applications (<10% solids) to forests were common. Slope restrictions are now being questioned due to the use of dewatered biosolids (typically 20% solids) and biosolids compost for fertilization, disturbed land restoration and hillside erosion control in hydrologically active areas. Dewatered biosolids are much more adhesive than liquid biosolids when applied over the canopy or onto the forest floor, and biosolids compost is typically incorporated into disturbed soils. Yet, a common observation in runoff studies from agricultural application of biosolids or manures is the strong linear relationship between increasing application rates (increasing nutrient loadings) and nutrient concentrations in runoff waters (Harris-Pierce et al., (1995); Khaleel et al., (1980). This relationship has not been established following biosolids fertilization to forested watersheds.

No studies have examined runoff water quality on a watershed scale following application of dewatered biosolids to forested sites. Two separate studies in the PNW have examined the mobility of liquid biosolids applied to forests. The University of Washington examined water quality in two small treated and control watersheds at Pack Forest, Washington following application of liquid biosolids at a rate of 45 Mg ha<sup>-1</sup> (Univ. of Washington, 1986). Investigators used a 15 meter buffer for ephemeral streams draining each watershed and found no significant difference in organic or mineral forms of N and P

in runoff waters comparing treated and untreated watersheds. The monitoring period was approximately one year following application and included several heavy rains during wet winter months.

In a similar examination, Kimmins et al., (1991) applied liquid digested biosolids to a 3.58 ha area within the East Creek Watershed in British Columbia. An extensive network of stream monitoring was established to determine if biosolids application would affect stream water quality. Concentrations of total-N,  $\text{NO}_3^-$ -N,  $\text{NH}_3$ -N, and total and  $\text{PO}_4$ -P in East Creek and ephemeral drainages were almost equal to or below pre-biosolids application levels. Stream data included the evaluation of a 100-year storm which occurred within one month following biosolids application. Fecal coliforms detected in ephemeral drainage channels during the 100-year storm indicated that subsurface soil-water flow may be a pathway for transfer of biosolids derived constituents, as 30 meter buffers from streams were used. The researchers found, in general, that fecal coliforms did not persist beyond one month in forest soils and detection in surface water was a storm-induced phenomena owing to subsurface soil-water flow.

The study of runoff from biosolids application on a plot scale has been done in agriculture and arid rangeland settings (Harris-Pierce et al., 1995; Bruggeman and Mostaghimi, 1993; Aguilar and Loftin 1992; Dunigan and Dick, 1980; Kladviko and Nelson, 1979; Kelling et al., 1977). However, reports in forestry literature are lacking. An inherent problem in comparing data on runoff water quality from any of these studies is the vastly different soils examined, differences in rainfall amounts and intensities used, and the contact distance between biosolids and collection devices before collecting runoff waters. Furthermore, it is difficult to locate replicate watersheds to study.

Loch et al., (1995) examined the effect of freshly applied and consolidated biosolids on surface water runoff quality from small plots within *Pinus radiata* plantations in Queensland, Australia (consolidated refers to biosolids that were surface applied and exposed to natural rainfall for six months before monitoring). The biosolids were aerobically digested and had been stored for one year before application. Researchers applied biosolids (dry weight basis) at a rate of 90 Mg ha<sup>-1</sup> to 0.8 x 2.0 meter plots on three different soil series (5% slope). Artificial rainfall was applied at a rate of 150 mm hr<sup>-1</sup> for one-half hour and runoff collected in gutters located directly below the plots. The rainfall amount and intensity corresponded to the 100-year storm event.

Runoff water quality was generally poor from all of the treated plots and exceeded Australian regulatory limits. This is not surprising given the study design. The authors did not use buffers between the plots and collection points nor did they examine the effectiveness of various buffer distances between treated plots and water collection points. Water contacting and moving through biosolids as shown in this study is essentially biosolids leachate and would in no way represent the quality of water moving through an operational application site where water is in direct contact with the soil. Concentrations of NO<sub>3</sub><sup>-</sup>-N and NH<sub>4</sub><sup>+</sup>-N were extremely high in runoff from freshly applied biosolids (330 mg L<sup>-1</sup> for both ions collected 5 minutes after initiating rainfall), but decreased rapidly during the rainfall event (16 and 30 mg L<sup>-1</sup> for NO<sub>3</sub><sup>-</sup>-N and NH<sub>4</sub><sup>+</sup>-N, respectively at 30 minutes). Concentrations of NO<sub>3</sub><sup>-</sup>-N and NH<sub>4</sub><sup>+</sup>-N from the consolidated biosolids were low throughout the rainfall event. In contrast, total P, in runoff from both fresh and consolidated biosolids was relatively high and showed only small decreases during the rainfall event. Total P concentrations in both treatments ranged from 10.5 to 4.3 mg L<sup>-1</sup> between 5 and 30 minutes after initiating rainfall.

### 3.5 Pathways of P to surface waters following biosolids fertilization

Runoff is an integrative term used to refer to the various processes that ultimately produce streamflow (Hewlett, 1982). These processes include overland flow, surface and subsurface stormflow, baseflow, streamflow, deep seepage, and underflow or hyporeic flow. Once rain water contacts biosolids, three primary pathways exist for the transfer of dissolved or suspended solid particles to surface or ground waters (Figure 3.2). These pathways include: (1) direct surface runoff (overland flow); (2) interflow (interflow is often referred to as lateral or subsurface flow; defined in Chapter 1) through the soil; and (3) vertical movement of soil water to ground waters. Overland flow (synonymous with surface water runoff) is defined as that part of streamflow derived from net precipitation which fails to infiltrate the mineral soil surface and runs over the surface of the soil to the nearest stream channel without infiltrating at any point (Hewlett, 1982).

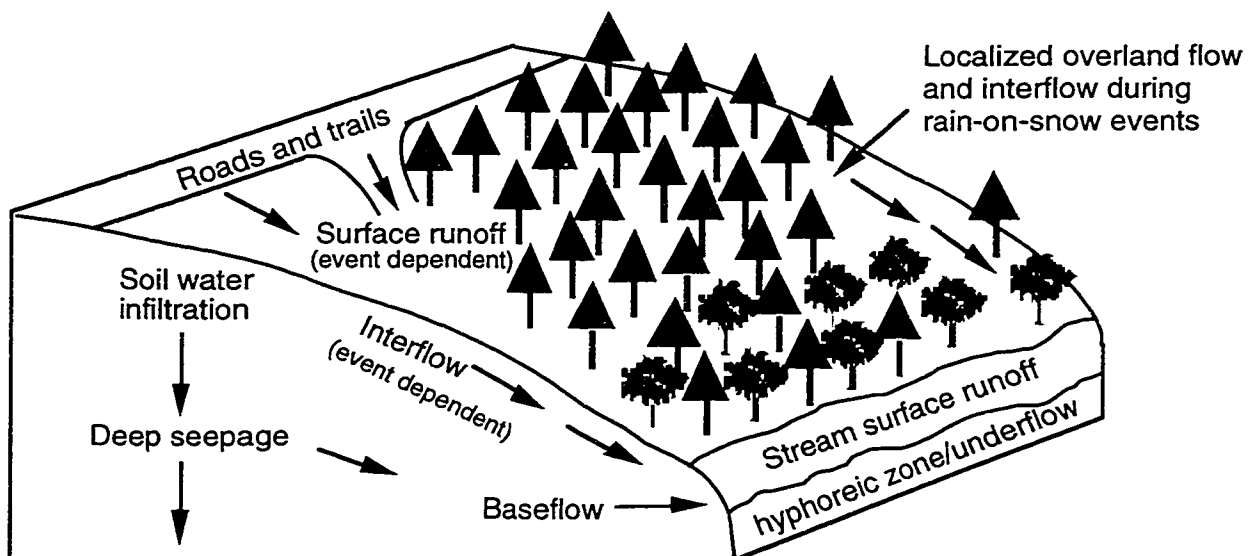


Figure 3.2. Possible pathways of water runoff from forested slopes.

All of the pathways shown in Figure 3.2 can contribute to surface water runoff depending on rainfall intensity and amount, forest floor composition, soil moisture conditions and texture, and topography. A conceptual diagram of pathways for transfer of P into surface waters is shown in Figure 3.3; primary transformations among P fractions are shown as well. Of the pathways shown, surface runoff may move soluble P or suspended P-rich inorganic and organic particles, while interflow and runoff will primarily move soluble P. Under certain soil conditions, however, interflow and vertical soil water have the potential to transfer particulate P; these conditions are discussed below. Water soluble P is the primary mobile P form susceptible to movement via surface runoff or interflow at the time of application. At a forest application site, direct transfer of particulates from biosolids is highly unlikely, as large buffers around water bodies are typically used. The exception is application roads and trails that can act as conduits for the direct transfer of biosolids particles into surface waters.

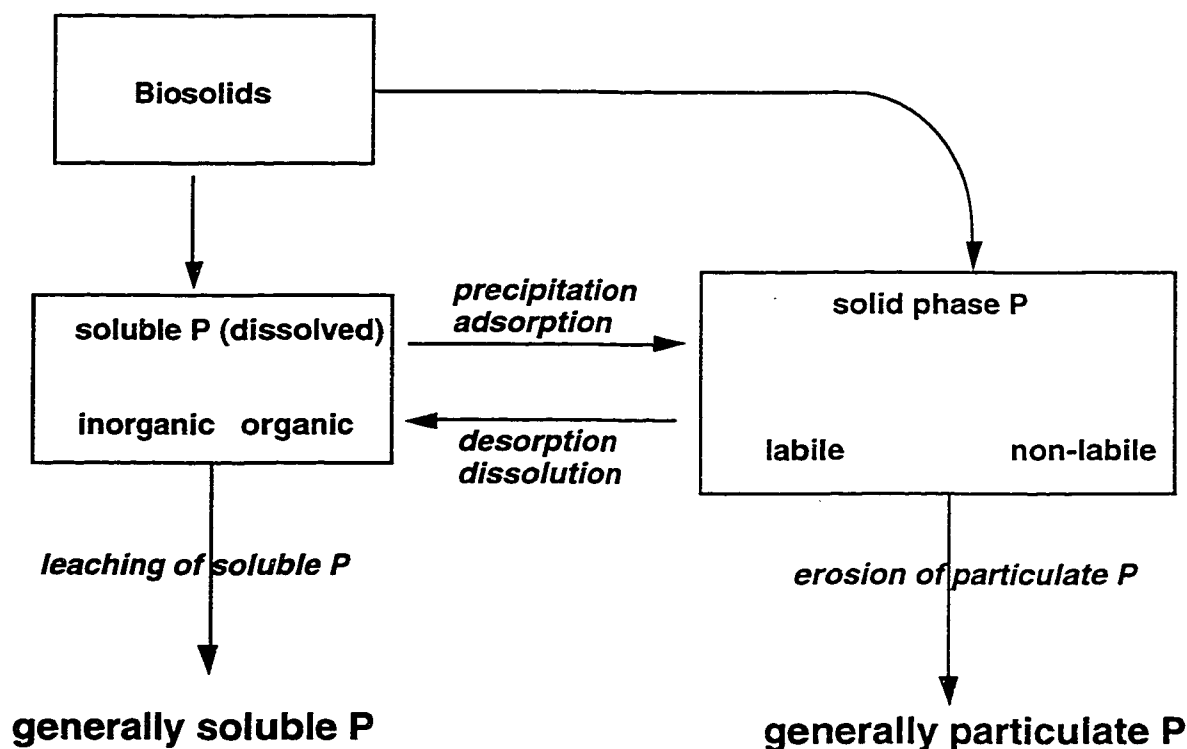


Figure 3.3. Pathways of phosphorus transfer to surface water and transformations among potentially mobile P pools in biosolids. Adapted from Harrison (1998).

### 3.5.1 Surface Runoff

Surface water runoff in many forested sites in the PNW is unlikely given the generally coarse textured soils and large organic horizons which promote rapid water infiltration. However, localized surface water runoff can occur but its widespread occurrence has not been reported for PNW soils. Harr (1977) found that overland flow rarely occurs on undisturbed forest soils in the Cascade Range in Oregon. The author attributed this to highly porous forest floor and surface soils with high unsaturated hydraulic conductivities and low rainfall intensities. In a review of literature at the time, the author suggested that researchers had substantial supporting information to show that overland flow in humid regions rarely occurs and that subsurface flow is the dominant pathway for runoff waters to enter streams. His work in Watershed 10 at the H.J. Andrews experimental forest in Oregon found that subsurface storm flow accounts for more than 97% of total storm flow in a stream draining the watershed. Beasley (1976) measured overland and subsurface flow for a three-year period covering 115 separate storm events in watersheds dominated by pine and mixed hardwoods. He found that subsurface flow from upper slopes can contribute significantly to storm hydrographs in forested areas where permeable surface soils overlie an impermeable stratum. This situation is common in some areas in the Puget Sound area, where permeable near-surface soils overlay a compacted till layer; numerous biosolids application sites overlie these soils.

### 3.5.2 Interflow

It is thought that in some forested watersheds runoff waters are transported via interflow on sloping terrain. This pathway (defined in Chapter 1) may be enhanced by large macrochannels (possibly decayed root channels and those created by soil fauna) which convey water rapidly through the soil profile and downslope (Hetherington, 1985; Feller

and Kimmons, 1979; Beven and Germann, 1982). Water and solute movement via macropore and micropore channels has been documented by a number of researchers working in forested ecosystems (Jardine et al., 1990; Wilson et al., 1990; Luxmoore, 1981). However, the extent to which these pathways contribute to the transport of dissolved or suspended particulates following biosolids application is unknown. The movement of constituents in biosolids via interflow pathways is, therefore, a consideration in evaluating runoff water quality effects from a biosolids application site.

In non-fertilized systems, the contribution of interflow to runoff generation and to the chemistry of runoff waters draining forested ecosystems has been examined by a number of researchers (Turton et al., 1995; Mulholland, et al., 1990; Wilson et al., 1991; Wilson et al., 1990; Harr, 1977; Beasley, 1976). Recent work on interflow water movement and solute dynamics suggests that both macropore and micropore flow contribute solutes to surface waters during runoff events (Wilson et al., 1991). The size of a macropore is an arbitrary measurement, but generally they are larger than 1000  $\mu\text{m}$  (Bevin and Germann, 1982), while mesopores are less than 1000  $\mu\text{m}$ . Micropores are typically defined as being between 5-30  $\mu\text{m}$  in diameter (SSSA, 1997). Wilson et al., (1990) found that preferential flow from hillsides through macro- and mesopores was the predominant stormflow mechanism in the West Fork, Walker Branch Watershed in Tennessee. Peak subsurface flow preceded peak streamflow and occurred primarily through the 1.0 to 2.5 m soil depth (Bt2 horizon). However, Luxmoore et al., (1990) working in the same watershed, concluded that macropores can transmit a substantial amount of water, but they have a small surface area and behave largely as physical conduits without much effect on water quality.

Jardine et al., (1990) showed that small pores retained water and solutes longer and had greater operational storage for ions than large pores within an undisturbed soil pedon located on a ridge top in the Walker Branch watershed, Tennessee. Solutes were transported by convection and diffusion from small pore regions to large pore regions via hydraulic and concentration gradients, respectively, with small pores shown to be a major source for solute transport in large pores. Wilson et al., (1991) monitored the subsurface transport of solutes within a 0.47 ha hillslope subcatchment in the west fork of the Walker Branch watershed. Their results showed that the most commonly observed solute transport pattern during storm events was an increase in concentration as flow rate increased, followed by a decrease in concentration during the recession limb of the stream hydrograph. The response was due to flushing of solutes primarily from water-filled mesopores, with macropores serving as conduits to streamwater.

The contribution of “old” versus “new” water in affecting stream water quality has undergone examination and this phenomenon may have implications for watersheds fertilized with biosolids. Biosolids provide a long-term source of N and P nutrition (Henry et al., 1994) and the resulting elevation in soil nutrient status may be measured in streams draining fertilized watersheds months and possibly years after application. For example, Bazemore et al., (1994) found that “old” soil water accounted for 65% of peak runoff for a large June rainstorm in a watershed located within Shenandoah National Park and a smaller November storm contributed 50% of peak runoff. The chemical composition of “old” water is important relative to water quality, as some researchers have suggested that contaminants dissolved in “old” water may be rapidly transported into streams if hydrologic factors that promote old water release predominate. These factors include soil porosity, macroporosity, antecedent soil water content, and precipitation amount and intensity.

### 3.6 The release and fate of phosphorus following biosolids applications

#### 3.6.1 Factors affecting the release of biosolids P into the soil solution

Phosphorus release into the soil following biosolids fertilization is mediated by the contact and movement of water through the applied material (Rydin and Ottabong, 1997). Water soluble P from biosolids moves into the forest floor and into mineral soil horizons with percolating rainwater. This may include both soluble inorganic and organic P. The retention of soluble reactive P by the soil will depend on the P sorption capacity and nature of sorption sites in the soil at the time of application (Sharpley, 1994). Phosphate sorption is concentration dependent and as solution concentrations of P increase, sorption increases as well. Desorption occurs when soil solution P concentrations decrease below the P concentration maintained on the soil surface, resulting in a release of P into the soil solution.

Following the initial release of water soluble P from biosolids, the release of additional P depends on a number of interrelated and complex factors: (1) water flux, (2) biosolids type (anaerobically digested versus aerobic), (3) dominant P forms and their solubility (Ca-, Fe- or Al-phosphates), and (4) pH changes within the near surface soil horizons induced by biosolids application and associated nitrogen transformations (Rydin, 1996; Hinedi and Chang, 1989; O'Connor, 1986; McLaughlin, 1983). For soils in general, the important properties that govern P solubility include pH, concentration of Fe, Al, and Ca, and the nature and surface areas of soil particles (Holford, 1997). In addition, organic anions which are abundant in rhizosphere of topsoil are believed to increase phosphorus solubility (Comerford and Skinner, 1989) and would presumably enhance the release of P from biosolids. However, the influence of organic anions on P solubility in biosolids or in biosolids-amended forest soils has not been examined.

Rydin (1996) found that the main factors controlling the release of P from biosolids under both anaerobic and aerobic conditions were water oxygen status and “flow size” (amount of water passing) through the biosolids. Anaerobic conditions dramatically increased P release from the biosolids studied (up to 95% of the original amount of P present) while the biosolids under aerobic conditions released much less, between 20% and 30% of the original P. Anaerobic conditions promote the release available P for several reasons: (1) reduction of ferric compounds; (2) higher solubilities of Al and Fe oxides resulting from hydrolysis due to increased pH in acid and strongly acid soils; (3) production of organic acids which form complexes with  $\text{Ca}^{2+}$  ions and disturb P solubility equilibria; and (4) release of phosphate ions from the exchange between organic anions and phosphate ions in Al-P and Fe-P compounds (Sanyal and De Datta, 1991).

Addition of flocculants has been shown to affect the amount of P released by biosolids amended soil under laboratory conditions. Rydin and Otabbong (1997) reported Al flocculated biosolids released up to 43% of the initial amount of P present in a sandy loam soil mixed with biosolids, while Fe-P flocculated biosolids mixed with the same soil released only 20%. The release process was described by a first order decay equation, with release rates varying between 0.04 and 0.07  $\text{d}^{-1}$ . The difficulty in using release rates as described is the relatively warm temperatures used during the incubation process, which can have a marked effect on biosolids nitrogen dynamics. Warm temperatures would tend to accelerate nitrogen transformations including the pH lowering processes of ammonia volatilization and nitrification. Ideal conditions for nitrogen transformations combined with a steady input of oxygenated, acidic water could conceivably increase the dissolution rate of biosolids rich calcium phosphates as well as the production of organic acids which can

participate in ligand exchange reactions that release P from Al-oxide surfaces (Fox et al., 1990).

Slight declines in soil pH (0.25-0.5 pH units) have been attributed to increases in P solubility following biosolids application to soil. For example, O'Connor et al., (1986) examined solid phase control of P release in calcareous New Mexico soils amended with anaerobically digested biosolids. Biosolids additions increased water and  $\text{NaHCO}_3$ -extractable P and plant uptake whereas fertilizer P was historically ineffective. Increased solubility of tri- and octacalcium phosphates were noted and this was attributed to a marked decline in soil pH following biosolids addition. In a study of excessively fertilized soils (including those fertilized with biosolids) in the midwest, Pierzynski et al., (1990) used a solubility equilibrium approach in studying solid phase control of P dissolution. Results showed that in an acidic agricultural soil fertilized with biosolids (pH 5.7 and total P concentration of 0.5%), the dominant solid phase controlling P solubility was the amorphous analog to variscite ( $\text{Al}(\text{OH})_2\text{H}_2\text{PO}_4$ ). Dispute exists whether or not crystalline variscite can form in soils, but the author suggests that under low pH conditions its presence may restrict P solubility years after fertilization has ceased.

### 3.6.2 Reversibility of phosphorus adsorption in biosolids-amended forest soils

An important concept in examining P release and retention following a biosolids application to forest soil is the extent to which added P is reversibly or irreversibly adsorbed by minerals or organics in the soil matrix. Reversibly adsorbed P could be considered potentially mobile and would be available for plant or microbial uptake or movement through the soil matrix if concentration gradients were favorable. Irreversibly adsorbed P could be considered relatively immobile and its release into the soil solution slow. In acidic soils, reversibly adsorbed P is thought to be primarily associated with

hydrous oxides of iron and aluminum, especially when organic amendments such as biosolids or composts are used (Harrison, 1998). Phosphate adsorption to amorphous Fe and Al oxide surfaces is thought to be a dominant mechanism for P retention in unfertilized PNW soils (Johnson et al., 1986) and in soils treated with wastewater (Johnson et al., 1979). Phosphate enters into a coordination with a metal oxide and displaces another anion, sometimes referred to as ligand exchange. At pH values such as those encountered in PNW forest soils (pH <6), surfaces can become positively charged because of H<sup>+</sup> sorption and phosphate sorption is enhanced.

Some reversibly adsorbed P may be associated with organo-metal complexes but direct evidence of this in biosolids-amended soils is lacking. Harter (1969) found that organic matter is important in the bonding of P in soils and he proposed that P is initially bonded to anion exchange sites on organic matter (the exchange likely involves a substitution of phosphate ions for hydroxyl ions in the organic matter), and subsequently transformed into less soluble iron and aluminum phosphates. The release of biosolids organic P via mineralization depends on biosolids type and it has been shown that decomposition of di- and monoesters in biosolids occurs quickly after application. Hinedi et al., (1988) examined mineralization of biosolids P from anaerobically and aerobically digested biosolids using <sup>31</sup>P NMR. Phosphorus diesters rapidly hydrolyzed and disappeared from soils amended with biosolids within 30 days since application, while P monoesters accumulated in acid soils but disappeared in alkaline soils; it was speculated that the monoesters in the acid soil could be sorbed by iron oxides.

In soils amended with anaerobically digested biosolids, a limited response has been noted with respect to increases in soil organic P pools. For example, Otabbong et al., (1997) reported slight decreases in soil Pi/Po ratios after a total of 6617 kg ha<sup>-1</sup> of biosolids

biosolids had been applied to experimental field plots (clay loam soil) over a 40-year period in Sweden. The organic P pool clearly increased due to biosolids application, yet the authors suggested that mineralization did not seem to be an important pathway for P transformations relative to the large pools of inorganic P that exist in the biosolids amended soil.

Some researchers working with biosolids have found that with time, P becomes more recalcitrant and less susceptible to release into the soil solution. For example, Rydin and Otabbong (1997) examined the release and forms of P remaining in biosolids amended soils and showed that the inert P pool (extractable in concentrated acid) increased following a series of leaching events. In an earlier study, Rydin (1996) found that the HCl extractable fraction of biosolids increased during an incubation experiment at the expense of a declining NaOH extractable fraction. This suggests that as biosolids P “ages” in the soil, some portion of it becomes more stable and resistant to release, presumably due to structural incorporation into secondary minerals or bridging with metal-humic complexes. It is widely reported that P added via fertilization can become less available for release into the soil solution over time. Once it contacts the soil mineral surface, P appears to become a more stable structural component of adsorbing minerals (Harrison and Adams, 1987).

### 3.6.3 Forms and fate of biosolids applied P in forest soils

The soil phosphorus cycle is a complex series of interactions governed by geochemical and biological subcycles (Figure 3.4). At the time of biosolids application several of the P pools (represented by gray shaded boxes) are enriched relative to existing levels, while over time, the secondary mineral pool of P appears to dominate P release. Working in agricultural soils, researchers have repeatedly demonstrated an increase in reversibly adsorbed P following manure and other organic amendment fertilization in near

surface horizons, but in some cases have shown that repeated applications result in marked declines in P sorption and increases in P concentrations in subsoils (Simard et al., 1995). Typically, increases have been most noticeable for the labile P fractions extractable in water, exchange resins, and sodium bicarbonate (Frossard et al., 1996b; Iyamuremye et al., 1996; O'Connor et al., 1986; Cline et al., 1985; Soon and Bates 1982). The practical consequences of increases in labile P pools in forest soils is potentially greater P availability and supply for tree uptake and growth.

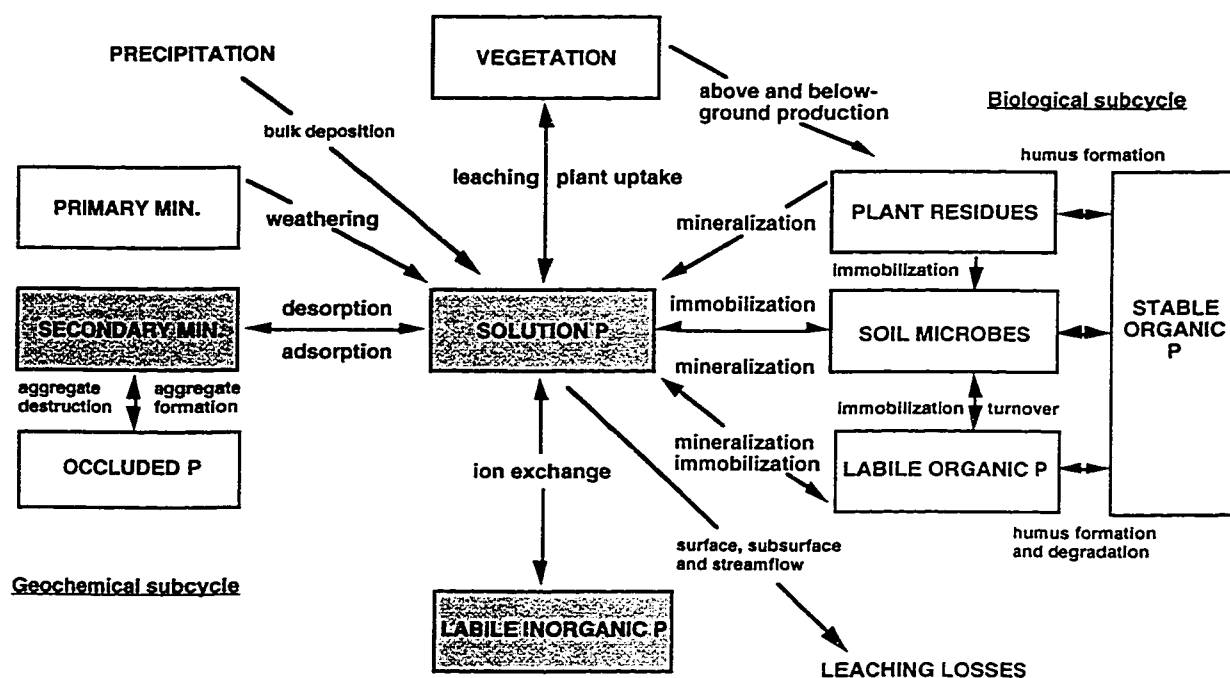


Figure 3.4. Phosphorus cycle in soils. Adapted from Walbridge et al., 1991.

One of the questions that remains unanswered specific to forest soils in the PNW is what is the depth in the soil profile where biosolids application ceases to affect the concentration, forms, and relative distribution of P pools. From a mobility standpoint, changes in P concentration with depth provide indications of the mobile nature, or lack thereof, of P following biosolids application. If significant changes are not noted with

increasing depth down the soil profile, then biosolids managers have some reasonable assurance that loading rates based on nitrogen are not exceeding the soil's capacity to store p with repeated biosolids applications. It could be argued that biosolids applications will have a long-term positive effect on soil P availability in acidic forest soils through the retention of added P in reversibly adsorbed, moderately labile pools.

Fertilization with biosolids has resulted in increases in nutrient availability on coarse textured soils. Working on glacial outwash soils at Pack Forest, Prescott et al., (1993) showed that application of biosolids at a rate of 142 Mg ha<sup>-1</sup> (4 Mg P ha<sup>-1</sup>) to 70-year-old Douglas-fir (site class IV) enhanced long-term availability of P in the forest floor and they reported evidence of long-term enhancement of P turnover in litter in plots treated with biosolids. They also reported greater P supply in forest floor material from biosolids treated plots as assessed by a greenhouse bioassay using Douglas-fir and Sitka spruce seedlings. Forest floor material from biosolids treated plots had significantly more P than either inorganic nitrogen fertilized or control plots more than 10 years after biosolids application.

The depth to which heavy biosolids applications (>400 Mg ha<sup>-1</sup>) affect total soil P concentrations has been addressed for forested glacial outwash soils. Harrison et al., (1994) assessed the long-term changes in soil chemical and physical properties due to a single heavy application (approximately 500 Mg ha<sup>-1</sup>) of municipal biosolids on an Everett series (glacial outwash) soil at Pack Forest, Washington. Biosolids-amended soil had higher total P (14 vs. 2.2 mg g<sup>-1</sup>) content in the 0-7 cm mineral soil horizon compared with an unamended soil of similar pedogenesis, yet no significant differences in total P concentrations were noted below 25 cm. The depth of sampling was performed to 185 cm. This study clearly demonstrates the strong P retention capacity of glacial, coarse textured

soils and it suggests that where lesser application rates are used the risk of P leaching below the rooting zone is minimal.

Using biosolids application rates of 250 and 625 Mg ha<sup>-1</sup> on an Everett series soil at Pack Forest, Riekerk (1978) found a significant reduction of solution phosphate in the B horizons with biosolids treatments as compared to A horizons in the same treatments. The author attributed the effect to the high P supply from biosolids interacting with abundant free iron oxides in the soils studied. However, Fe adsorption of phosphates were not confirmed as the mechanism responsible for low solution P concentrations in B horizons of treated soils.

### 3.7 Summary

Most municipal biosolids contain one to four percent phosphorus on a dry weight basis. Important pathways for the transfer of constituents in biosolids to surface waters include direct runoff via overland flow and soil water interflow. In forests within temperate, humid regions, overland flow is believed to be minimal due to the infiltrative properties of the forest floor and porous surface soils. Thus soil water interflow can be a dominant pathway for generation of runoff event flow as well as a pathway for ion movement. Movement of P from biosolids via this or other pathways has not been well documented. Important processes governing the release of P from forest soils fertilized with biosolids include biosolids type, dominant P forms and their solubility, water flux through the applied material, and soil pH. Researchers working with soils derived from glacial outwash that received from 140 to nearly 500 Mg ha<sup>-1</sup> of biosolids report increased soil P availability near the forest floor. However, significantly different mean concentrations of soil total P have not been reported below a depth of 25 cm.

## CHAPTER IV

RUNOFF OF PHOSPHORUS AND NITROGEN FROM A STEEP, FORESTED  
WATERSHED FERTILIZED WITH BIOSOLIDS

This chapter examines the runoff water quality implications of using biosolids within a steep, forested watershed at Pack Forest, Washington. A study was established to measure the effect of biosolids application on water quality during baseflow and runoff event conditions. Water quality (baseflow only) and discharge were monitored for approximately one year before biosolids application within the 27 Creek watershed, with runoff event water quality sampling commencing four months prior to application. After biosolids application, both baseflow and runoff event water quality sampling and Creek discharge measurements continued for about two years.

#### 4.1 Experimental design

Biosolids are not ordinarily applied to forested slopes greater than 30%, which is the guideline for biosolids application to forested areas (WDOE, 1994). The guideline may be too conservative and slopes greater than 30% have never been tested with regard to the effect of biosolids application on runoff water quality. To test this, biosolids were applied to forested slopes in excess of 30% (within a headwater watershed) in which runoff water directly contacting biosolids could be collected.

The experiment tests the assumption that if constituents in biosolids are to move from a site, it would occur during runoff events which are induced by heavy rainfall and high soil moisture conditions. Under heavy rainfall conditions, stream discharge increases and the source area for runoff water expands within a watershed. This situation could be encountered anytime between October and June at Pack Forest. In order to examine

“worst-case” conditions for runoff from biosolids, application during January was selected.

Conversely, biosolids applied during the previous winter decompose during the ensuing growing season, releases nutrients through mineralization and dissolution processes. Depending on the extent of uptake and soil immobilization, the concentration of nutrients in the soil solution may be elevated. This could create a situation where available P production exceeds uptake. The remaining P not immobilized in the soil could be mobile and transferred to runoff water as the Creek’s source area expands and discharge increases.

## 4.2 Methods and materials

### 4.2.1 Study site characteristics

The 27 Creek Watershed is located within the University of Washington’s 1720 ha Charles Lathrop Pack Demonstration Forest. Pack Forest is at the base of the Cascade foothills about 110 km south of Seattle. Dominant vegetation on the forest is second growth Douglas-fir with some western hemlock, western red cedar and red alder. The climate is typical maritime, with relatively dry summers and wet winters, and moderate temperatures throughout the year. Annual precipitation is about 120 cm, with approximately 50% falling between October through January. Rainfall during the period of July through August is usually less than 12 cm, often resulting in drought-like conditions on well drained soils. For normal temperatures and precipitation, evapotranspiration is estimated between 38 to 56 cm annually.

The study site is a 21.4 ha headwater watershed and is drained by a first-order perennial stream (27 Creek). The watershed ranges between 420 and 600 meters with a northerly aspect (Figure 4.1). Topography is steep, with some slopes exceeding 60%.

Nearly all of the watershed was clear-cut in 1982, replanted the following year, and currently consists of 16-year-old second growth Douglas-fir intermixed with naturally regenerated western hemlock and red alder. Most of the watershed was pre-commercially thinned in March and April 1996; felled trees were left in place.

#### 4.2.2 Biosolids and soil chemical composition and biosolids application rate

Anaerobically digested, dewatered (~20% solids) biosolids from King County's Renton Wastewater Treatment Plant were used; its chemical composition at the time of application is shown in Table 4.1. Biosolids samples were analyzed after air-drying for one week and light grinding to pass through a 2-mm sieve. The soil within the watershed is mapped as the Wilkeson soil series (fine-loamy, mixed, mesic Ultic Haploxeralfs). Soil samples were collected from five separate soil pits excavated to a depth of 15 cm in October 1995 (soil removed from the A and top of the B horizon). Soil samples were air-dried for 72 hours and sieved to 2 mm before analysis. Values shown in Table 4.1 are expressed on a dry weight basis.

Biosolids were applied to 8.4 of 21.4 hectares of the watershed during the third week of January, 1997 (95% of total application area) and the first week of May, 1997 (5% of total application area) to the hatched areas shown in Figure 4.1 at a dry weight rate of  $13.5 \text{ Mg ha}^{-1}$ . Wet conditions and unstable roads in January 1997 prevented application from being completed at one time due to safety concerns. The application rate was based on nitrogen demand for a 15-year old Douglas-fir stand on soils never fertilized with biosolids. The approximate loading rates are  $700$  and  $500 \text{ kg ha}^{-1}$  for nitrogen and phosphorus, respectively. Total buffer distance around 27 Creek and ephemeral drainages (noted in Figure 4.1) was 40 meters.

Table 4.1. Chemical composition of Renton biosolids and 27 Creek Soil.

	C	N	P	Al	Ca	Fe	pH
	-----%-----						
Biosolids n=8	34±4	5.2±0.3	3.7±0.6	1.5±0.1	2.8±0.2	2.6±0.2	8.6±0.2
Soil n=5	3.4±0.5	0.1±0.1	0.4±0.2	0.9±0.3	1.4±0.3	1.1±0.5	4.2±0.2

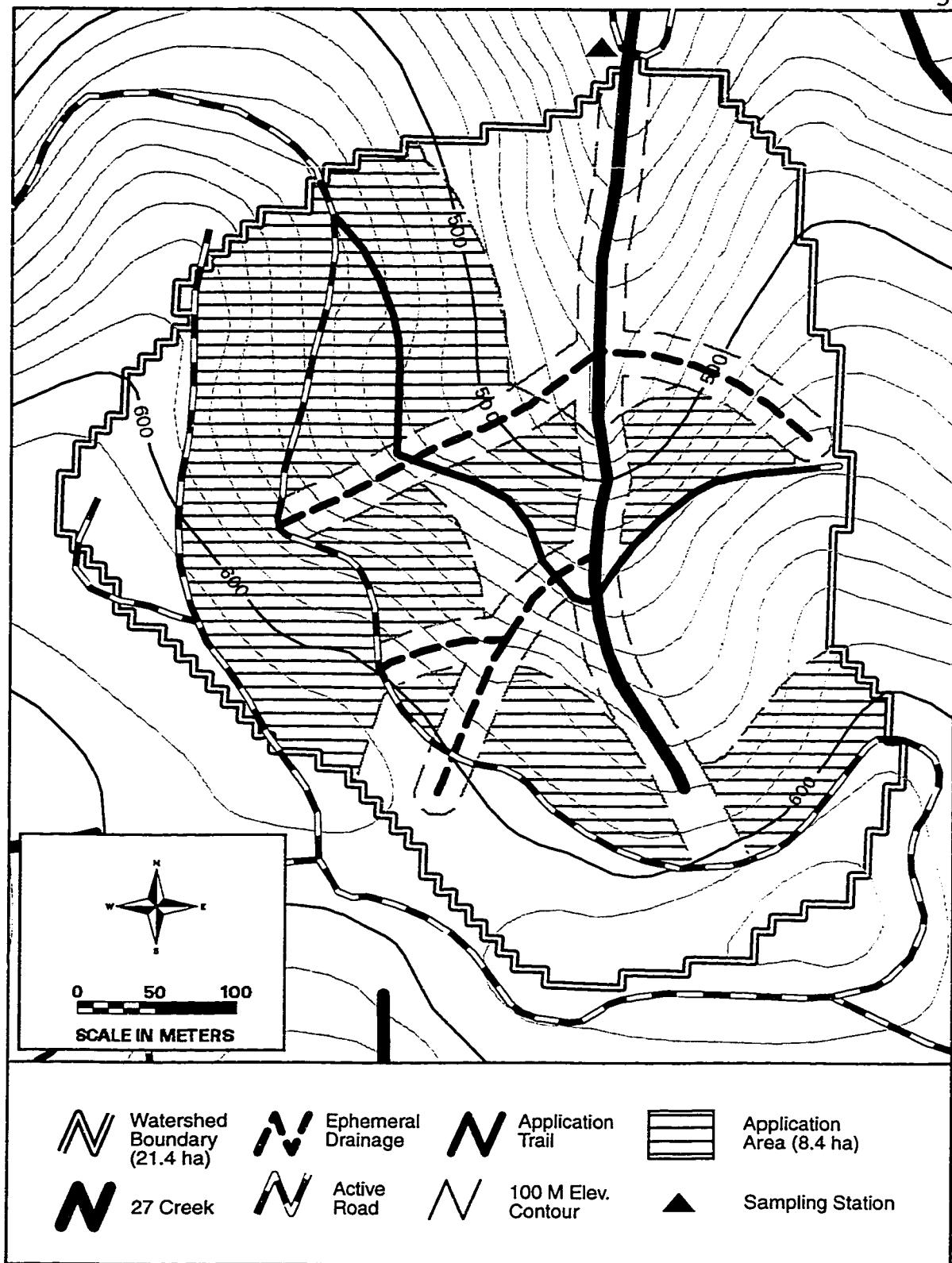


Figure 4.1. 27 Creek Watershed, Pack Forest, Washington

### 4.2.3 27 Creek Watershed Hydrology

#### 4.2.3.1 Hydrologic measurements

An ISCO model 4120 submerged probe flow logger was installed inside a 61 cm diameter galvanized culvert. Flow rate was determined using the Manning equation fitted for closed conduits. A roughness coefficient of 0.24 was used. Calibration was done using a small ruler to measure water level over the top of the submerged probe. Frequent recalibration was performed and observed readings were compared to measured discharge using a 121 liter plastic container and stop watch. The flow logger was integrated with an ISCO 3700 portable water sampler and model 510 rain gauge located in a clearing near the culvert. Daily average discharge and daily rainfall for water years 1996-97 and 1997-98 are shown in Figures 4.2 and 4.3.

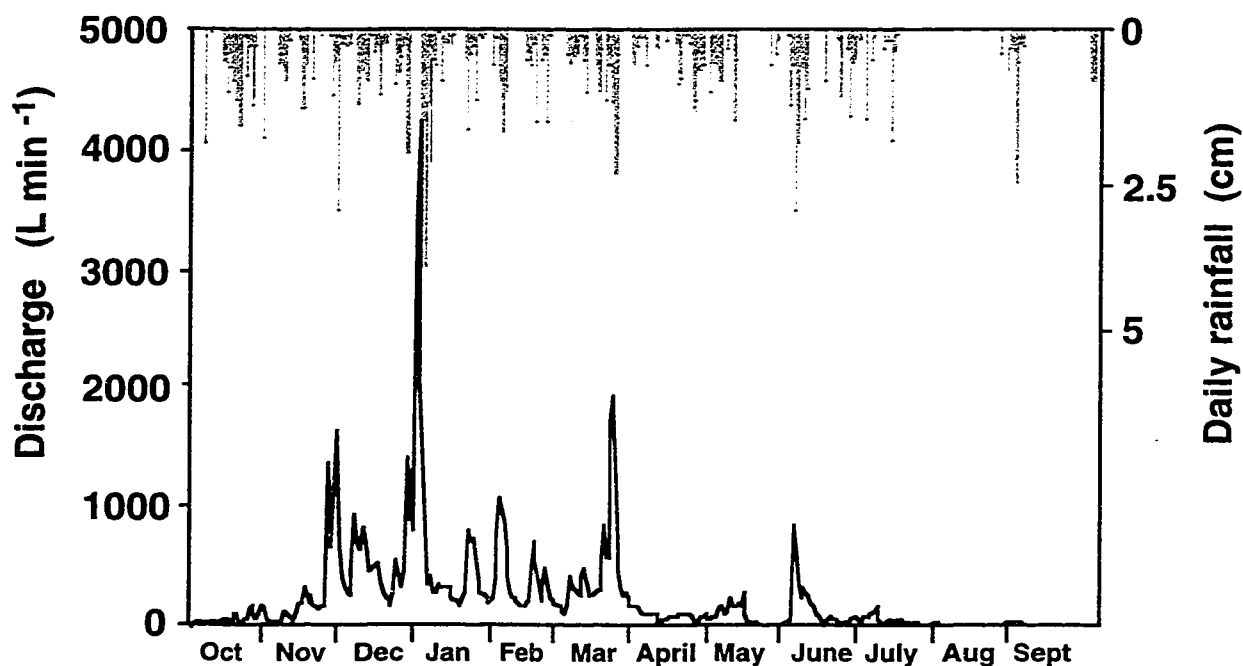


Figure 4.2. 27 Creek discharge and rainfall for the water year 1996-97.

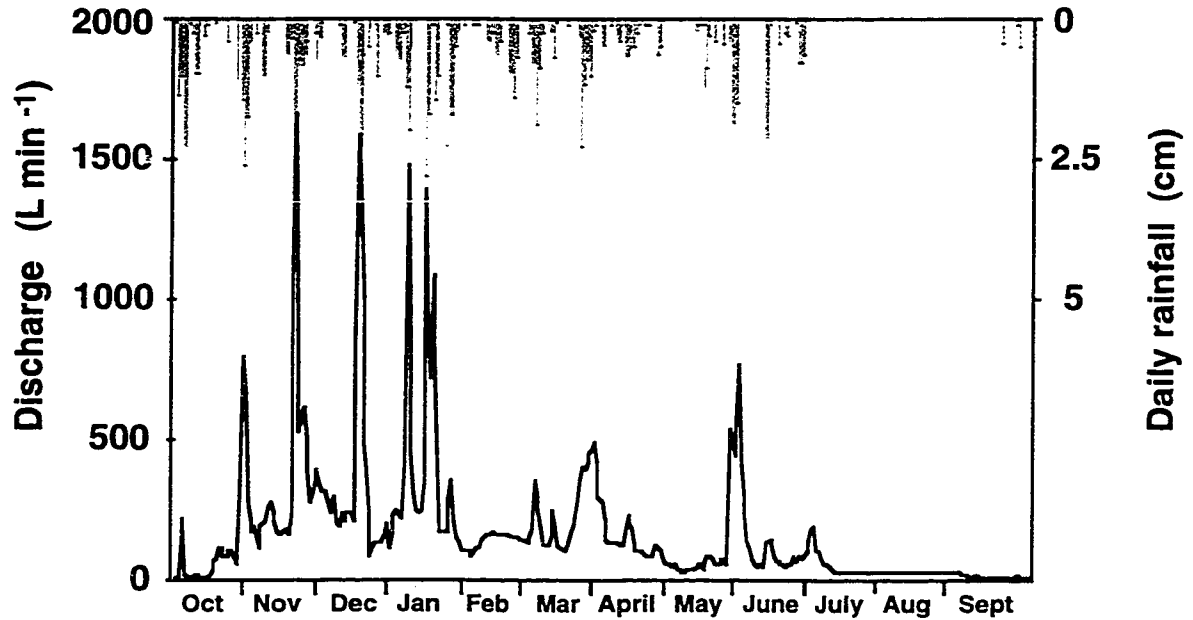


Figure 4.3. 27 Creek discharge and rainfall for the water year 1997-98.

#### 4.2.3.2 Runoff event and baseflow separation

Several runoff events were selected for analysis, with an attempt made to include at least one runoff event per season exclusive of mid July-September rainstorms (during this time, relatively little runoff is generated within the 27 Creek watershed). Runoff events chosen for analysis were separated from baseflow using the technique of Hewlett and Hibbert (1967). From the point of initial hydrograph rise, a line sloping upward at a rate of  $(1.42 \text{ l s}^{-1}) * 2.59(\text{km}^2)$  is plotted and extended until it intercepts the hydrograph. This method is acceptable for separating runoff hydrographs in watersheds less than  $52 \text{ km}^2$ .

#### 4.2.4 Water quality sampling and analytical methods

From November 1995 until November 1998, water samples were removed at least once a month by taking a grab sample at a single point in the Creek, followed by analysis for total P and total N (total N=organic N plus  $\text{NH}_3\text{-N}$  and  $\text{NO}_3\text{-N}$ ). Beginning in October 1996 numerous rainfall events causing a substantial rise in the stream hydrograph initiated automatic water sampling. After sampler initiation, water samples remained in the automatic sampler on ice until removal and transport. Water samples were also removed periodically during baseflow conditions after October 1996. After October 1996, almost all water samples were analyzed for total P,  $\text{PO}_4\text{-P}$ , BAP, total N,  $\text{NH}_3\text{-N}$ , and  $\text{NO}_3\text{-N}$ . All water analyses were performed by the King County Water and Land Resources Division Environmental Laboratory in Seattle, Washington.

Total N and P on unfiltered water samples as well as  $\text{PO}_4\text{-P}$ ,  $\text{NH}_3\text{-N}$ ,  $\text{NO}_3\text{-N}$  were determined using standard methods for the examination of water (APHA-AWWA-WPCF, 1994). Biologically available P (BAP) was determined by filtering a known volume of Creek water ( $0.45\mu\text{m}$  filter) and analyzing the extract for orthophosphate (APHA-AWWA-WPCF, 1996). The particulate material remaining on the filter paper is extracted in a dilute sodium hydroxide/sodium chloride solution overnight, neutralized, filtered, and analyzed for orthophosphate. The sum of both determinations is BAP.

#### 4.2.5 Analytical methods used for soil and biosolids

Total soil and biosolids N and C were determined by dry combustion (Perkin-Elmer CHN Analyzer Model 2400). Total elements were determined using a  $\text{HNO}_3\text{-H}_2\text{O}_2\text{-HCl}$  acid digestion (EPA Standard Method 3050) and inductively coupled argon plasma spectroscopy (EPA Standard Method 6010. ICP; Thermo Jarrel Ash ICAP 61E, Thermo

Jarrel Ash, Franklin, MA). Total soil and biosolids P was determined by digesting soil samples in  $\text{HNO}_3\text{-H}_2\text{O}_2\text{-HCl}$  and determining P colorimetrically (Murphy and Riley, 1962) after neutralization of sample aliquots. A Perkin-Elmer model 55E spectrophotometer was used for all colorimetric analyses using a wavelength of 880 nm. Soil and biosolids pH were determined using a VWR model 3000 pH meter. A 1:2 soil/biosolids-distilled deionized water ratio was used with an equilibration time of 30 minutes before pH measurement.

#### 4.2.6 Data transformation and statistical analysis

Phosphorus and nitrogen concentrations ( $\text{mg L}^{-1}$ ) were log transformed in order to meet normality assumptions necessary in exploratory statistical analyses. For examination of concentration and discharge relationships, both linear and non-linear regression analyses were performed on untransformed and log-transformed data.

Flow-weighted P and N parameters were calculated using the following formula:

$$C_i (\text{mg L}^{-1}) = \sum C_i Q_i / \sum Q_i, \text{ where } C = (\text{mg L}^{-1}) \text{ and } Q = (\text{L min}^{-1})$$

### 4.3. Results and discussion

#### 4.3.1 Concentration range of phosphorus and nitrogen in 27 Creek before and after biosolids application

##### 4.3.1.1 Phosphorus

The frequency distributions of dissolved  $\text{PO}_4\text{-P}$ , BAP, and total P concentrations in 27 Creek before and after biosolids application are shown in Figures 4.4. The data are untransformed and data points represent either a single grab or automatic sample taken from 27 Creek from October 1996 to November 1998 for  $\text{PO}_4\text{-P}$  and BAP, and from October

1995 to November 1998 for total P. For all parameters analyzed in this study, more post application samples than pre-application samples were taken. The median concentration of  $\text{PO}_4\text{-P}$  and BAP decreased after biosolids application (Fig 4.4 A). The generally narrow range of labile P concentrations in 27 Creek suggest that biosolids has had little effect on 27 Creek labile P concentrations.

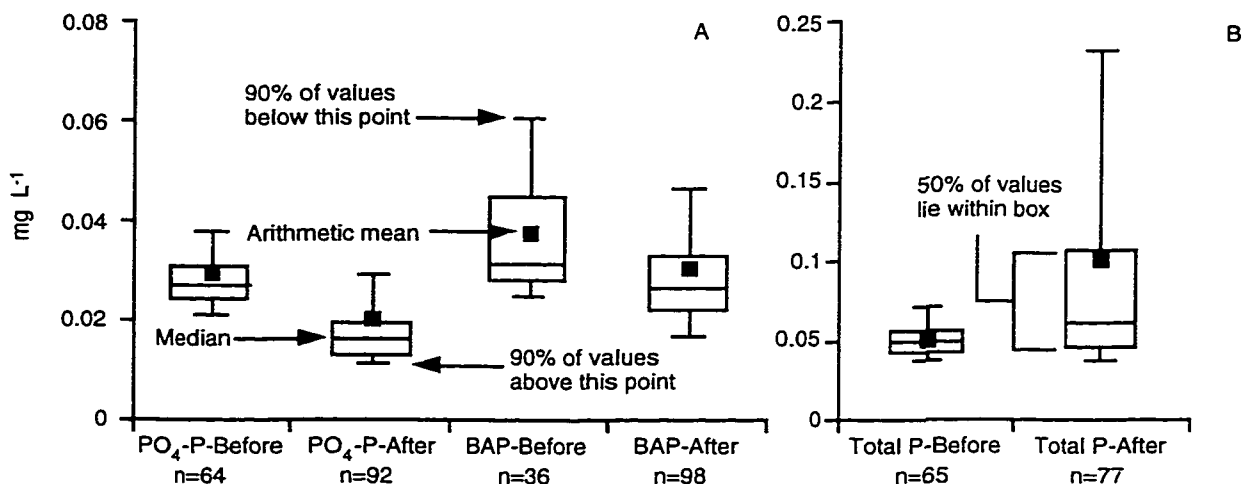


Figure 4.4 A-B. Frequency distribution of  $\text{PO}_4\text{-P}$  and BAP (4.4 A) and total P concentrations (4.4 B) in 27 Creek before and after biosolids application. Note different scales between the two figures. Horizontal lines above and below each box represent the 10th and 90th percentiles of each parameter, while the upper, lower, and middle line within each box represent the 75th, 25th and 50th percentiles, respectively. The arithmetic mean of each sample group is represented by the black square.

The median and mean total P concentration in 27 Creek is higher after application than before application (Figure 4.4 B), while the range of concentrations increased markedly. The disparity may be due in part to sample collection differences with respect to Creek discharge at the time of sampling. When the average monthly flow-weighted total P concentration is plotted over time (Figure 4.5), the increase in total P is less apparent, but a seasonal trend develops in elevated total P concentrations during spring and autumn months.

Interpreting the trend of increases in 27 Creek total P concentration after biosolids application is problematic for several reasons. Runoff events prior to October 1996 were not monitored, and total P was not determined for some of the runoff events during early autumn 1996. An analysis of post-application data shows that elevated total P concentrations were noted primarily during spring months and occasionally during periods of increased water discharge from the watershed. The highest total P concentration noted before application was approximately  $0.1 \text{ mg L}^{-1}$  in early November 1996, while the highest concentration after application was fourfold greater ( $0.4 \text{ mg L}^{-1}$ ) in May 1997. Natural variation in P movement and export from the watershed is expected and it appears certain periods of increased discharge are important in total P export. The limited number of storm events monitored prior to application and exclusion of spring events may not adequately represent the pattern of total P movement from the watershed.

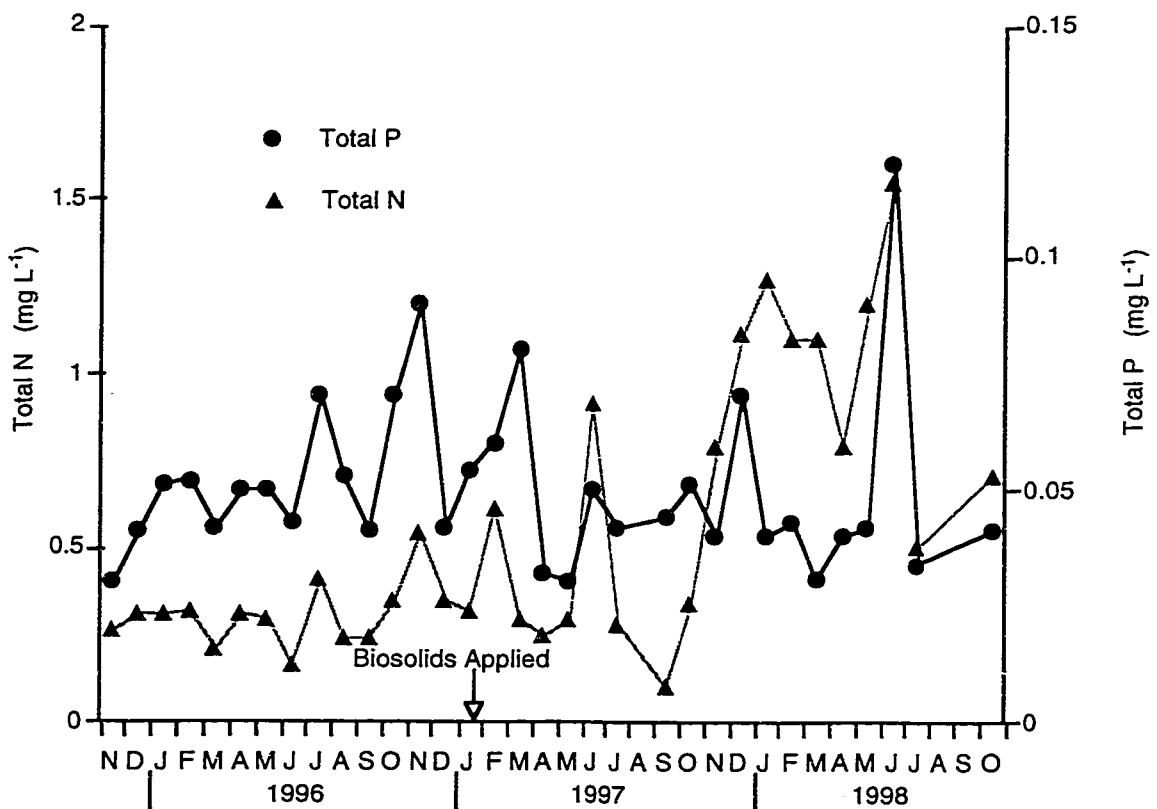


Figure 4.5. Monthly average total P and N concentrations in 27 Creek, Nov. 95-Oct. 98.

#### 4.3.1.2 Nitrogen

The frequency distributions of  $\text{NH}_3\text{-N}$  and  $\text{NO}_3^-\text{-N}$  concentrations before and after biosolids application are shown in Figure 4.6. Ammonia-N has remained relatively constant, ranging from below the detection limit ( $0.01 \text{ mg L}^{-1}$ ) to  $0.1 \text{ mg L}^{-1}$ . The distribution of  $\text{NH}_3\text{-N}$  includes zero values in Figure 4.6 A to reflect the frequency of concentrations falling below the detection limit. Despite fertilization of the watershed with biosolids, which contains up to 1.5% ammonia-N and 7% total N on a dry weight basis, no change in 27 Creek  $\text{NH}_3\text{-N}$  concentrations was observed at any time after application. No seasonal trends were observed as well.

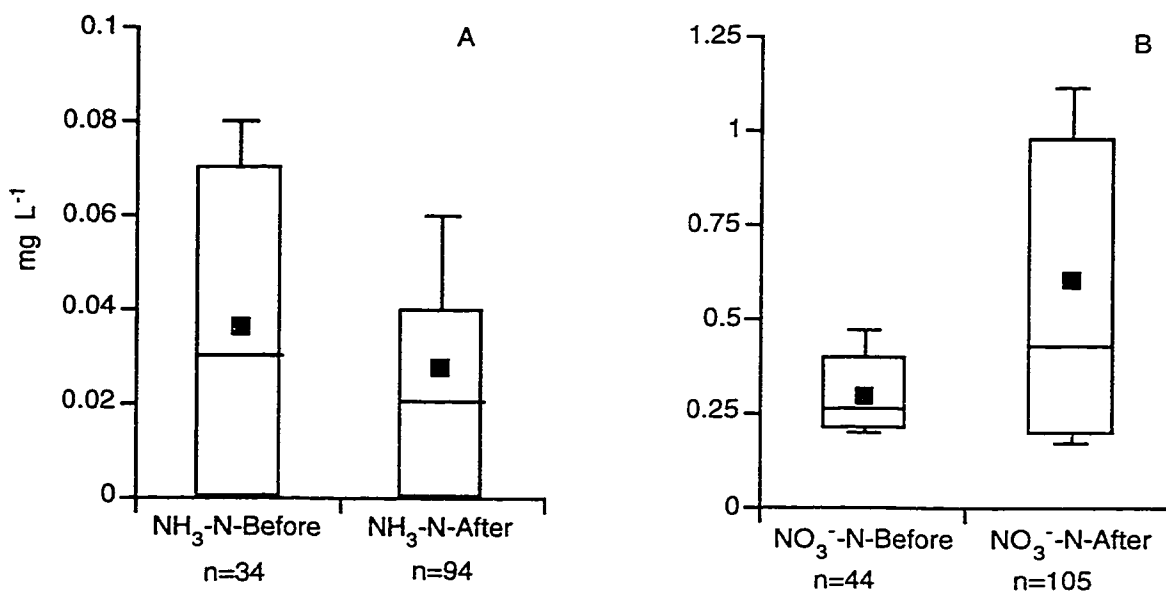


Figure 4.6 A-B. Frequency distribution of  $\text{NH}_3\text{-N}$  and  $\text{NO}_3^-\text{-N}$  concentrations in 27 Creek before and after biosolids application. Horizontal lines above and below each box represent the 10th and 90th percentiles of each parameter, while the upper, lower, and middle line within each box represent the 75th, 25th and 50th percentiles, respectively. The arithmetic mean of each sample group is represented by the black square.

The lack of any noticeable change in  $\text{NH}_3\text{-N}$  concentrations may be due to moderate volatilization losses of ammonia-N in the days and weeks following application as well as

rapid conversion to  $\text{NH}_4^+$ -N and adsorption by the soil. After a winter application, uptake of  $\text{NH}_4^+$ -N by plants and immobilization by microorganisms following application may be minor compared to sorption reactions; over time the importance of these processes reverse and uptake and microbial immobilization strongly limit  $\text{NH}_3$ -N mobility.

Watershed scale studies evaluating water quality effects of urea-N fertilization have shown much more dramatic increases in stream water  $\text{NH}_3$ -N concentrations. For example, Hetherington, 1985 reported peak  $\text{NH}_3$ -N concentrations of up to  $1.5 \text{ mg L}^{-1}$  24 hours after fertilization, with concentrations returning to prefertilization conditions within 14 days. Elevated levels of  $\text{NH}_3$ -N in streamwater have been reported to persist following urea fertilization of watersheds dominated by Douglas-fir for several months (Bison et al., 1992).

Nitrate-N concentrations in 27 Creek increased after application of biosolids (Figure 4.6 B). Pre-application concentrations ranged from  $0.05$  to  $0.5 \text{ mg L}^{-1}$ , while post-application concentrations have been as high as  $1.5 \text{ mg L}^{-1}$ . The effect of biosolids on increasing 27 Creek  $\text{NO}_3^-$ -N concentrations was observed approximately nine months after the January 1997 application, and elevated concentrations (approximately  $1.0 \text{ mg L}^{-1}$ ) have generally persisted since that time. The increase in  $\text{NO}_3^-$ -N concentrations is reflected in a marked increase in the average monthly concentration of total N in 27 Creek after biosolids application (Figure 4.5). Elevated  $\text{NO}_3^-$ -N levels in streams draining watersheds fertilized with urea-N have been reported to persist for a year or more (Bisson et al., 1992); in many instances buffers around drainages were not used. In this case an increase in Creek  $\text{NO}_3^-$ -N concentration is clearly an effect of biosolids decomposition, mineralization of organic N, and nitrification of  $\text{NH}_4^+$ -N which has elevated soil solution concentrations of  $\text{NO}_3^-$ -N.

### 4.3.2 Water quality in 27 Creek during runoff events before and after biosolids application

#### 4.3.2.1 Phosphorus

Several runoff events were monitored before and after biosolids application, with at least one runoff event during each season selected for analysis except low-flow, July-October, conditions. More events were monitored after biosolids application than before it. Runoff event flow was separated from base flow using the method of Hewlett and Hibbert (1967). Flow-weighted concentrations for PO<sub>4</sub>-P, BAP, and Total P during selected runoff events are shown in Table 4.2.

Table 4.2. Flow-weighted phosphorus and nitrogen concentrations in 27 Creek during runoff event conditions, 1996-1998.

Event Date	PO <sub>4</sub> -P	BAP	Total P	NH <sub>3</sub> -N	NO <sub>3</sub> <sup>-</sup> -N
	-----mg L <sup>-1</sup> -----				
11/26-28/96b	0.03	0.05	0.05	nd	0.4
12/20-26/96b	0.02	0.03	0.08	0.07	0.2
12/31/96-	0.03	0.03	0.05	0.07	0.2
1/17-21/97a	0.02	0.03	0.06	0.04	0.2
3/15-22/97a	0.01	0.03	0.09	0.04	0.2
5/31-6/4/97a	0.04	0.05	0.30	0.07	0.3
10/31-11/4/97	0.02	0.02	0.05	0.01	0.9
11/19-23/97a	0.02	0.03	0.07	0.01	1.0
12/12-15/97a	0.05	nm	0.08	0.04	1.0
1/14-20/98a	0.01	0.03	0.10	0.01	1.3
5/28-31/98a	0.01	0.03	0.10	0.04	1.0

Notes: b=before application; a=after application.  
nd=not detected; nm=not measured.

Flow-weighted PO<sub>4</sub>-P and BAP concentrations during runoff events were consistent throughout the study. Phosphate-P concentrations peaked in early October 1996

at  $0.07 \text{ mg L}^{-1}$  during a small autumn runoff event (data not shown) but dropped at this point and remained relatively constant between  $0.01$  to  $0.05 \text{ mg L}^{-1}$ . BAP has been remarkably consistent throughout the study and over several seasons; rarely have flow-weighted concentrations exceeded  $0.03 \text{ mg L}^{-1}$ .

Both dissolved  $\text{PO}_4\text{-P}$  and BAP are useful in assessing the potential effect of biosolids application on 27 Creek water quality during runoff events. The average concentration of water soluble  $\text{PO}_4\text{-P}$  in biosolids is 0.5% (Chapter V), while that of labile P (analogous to BAP in natural waters) is approximately 1% on a dry weight basis (labile P as defined here is equal to the sum of sequential  $\text{H}_2\text{O}$  and  $0.5 \text{ M NaHCO}_3^-$ -extractable P fractions). If direct runoff of P from biosolids occurred at any time following application, even slight  $\text{PO}_4\text{-P}$  increases in runoff water should be measurable given: (1) the analytical sensitivity for detecting  $\text{PO}_4\text{-P}$  (detection limit =  $0.005 \text{ mg L}^{-1}$ ) and (2) the study design's emphasis on sampling 27 Creek water over a wide range of discharge rates. Likewise, BAP (which measures labile particulate P in addition to dissolved  $\text{PO}_4\text{-P}$ ) concentrations during runoff events did not change following biosolids application, suggesting that labile, P-rich particles in biosolids are not mobile during periods of heavy rainfall and subsequent runoff.

Flow-weighted total P concentrations range from  $0.05$  to  $0.3 \text{ mg L}^{-1}$  (Table 4.2). Concentrations during runoff events were generally comparable, but tended to be higher after biosolids application. Increases in total P were noted during a late spring 1997 runoff event five months after biosolids application, and again to a lesser extent during two events in 1998. As labile P concentrations have varied little, an increase in total P during certain runoff events may be within the normal concentration range for this watershed.

An examination of P fractions provides some insight. Total P, soluble P, and BAP were measured directly. Through subtraction, the concentration of particulate P (PP) and bioavailable particulate P (BPP) can be calculated ( $TP - SP = PP$ ;  $BAP - SP = BPP$ ). The relative amount of organic versus inorganic particulate P was not determined nor was the concentration of dissolved organic P. The concentration of the PP fraction has increased following biosolids application due to increases in total P. However, the concentration of labile particulate P (BPP) has not changed. Therefore, episodes of elevated total P and PP in Creek runoff water while that of  $PO_4$ -P, BAP, and BPP remain constant suggests that P in Creek water is primarily in particulate form and not labile. It is important to note that the 27 Creek riparian corridor is heavily vegetated and densely covered. In addition, the watershed—including the Creek corridor and ephemeral drainages—was precommercially thinned in March and April 1996 with felled trees left in place.

Most of the P in anaerobically digested, dewatered biosolids is in an inorganic solid phase, and of this fraction, most is found as Al, Ca, or Fe-phosphates of varying stability and reactivity (Frossard et al., 1994; Hinedi et al., 1989a). Organic P in anaerobically digested, dewatered biosolids is a minor fraction on a dry weight basis and occurs primarily as mono- and di-esters and polyphosphates (Hinedi et al., 1989a) and these compounds are readily hydrolyzed upon application and reaction with the soil and theoretically persist for short periods of time. Organic P compounds added in biosolids presumably decompose and release phosphate soon after application, minimizing the potential for movement of P rich particles. Thus, transfer of particles rich in inorganic or organic P from biosolids to surface waters is unlikely and the data support this assumption.

#### 4.3.2.2 Nitrogen

Flow-weighted ammonia-N ( $\text{NH}_3\text{-N}$ ) concentrations, when detected, were low, averaging between 0.01 and 0.07  $\text{mg L}^{-1}$  (Table 4.2). In approximately 30% of water samples taken for this study,  $\text{NH}_3\text{-N}$  has been below detection limits (0.01  $\text{mg L}^{-1}$ ). Ammonia-N concentrations in biosolids are relatively high compared to other nutrients, ranging from 0.5 to 1.5% on a dry weight basis (King County data, 1997). Consequently, runoff waters directly contacting and moving through biosolids would be susceptible to high  $\text{NH}_3\text{-N}$  concentrations immediately after biosolids application. Conversely,  $\text{NO}_3\text{-N}$  concentrations in anaerobically digested biosolids are often below 50  $\text{mg kg}^{-1}$ . Therefore, in assessing effects of biosolids application on water quality,  $\text{NH}_3\text{-N}$  is a useful early indicator, while  $\text{NO}_3\text{-N}$  is useful over the long-term as biosolids decomposes and organic N mineralizes and nitrifies.

Flow-weighted  $\text{NO}_3\text{-N}$  concentrations during runoff events were relatively constant before biosolids application, ranging between 0.23 and 0.35  $\text{mg L}^{-1}$  (Table 4.2). The pre-biosolids application  $\text{NO}_3\text{-N}$  concentration in 27 Creek water generally mirrored that of precipitation. The five-year (1992-96) average annual volume-weighted mean  $\text{NO}_3\text{-N}$  concentration in precipitation at Pack Forest is 0.34  $\text{mg L}^{-1}$  (NADP, 1998). Beginning in November 1997, the average flow-weighted  $\text{NO}_3\text{-N}$  concentration noticeably increased to approximately 1  $\text{mg L}^{-1}$  (Table 4.2). In addition, total N concentrations increased after biosolids application (Figure 4.5). The increase in  $\text{NO}_3\text{-N}$  concentration in 27 Creek is clearly an effect of biosolids in increasing the soil-water  $\text{NO}_3\text{-N}$  concentration due to biosolids decomposition and N mineralization and nitrification processes. Nitrate-N concentrations in 27 Creek after biosolids application are approximately 10% of drinking water standards, however.

### 4.3.3 The effect of discharge on phosphorus and nitrogen concentrations in 27 Creek

#### 4.3.3.1 Phosphorus

The concentration of  $\text{PO}_4\text{-P}$  and BAP in 27 Creek did not change with increasing discharge before and after biosolids application (Figures 4.7 and 4.8). For separate runoff events, changes in  $\text{PO}_4\text{-P}$  and BAP concentrations were not related to changes in discharge at any time ( $r^2 < 0.1$ ). This is not unexpected, as the lack of a relationship between dissolved phosphate concentration and discharge has been reported for a number of forest types (Meyer and Likens, 1979; Schreiber et al., 1976; Hobbie and Likens, 1973). Biologically available P is not commonly used in studies of runoff from forested watersheds. It is useful in this case because of the high concentration (~1%) of labile P in municipal biosolids and the potential for transfer of fine particulates from steep slopes via lateral flow networks (Dunne, 1978).

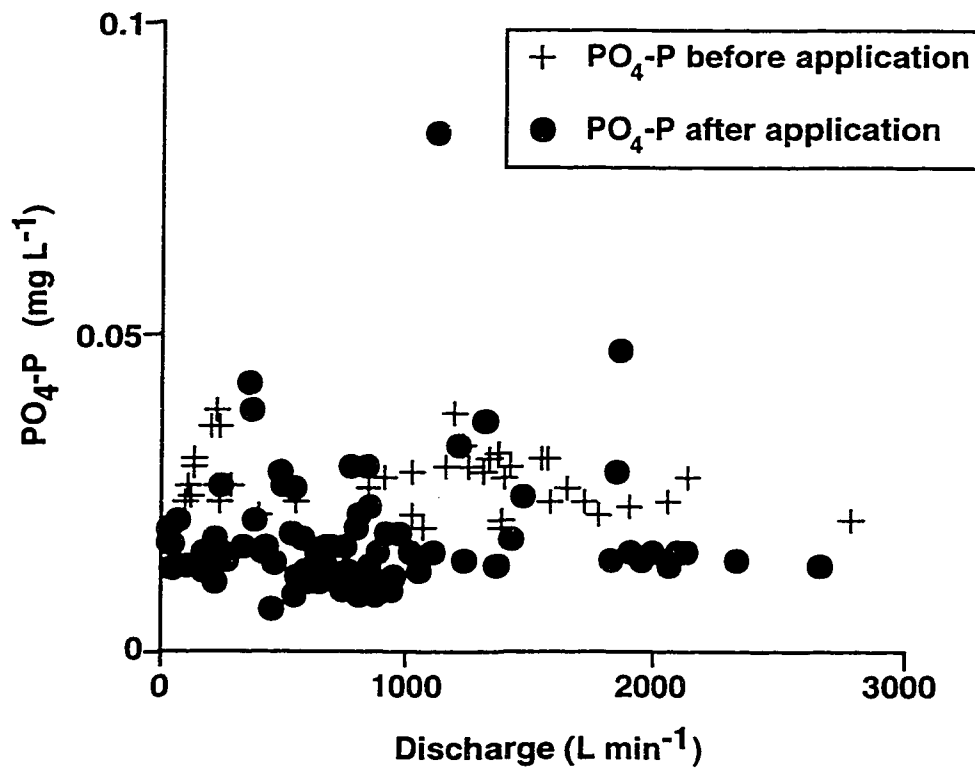


Figure 4.7.  $\text{PO}_4\text{-P}$  versus discharge in 27 Creek before and after biosolids application.

Dilution effects were not observed for  $\text{PO}_4\text{-P}$  and BAP. The lack of any dilution effect suggests that soil water within the Creek's source area and runoff water  $\text{PO}_4\text{-P}$  and BAP concentrations may be in equilibrium. Thus, a reasonable assumption is that mass export of labile P would increase linearly with increasing discharge and variation in amounts exported during runoff events are controlled by changes in discharge. Furthermore, for  $\text{PO}_4\text{-P}$  and BAP a reasonable assumption is that annual variation in discharge is probably more important than variation in runoff event discharge in controlling labile P export from this watershed.

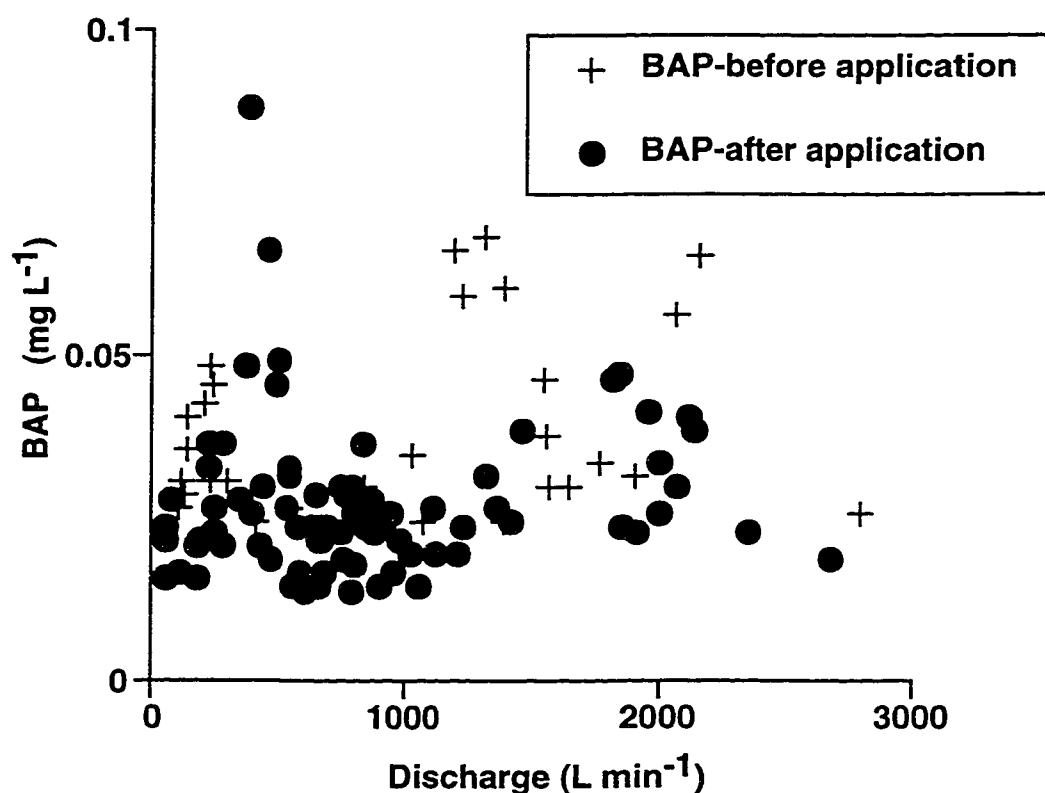


Figure 4.8. BAP versus discharge in 27 Creek before and after biosolids application.

The lack of any concentration discharge relationship is important relative to the mobility of P following biosolids application. In general, low soil solution phosphate concentrations are maintained by the soil's ability to buffer phosphate additions, primarily

through P sorption reactions with Al and Fe oxides in low pH soil environments (Berkheiser et al., (1980). Soil water and subsurface runoff water must maintain a low equilibrium phosphorus concentration and this concentration is nearly equal to that of streamwater under the discharge range within the 27 Creek watershed. Biosolids, while adding approximately 500 kg total P ha<sup>-1</sup>, did not exceed the soil's retention capacity for added P and any phosphate that was released into solution from biosolids was rapidly sorbed by the soil near the application zone.

In general, there is little relationship ( $r^2 < 0.1$ ) between total P concentrations and discharge from the 27 Creek watershed (Figure 4.9). However, in some cases elevated total P concentrations have been measured seasonally and during periods of increased discharge following biosolids application, but there has been no consistent pattern during the runoff events selected for analysis. A runoff event during late May 1997 produced the highest total P concentrations in runoff water measured during the study, but total discharge was moderate compared to other runoff events.

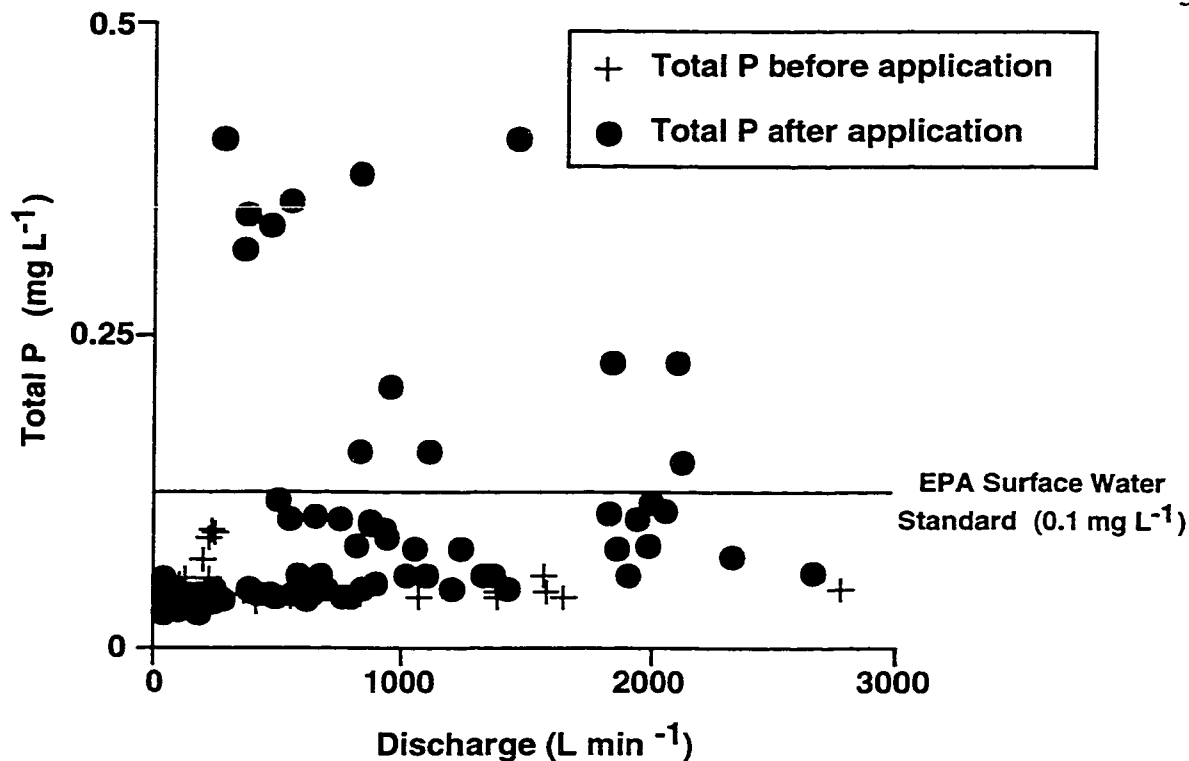


Figure 4.9. Total P versus discharge in 27 Creek before and after biosolids application.

A positive relationship between total P concentration and discharge has been reported for several streams draining forested areas (Meyer et al., 1988; Meyer and Likens, 1979) and the increase in total P concentration has usually been attributed to mobilization of organic detritus (particulates) from source areas in stream networks. Mobilization of particulate P is commonly part of the natural cycle of P export from most forested watersheds and mass export is strongly dependent upon episodic runoff events.

The trend apparent from Figure 4.9 is the elevation of total P concentrations after biosolids application over most of 27 Creek's discharge range. Elevated total P concentrations have been measured during both spring seasons after biosolids application, as well as during runoff events in November 1997 and January 1998. This may be an effect of biosolids in increasing the equilibrium P concentration supported in the soil

solution for a P fraction other than  $\text{PO}_4\text{-P}$  or BAP (such as soluble organic P that was not hydrolyzed during determination of soluble P using the Murphy and Riley (1962) procedure. Another possible explanation may be P release from Creek sediments or organic matter mineralization in response to warm temperatures (spring events) and abundant detrital sources near the stream corridor (autumn and spring events). Research has shown that stream sediments can sorb and release added phosphate under some conditions (Meyer, 1979).

Lack of pre-application spring runoff data hinders the analysis of biosolids effect on total P in runoff waters. However, the variation in the total P concentration-discharge relationship after biosolids application and the consistency in BPP concentrations suggests that runoff events do not induce widespread movement of P from application areas nor would these events likely change the P export pattern. Certainly it would be expected that an increasing mass of total P is exported from the watershed during high discharge events and the relationship between mass export of P on a per hectare basis and discharge would be linear. Changes in observed total P concentrations in 27 Creek following biosolids application may have more to do with seasonal and event-related source area dynamics than with biosolids application.

#### 4.3.3.2 Nitrogen

There is no relationship between  $\text{NH}_3\text{-N}$  concentrations and discharge ( $r^2 < 0.1$ ) from the 27 Creek watershed (Figure 4.9). The absence of a concentration-discharge relationship prior to biosolids application is consistent with other studies examining runoff water quality in forested watersheds (Meyer, 1988; Feller and Kimmons, 1979). It is clear biosolids have not altered the  $\text{NH}_3\text{-N}$  concentration-discharge relationship in any way nor has the application of biosolids had any effect on  $\text{NH}_3\text{-N}$  concentrations in 27 Creek. This

situation is similar to that of labile P and suggests that the  $\text{NH}_3\text{-N}$  concentration in 27 Creek is independent of discharge.

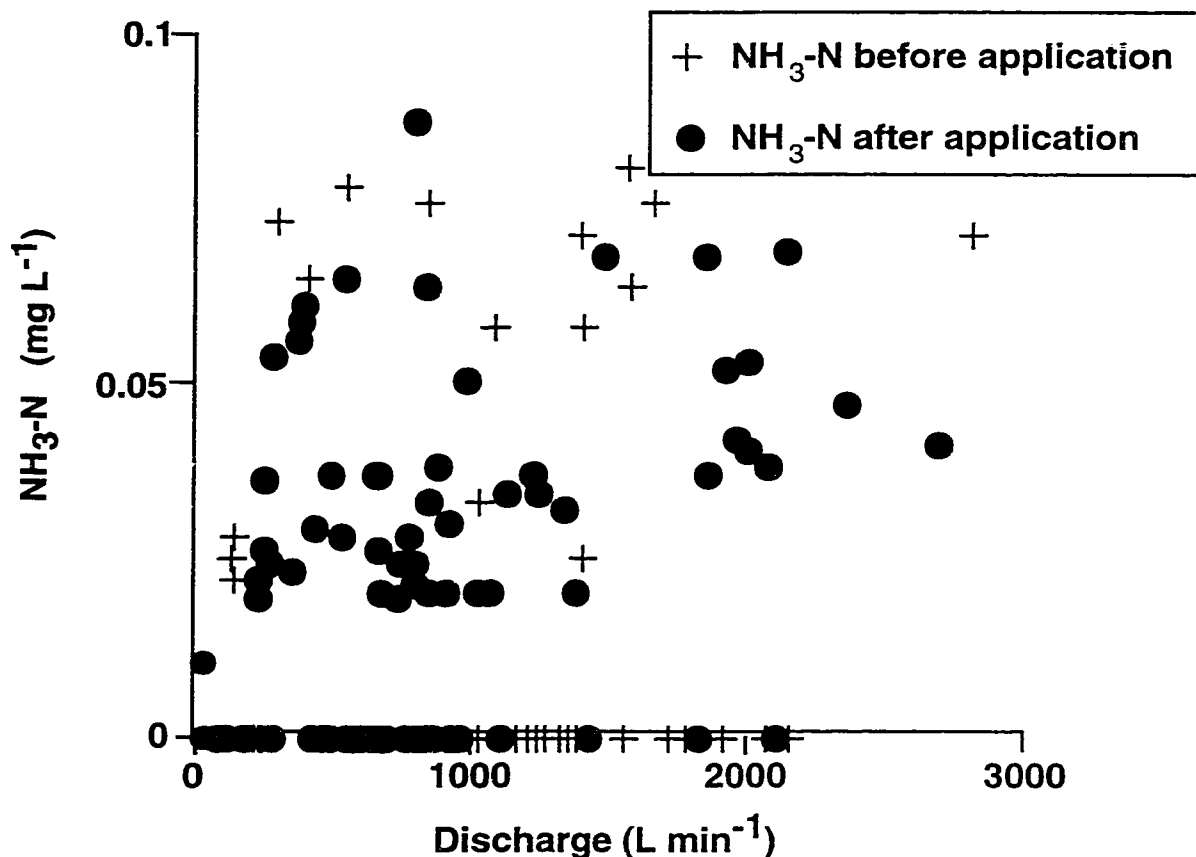


Figure 4.10.  $\text{NH}_3\text{-N}$  versus discharge in 27 Creek before and after biosolids application.

The lack of any change in  $\text{NH}_3\text{-N}$  concentration following biosolids application is an important finding in that biosolids contains high concentrations of  $\text{NH}_3\text{-N}$  and because elevated levels of  $\text{NH}_3\text{-N}$  can be toxic to fish populations. It is also important in determining whether or not biosolids applied to steep forested slopes results in direct runoff of nutrient rich water into streams draining biosolids treated areas. Clearly, this has not occurred for  $\text{NH}_3\text{-N}$ , both in the wet months immediately after biosolids application and over several seasons.

The relationship between  $\text{NO}_3^-$ -N concentrations in 27 Creek and discharge has been altered by biosolids application (Figure 4.11). Before application, the  $\text{NO}_3^-$ -N concentration in 27 Creek was not related to changes in discharge as shown by the horizontal scatter of pre-application data over a wide discharge range;  $\text{NO}_3^-$ -N concentrations in 27 Creek rarely exceeded  $0.5 \text{ mg L}^{-1}$ .

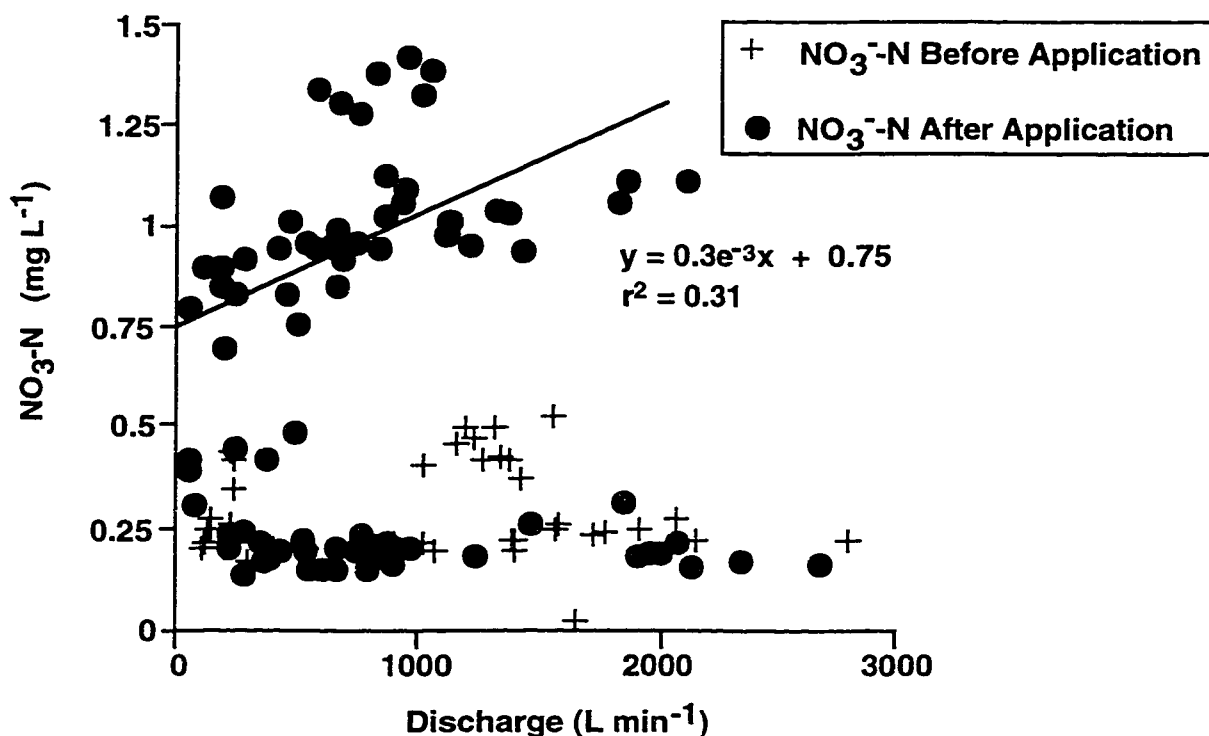


Figure 4.11.  $\text{NO}_3^-$ -N versus discharge in 27 Creek before and after biosolids application.

Nine months after biosolids application, a noticeable increase in  $\text{NO}_3^-$ -N concentrations occurred, and in general, increases in discharge result in increases in  $\text{NO}_3^-$ -N concentrations in 27 Creek ( $r^2=0.31$ ,  $p<0.0001$ ). The elevation of  $\text{NO}_3^-$ -N concentrations was observed beginning in October of 1997 and it continued for the duration of the study. The data cluster beginning at approximately  $0.75 \text{ mg L}^{-1}$  and extending upward coincides with the onset of autumn 1997 runoff events.

The lag effect of increasing  $\text{NO}_3^-$ -N soil-water and runoff water concentrations nine months after application is consistent with the current understanding of biosolids nitrogen dynamics and the release of organic N through the mineralization process. Organic N mineralization from anaerobically digested biosolids occurs slowly and, within one year of application for western Washington Douglas-fir forests, approximately 40% of the organic N is mineralized (Henry, et al., 1999). Therefore, organic N mineralization provides a large pool of  $\text{NH}_4^+$ -N from which  $\text{NO}_3^-$ -N is ultimately produced through microbially mediated transformations. The mobility of  $\text{NO}_3^-$ -N in the soil following biosolids application in the Pacific Northwest has been demonstrated repeatedly and for several different soil types (Henry et al., 1994).

Plant uptake, microbial immobilization, and soil storage probably removed a portion of the organic N released through mineralization and nitrification between January and October 1997. No changes in 27 Creek  $\text{NO}_3^-$ -N concentrations were noted during this time (Figure 4.11). The data are scattered horizontally across the full range of 27 Creek discharge rates and concentrations are similar comparing before and after conditions.

Autumn rain storms beginning in late October 1997 mobilized  $\text{NO}_3^-$ -N from soil-water in response to the input of low  $\text{NO}_3^-$ -N concentration rain water, elevating concentrations in subsurface runoff water and noticeably in 27 Creek runoff. The replenishment of soil water  $\text{NO}_3^-$ -N has continued, due in part to the moderate rate of biosolids organic N mineralization and nitrification of  $\text{NH}_4^+$ -N, followed by its release as  $\text{NO}_3^-$ -N during runoff events. Elevated  $\text{NO}_3^-$ -N concentrations in 27 Creek and the development of a positive concentration-discharge relationship should be placed into context, however, with the mass of N applied to the watershed versus mass exported. Approximately 5900 kg of total N was added to the watershed. From October 1, 1997 to

June 30, 1998, 90 kg of  $\text{NO}_3^-$ -N was exported via surface water runoff assuming a constant  $\text{NO}_3^-$ -N concentration of  $1 \text{ mg L}^{-1}$  and total discharge of approximately  $9.0 \times 10^7$  L). Export of 90 kg  $\text{NO}_3^-$ -N is relatively small and includes nitrate produced from biosolids and natural sources. Given background nitrate concentrations below  $0.4 \text{ mg L}^{-1}$ , nitrate loss from biosolids represents less than 1% of the original mass of total N applied.

#### 4.4 Summary

##### 4.4.1 Phosphorus mobility following biosolids application to a forested watershed

Biosolids increase the nutrient capital of a site and the addition of  $400\text{-}475 \text{ kg P ha}^{-1}$  appears to have a limited effect on water quality. The application of biosolids did not change the concentration of  $\text{PO}_4\text{-P}$  or BAP compared to pre-application conditions and it had no effect on the relationship between 27 Creek labile P concentrations and discharge. In fact,  $\text{PO}_4\text{-P}$  and BAP concentrations varied little over the 27 Creek discharge range, suggesting that runoff events do not induce mobilization and transport of biosolids P.

For total P, the same patterns generally hold. However, some runoff events have produced a noticeable increase in total P concentrations relative to pre-application conditions and increases in concentration can be attributed to increases in discharge; this relationship is episodic and appears to be seasonal. These episodes began nearly five months after application and occur primarily in late spring. The relationship (occasionally) between total P and discharge, the consistency of labile P while total P has fluctuated, and the seasonal nature of elevated total P concentrations during runoff events suggest that particulate P may be responsible for increases in total P concentrations in 27 Creek.

One of the primary objectives of this research was to determine if runoff events induce movement of P compounds from biosolids into surface water. No difference in 27

Creek  $\text{PO}_4\text{-P}$  and BAP concentrations were observed before or after biosolids application under any discharge condition. Elevated concentrations of total P were noted after biosolids application, but its appearance was episodic and inconsistent. Moreover, increases in non-labile particulate P coinciding with seasonal runoff events suggest that the source of increase in total P after application may not be related to biosolids, but rather to near-stream detrital P sources. Lack of pre-application runoff event monitoring hinders comparison between the before and after periods, as natural variation in total P may be responsible for the differences noted in total P concentrations, and runoff monitoring was not performed early enough in the study to detect differences due to biosolids application. Consistently low concentrations of  $\text{PO}_4\text{-P}$ , BAP, and BPP in 27 Creek suggest, however, that biosolids are not the sole cause of increases in total P concentrations and export from the watershed during some runoff events.

#### 4.4.2 Nitrogen mobility following biosolids application to a forested watershed

Trends in 27 Creek  $\text{NH}_3\text{-N}$  and  $\text{NO}_3\text{-N}$  concentrations before and after biosolids application and during runoff events show contrasting processes. Ammonia-N appears to be strongly conserved within the watershed, presumably due to plant uptake, microbial immobilization, and retention on soil cation exchange sites. Runoff water concentrations before and after biosolids application were consistently low and in many cases, concentrations were below analytical detection limits. Ammonia-N concentrations after biosolids application are comparable to pre-application concentrations and, in general, concentrations are below established standards for the protection of water quality in Washington state ( $0.05 \text{ mg L}^{-1}$ ; this is pH and temperature dependent). There was no relationship between  $\text{NH}_3\text{-N}$  concentrations and discharge and the application of biosolids had no effect on this relationship.

Conversely,  $\text{NO}_3^-$ -N concentrations noticeably increased after biosolids application, but the mean concentration is an order of magnitude lower than the drinking water standard of  $10 \text{ mg L}^{-1}$  in Washington state. Nitrate has a low affinity for negatively charged soil particles and it is mobilized from the soil and soil water to stream water via displacement by low concentration input waters as a result of heavy rainfall. Runoff event  $\text{NO}_3^-$ -N concentration increased after biosolids application and increases in concentration were positively related to discharge; no relationship existed prior to biosolids application. However, of the nearly 5900 kg total N applied in biosolids, less than 1% was removed from the watershed in surface water runoff as  $\text{NO}_3^-$ -N after biosolids application.

#### 4.5 Conclusions

1.  $\text{PO}_4$ -P, BAP, BPP, and  $\text{NH}_3$ -N are not mobile following biosolids application. Direct runoff of these compounds into 27 Creek during runoff events was not observed.
2. Total P appears to be immobile following biosolids application. Seasonal episodes of elevated total P concentrations were noted during some periods of increased discharge. However, native particulate P entering 27 Creek during runoff events or release of P from sediments cannot be ruled out in elevating total P concentrations.
3. The concentration of  $\text{PO}_4$ -P, BAP, BPP, and  $\text{NH}_3$ -N in 27 Creek is not related to discharge; for most events, discharge had no effect on total P concentrations as well.
4. Biosolids changed the 27 Creek concentration-discharge relationship for  $\text{NO}_3^-$ -N. Before application, no relationship existed. Beginning nine months after biosolids application, increases in discharge were positively related to increases in  $\text{NO}_3^-$ -N concentrations. The longevity of this effect was not determined.

## CHAPTER V

MOBILITY AND FATE OF PHOSPHORUS FOLLOWING  
BIOSOLIDS APPLICATION TO A FORESTED SLOPE

This chapter examines the vertical and lateral mobility of P and N following a single biosolids application to a forested slope. Soil water interflow (herein referred to as interflow) discharge rates and the concentration of phosphate and nitrate in soil water were measured under a wide range of hydrologic conditions before and after biosolids application using lysimeters and interflow collectors installed into a steep hillside at Tiger Mountain State Forest near Preston, Washington. This site has suitable hydrologic characteristics for monitoring interflow during periods of heavy rainfall, which produces marked increases in interflow and surface water runoff discharge. Fourteen months after biosolids application, the vertical mobility of P was assessed and predominant retention mechanisms identified using a sequential fractionation approach. Soil sampling included O horizon material of variable thickness and mineral soil samples from two regions near the forest floor (0-15 and 15-30 cm deep).

## 5.1 Experimental design

## 5.1.1 Hypotheses

Hypothesis 1. The concentration of soil P fractions will be significantly increased by a single biosolids application to a Tokul series soil.

## 5.1.2 Testing of hypotheses

A study site was selected within the Tiger Mountain State Forest. A 0.25 ha area was divided and separate control and biosolids treated areas established (each ~0.1 ha).

Fourteen months after biosolids application, the release of phosphorus from biosolids and its vertical mobility were measured. Organic horizon material (variable thickness to 3 cm) and mineral soil at depths of 0-15 cm and 15-30 cm in six separate locations in control and treated areas, respectively, were removed. This was followed by sequential phosphorus fractionations using chemical extractants and related chemical analysis of O horizon and mineral soil material. Soil phosphorus data were log transformed, then statistical comparisons made using a paired-sample t-test,  $n=6$ . An alpha level of significance of 0.05 was used.

## 5.2 Methods and materials

### 5.2.1 Study site characteristics and plot establishment

The study area is located within the Tiger Mountain State Forest, near Preston, Washington (Figure 5.1). The study site (Figure 5.2) is located within a large area clearcut in 1985 and is dominated by 3rd rotation Douglas-fir (~10-yr-old) and naturally regenerated western hemlock, western red cedar, and a large component of red alder. Some of the forest near the study site was used for operational biosolids application in August and September, 1997. Topography in and near the site is moderately sloping, with slopes ranging from 5 to 50%; the study site is located on a 45% slope. Separate control and treated plots were established side-by-side, with each plot approximately 0.1 ha. The biosolids treated plot was positioned downslope of the control area. A preliminary investigation of the site during operational biosolids application planning revealed strong potential for measuring interflow on forested slopes given the areas northerly aspect, mean annual precipitation of 200 cm, and glacial soil characteristics.

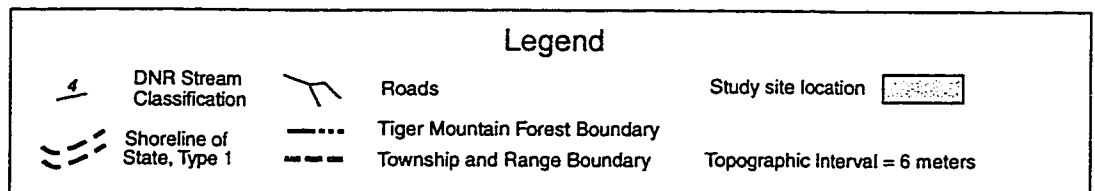
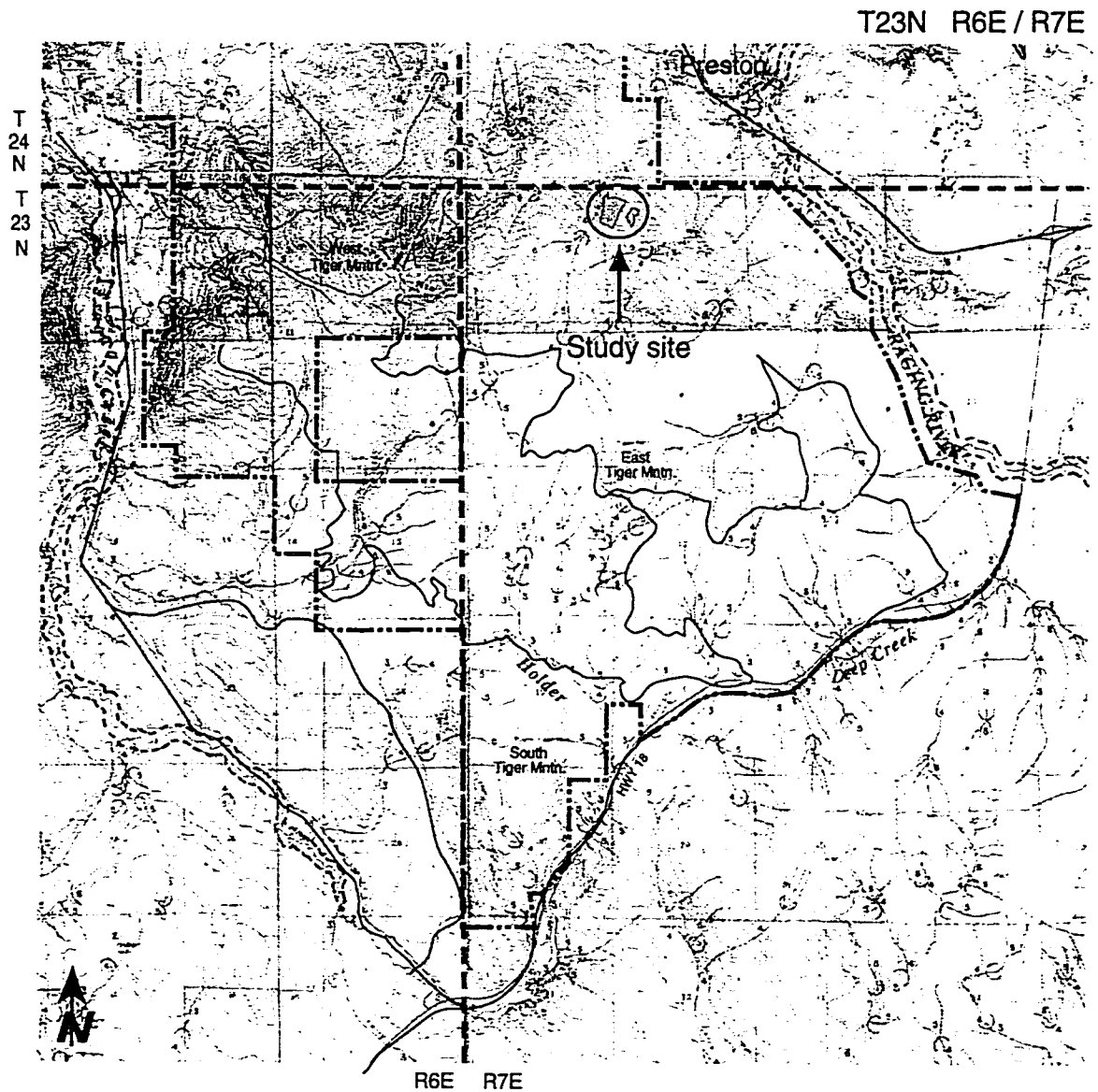


Figure 5.1. Vicinity Map, Tiger Mountain State Forest, King County, Washington

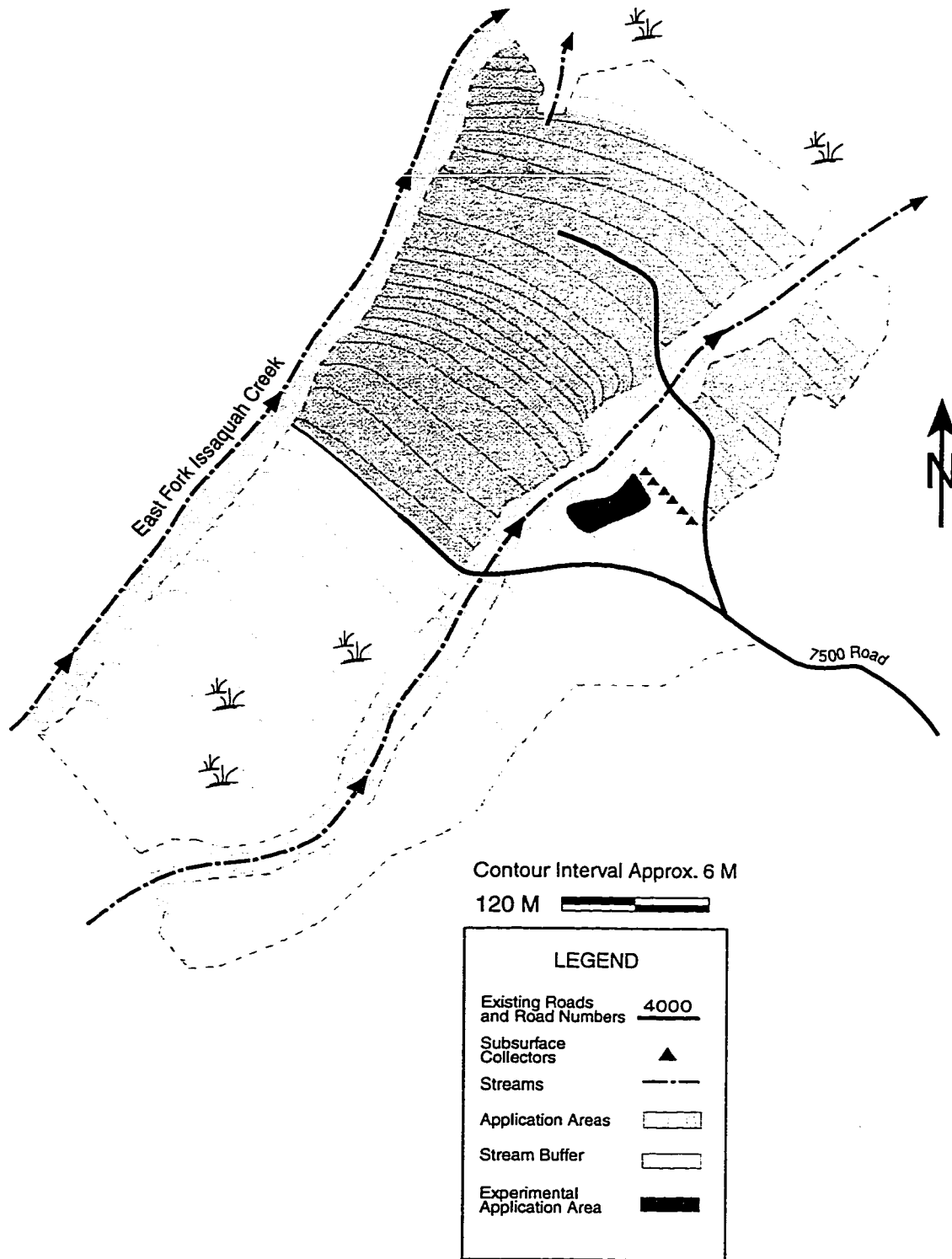


Figure 5.2. Study site location and topography

### 5.2.2 Site Hydrology

Precipitation has been measured at the Tiger Mountain site since November 1996 using an ISCO model 510 rain gauge. Monthly total precipitation recorded between November 1996 and October 1998 is shown in Figure 5.3. Interflow discharge from separate soil horizons was measured periodically between November 1996 and June 1998. The site is remote; thus some runoff events following snow were missed. As many events as possible which produced interflow were monitored during all weather conditions. The rain on snow events that were monitored always produced measurable interflow in all horizon positions. Interflow discharge increases with depth and, in general, appears to vary with season, rainfall amount and frequency, and ground water level at the onset of rainfall. No attempt was made to correlate interflow rates with any of the above variables.

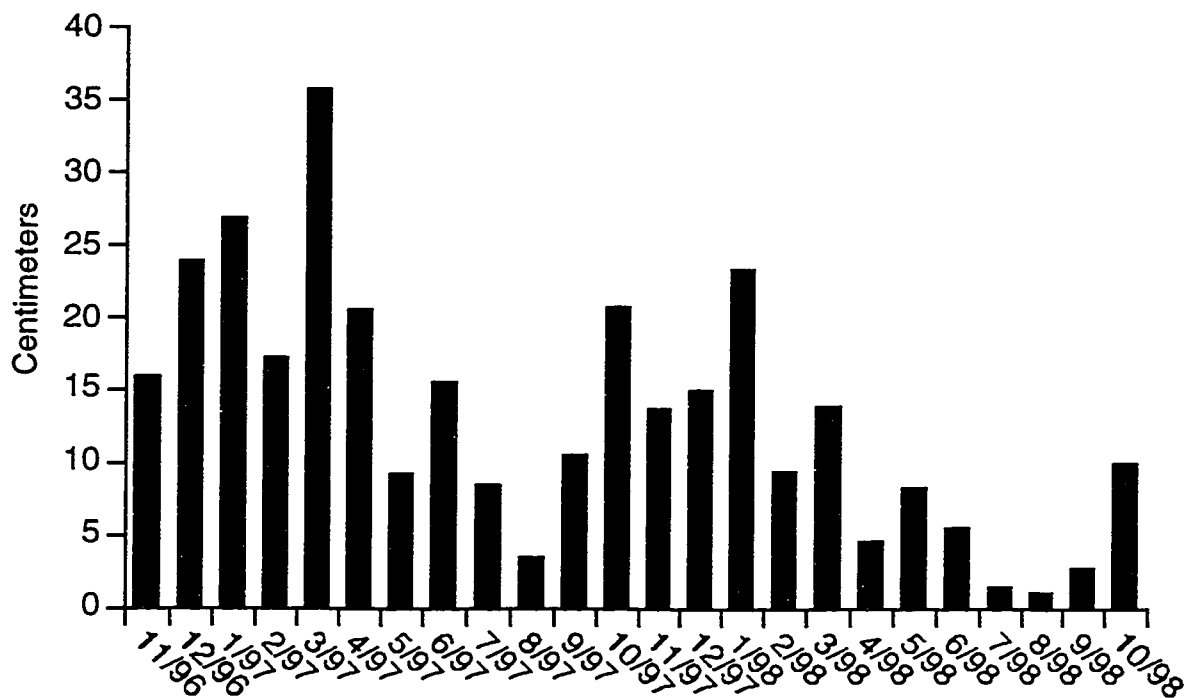


Figure 5.3. Monthly precipitation, Tiger Mountain State Forest, November 1996 to October 1998.

### 5.2.3 Interflow collection technique

In August 1996 six separate interflow collectors were installed within the study site (Figure 5.4). The collectors intercept soil water during saturated conditions and each collector has either three or four separate horizon collectors depending on horizon differentiation at each collector location. The collectors are designed to intercept interflow at points between the A, B, BC or CB (where present), and C horizons (Figure 5.4). The soil was excavated to a depth of approximately 2.5 meters with a trackhoe, with refinements made by hand before construction.

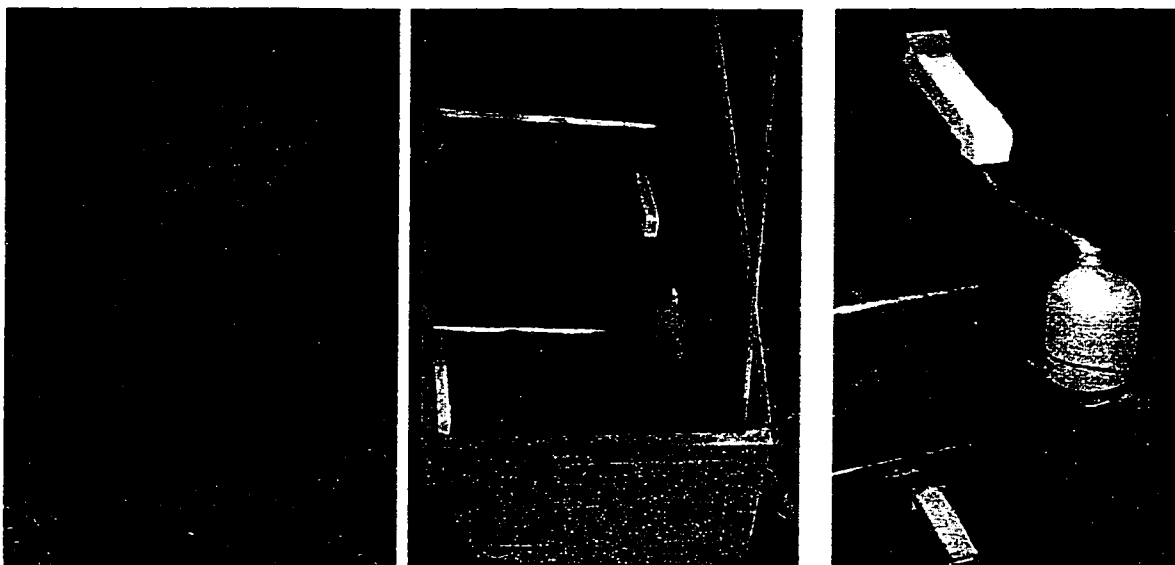


Figure 5.4. Typical interflow collector installed at Tiger Mountain.

The collectors are constructed of ground-contact treated wood and use plastic gutters tightly fitted into excavated channels dug into the soil face. The gutters are connected to the back side of a wood face and an elbow and short piece of pipe are used to transmit water from the gutter to the front side of the wood face to remove water samples and measure flow rates. Fiberglass mesh is packed into the gutters to avoid debris from clogging the water collection and delivery system and an aluminum (roof flashing) plate positioned over the top of the gutter to prevent massive soil movement into the gutter. An

aluminum plate made from roof flashing is driven back into the soil as far as possible and positioned above the gutter. The plate directs water from discrete soil horizons into the appropriate gutter.

It is important to consider how installation of an interflow collector affects the pattern of water movement through the soil. Any technique that involves collecting water flowing from a free face will collect only saturated lateral flow (Atkinson, 1978). Water at the free face must be in equilibrium with atmospheric pressure in order to leave the pore. Thus, soil at this face must be saturated and it follows that a saturated wedge develops above this point. Consequently, the elevation of interflow may be increased due to the installation of interflow collectors and the hydrograph generated is not entirely representative of natural conditions. In fact, it could be argued that this technique changes the pattern of interflow and the movement of ions in soil water by inducing saturated flow during periods when it may not normally occur. This collection technique has been used in similar studies examining the movement of nutrients from wastewater spray application sites (R. Harrison, personal communication).

In May 1997, 10 ceramic cup tension lysimeters (Soil Moisture Co. model 1900) were installed between 15 and 45 cm below the soil surface within the study area. Six were placed within the biosolids treated area and four in a control area. Lysimeters installed in the biosolids treated plot were positioned 2 meters from each collector at the biosolids-buffer interface. All lysimeters were periodically charged at a light tension of 0.01 MPa and soil water removed within one week of charging and more frequently during periods of heavy rainfall.

#### 5.2.4 Soil-water sampling procedures and chemical analysis

Soil water moving in interflow through the study site was collected primarily during heavy rainfall conditions from November 1996 to June 1998. Interflow measurements were made for 24 months following installation of collection devices and for nearly 12 months after biosolids application. Samples were removed from all soil horizon positions within collectors draining both control and treated areas, before and after biosolids application. Water samples were collected during some runoff events in large plastic bottles and transferred to “Whirl-pak” brand plastic bags before analysis, or samples were placed in sterile “Whirl-paks” at the time of sampling. Because the site was remote, occasionally water bottles filled up and overflowed before sampling, so the water sampled may reflect a grab versus composite sample. Discharge rates were recorded at the time of sampling whenever possible. The clarity of water samples was always excellent, thus no filtration to remove suspended particles was needed. Undiluted water samples were analyzed at the University of Washington’s College of Forest Resources laboratory for  $\text{PO}_4^{3-}\text{-P}$ ,  $\text{NO}_3^{-}\text{-N}$ ,  $\text{SO}_4^{2-}\text{-S}$ , Br, Cl, and F using ion chromatography (Dionex Model 2100); instrument detection limits for these anions are shown in Table 5.1.

Table 5.1. Ion chromatography equipment detection limits.

<u>Parameter</u>	<u>mg L<sup>-1</sup></u>
Br	0.01
Cl	0.01
F	0.002
$\text{NO}_3^{-}\text{-N}$	0.003
$\text{SO}_4^{2-}\text{-S}$	0.006
$\text{PO}_4^{3-}\text{-P}$	0.01

### 5.2.5 Tracer examination

Conservative tracers were used to better understand the pattern of interflow movement through the site and to assess the likelihood of water contacting biosolids treated soil and moving to control interflow collector positions. The tracers used initially were bromide, fluoride, and chlorine. Ten L of 100 mg L<sup>-1</sup> solutions of NaBr, NaF, and KCl were applied evenly using a backpack sprayer to separate 80m<sup>2</sup> areas above specific collectors in the first week of February 1997. After this, water samples removed from collectors during and following runoff events were analyzed for Br, F, and Cl using ion chromatography; measurement of these parameters was done four months prior to application to attempt to establish background concentrations in soil water.

Results of the initial tracer application showed that some cross contamination could possibly occur between certain plots above the various collectors, but that transfer of water from the area eventually treated with biosolids into the control area was unlikely. Thus, separate control and treated areas were established rather than assigning control and treatment plots randomly. Subsequent application of 30 liters of 100 mg L<sup>-1</sup> NaBr during November 1997 to the 720 m<sup>2</sup> area above collectors 1-3 (which received a biosolids treatment) revealed that water moving through this area does not move into nearby control collectors. On two separate occasions bromide was detected within interflow collectors 5 and 6, respectively, but this is attributed to the initial application of bromide above interflow collector 5 in February 1997. Bromide was never detected in interflow collector 4, which is the closest collector to the biosolids treated area. Details of the investigation and interflow tracer data for Cl, Br, and F are given in Appendix A.

### 5.2.6 Soil characteristics and sampling procedure

Soils at the study site are mapped as the Tokul soil series, coarse-loamy, mixed, mesic, ortstein Typic Haplorthods (SCS, 1986). A soil profile description specific to the study site is given in Table 5.2. A distinguishing feature of the soil at this site is an indurated layer beginning 60-90 cm below the forest floor. From October to June, the ground water level rises in response to rainfall and soil water flows in and above the indurated layer. On sloping terrain, the indurated layer in combination with rainfall and a high ground water table induces interflow, especially during heavy rainfall events and during rain-on-snow events. Mottling was noted throughout CB and C horizons, but was never detected above this in six separate soil pits excavated for soil water collectors. Charcoal was noted throughout the A and B horizons in all soil pits excavated.

Soil sampling was performed 14 months after biosolids application on September 30, 1998. Twelve separate soil pits were excavated in control and treatment areas to a depth of 45 cm (six replicates from control and treated areas, respectively). Soil was removed from the O horizon (variable thickness to 8 cm), 0-15 cm (A horizon), and 15-30 cm (B horizon) depths and placed in plastic bags. All samples were stored aerobically at 4 C° for less than one week before air drying. An important feature was the noticeable amount of undecomposed biosolids remaining on the forest floor 14 months after application. To eliminate possible interferences from biosolids in the chemical analysis of O horizon material and to prevent contamination of mineral soil during sampling, visible biosolids particles were removed prior to sampling. In the laboratory, O horizon material was air-dried, living plants and roots removed, and sieved to <4 mm. Mineral soil was air dried, passed through a 2-mm sieve with gentle shaking, and placed in covered containers until analysis. Selected soil chemical characteristics are shown in Table 5.3.

Table 5.2. Profile description of the Tokul series soil (coarse-loamy, mixed, mesic, ortstein Typic Haplorthods), Tiger Mountain State Forest, T23N R7E. Interflow collector #4.

<u>Horizon</u>	<u>Depth</u>	<u>Description</u>
Oi	3-0 cm	Undecomposed needles and leaves; moss; abundant micro, very fine, and fine roots; smooth boundary
A	0-25 cm	Very dark brown (10 YR 2/2) moist; sandy loam; weak very fine crumb; very friable; nonsticky and nonplastic; many micro, medium roots; many very fine to medium vesicular and interstitial pores; abrupt smooth boundary
Bs	25-71 cm	Dark yellowish brown (10 YR 3/6) moist; sandy loam; moderate fine subangular blocky; very friable; nonsticky and nonplastic; common micro, fine roots; common fine to medium vesicular and interstitial pores; clear wavy boundary
Bw	71-125 cm	Olive brown (2.5 Y 4/4) moist; sandy loam; moderate fine to medium subangular blocky; firm; nonsticky and nonplastic; common micro, fine roots; few fine vesicular pores; abrupt smooth boundary
CB	125-165 cm	Grayish brown (2.5 Y 5/3) moist; sandy loam; strong medium subangular blocky; friable; nonsticky and nonplastic; very few medium roots; few medium interstitial pores; about 25% gravel; clear wavy boundary
C	165-200 cm	Grayish brown (2.5 Y 4/3) moist; sand; indurated; nonsticky and nonplastic; very few roots; many fine to coarse interstitial pores; about 50% gravel

### 5.2.7 Analytical methods used for soil and biosolids analysis

The vertical mobility of phosphorus from biosolids applied at this site was assessed using several methods for soil phosphorus determination. This included a modified sequential extraction procedure (Hedley et al., 1982) using progressively stronger reagents to solubilize phosphorus from inorganic and organic soil pools; biosolids P was also fractionated using this procedure. The fractionation methods used on mineral soil and the interpretation of the various fractions are described in detail in Chapter VI. Microbial P was determined using the chloroform/bicarbonate technique (Hedley et al., 1982).

For this study, air dried O horizon material was sieved to <2 mm and extracted sequentially with 0.5 M NaHCO<sub>3</sub> and 0.1 M NaOH. Separate O horizon material samples were digested in hot acid and liberated orthophosphate determined colorometrically. The 0.1 M NaOH extracts were extremely dark due to solubilization of organic matter during the extraction and this adversely affects color development in the molybdate blue method (Murphy and Riley, 1962). Thus, only total P was determined colorometrically in 0.1 M NaOH O horizon extracts following persulfate digestion and sample neutralization.

Biosolids and soil total P was measured by using an HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub>-HCl acid digestion (EPA Standard Method 3050), followed by colorometric determination of liberated orthophosphate using the method of Murphy and Riley (1962).

Total soil and biosolids N and C were determined by dry combustion (Perkin-Elmer CHN Analyzer Model 2400). Total elements were determined using a HNO<sub>3</sub>-H<sub>2</sub>O<sub>2</sub>-HCl acid digestion (EPA Standard Method 3050) and inductively coupled argon plasma spectroscopy (EPA Standard Method 6010. ICP; Thermo Jarrel Ash ICAP 61E, Thermo

Jarrel Ash, Franklin, MA). Soil and biosolids pH were determined using a VWR model 3000 pH meter. A 1:2 soil/biosolids-distilled deionized water ratio was used with an equilibration time of 30 minutes before pH measurement. Selected soil chemical characteristics are shown in Table 5.3.

#### 5.2.8. Biosolids application and chemical characteristics

Anaerobically digested, dewatered (~20% solids) biosolids from King County's Renton Wastewater Treatment Plant were used; its chemical composition at the time of application is shown in Table 5.3. Biosolids samples were analyzed after air-drying for one week and light grinding to pass through a 2-mm sieve. Values shown in Table 5.3 are expressed on a dry weight basis.

Biosolids were applied ( $13.5 \text{ Mg ha}^{-1}$ ) to 0.1 ha using King County's Aero-spread applicator in late June 1997 and by hand to the remaining portion near the subsurface soil water collectors two weeks later. A two-meter buffer was maintained between the biosolids and interflow collectors. The application rate was approximately . The total phosphorus loading was approximately  $500 \text{ kg ha}^{-1}$  while that of nitrogen was  $675 \text{ kg ha}^{-1}$ .

Table 5.3. Selected characteristics (total elemental concentrations and pH) of King County biosolids and Tiger Mountain soil. Standard deviations given. Biosolids n=8; Soil n=5.

	C	N	P	Al	Ca	Fe	pH
	-----%						
<u>Biosolids</u>	34±4	5.2±0.3	3.7±0.6	1.5±0.1	2.8±0.2	2.6±0.2	8.6±0.2
<u>Tiger Soil</u>							
0-15 cm	7±2	0.3±0.1	0.06±0.01	2.9±0.4	0.3±0.1	2.0±0.1	5.5±0.2
15-30 cm	6±2	0.3±0.1	0.06±0.01	3.8±0.3	0.3±0.1	2.1±0.1	5.5±0.1

### 5.2.9 Data and statistical analysis

Untransformed water quality data was used in all cases for this study. No attempt was made to perform statistical comparisons on water quality data because of lack of replication for control and biosolids treated plots. Interflow discharge values were log transformed using the following formula:

$$\log(1 + X), \text{ where } X = \text{discharge in ml sec}^{-1}$$

For the assessment of phosphorus vertical mobility following a one-time biosolids application, a paired soil sampling procedure was used. Six replicate soil pits each were randomly selected and excavated in control and biosolids treated areas, respectively. Soil phosphorus and related chemical data were log transformed, then analyzed using a paired-sample t-test,  $n=6$ . An alpha level of significance of 0.05 was used in all cases.

## 5.3 Results and Discussion

### 5.3.1 Phosphorus forms in biosolids applied at Tiger Mountain

The concentration and forms of P in biosolids using a modified Hedley et al., (1982) sequential extraction procedure are shown in Figure 5.5. The fractions, in descending order, remove progressively more biologically and chemically resistant P forms. Water and sodium bicarbonate remove the most biologically available (theoretically the most mobile) P forms first, followed by more resistant fractions. A deionized water extraction was performed instead of using anion exchange resins because of particle adherence to the resin bags, which can introduce error into subsequent sequential extractions due to sample mass loss. It is clear that P is found in high concentrations in biosolids, and these dwarf that of total soil P found at Tiger Mountain (Table 5.3).

Combined, the water and sodium bicarbonate extractable (labile P) fractions represent more than 1% total P of biosolids on a dry weight basis. Thus, it was expected that vertical migration of labile phosphorus would result following biosolids application, with enrichment of the most labile fractions in near surface soil horizons. Also it was expected that movement of phosphate would occur in soil water during periods of elevated interflow discharge.

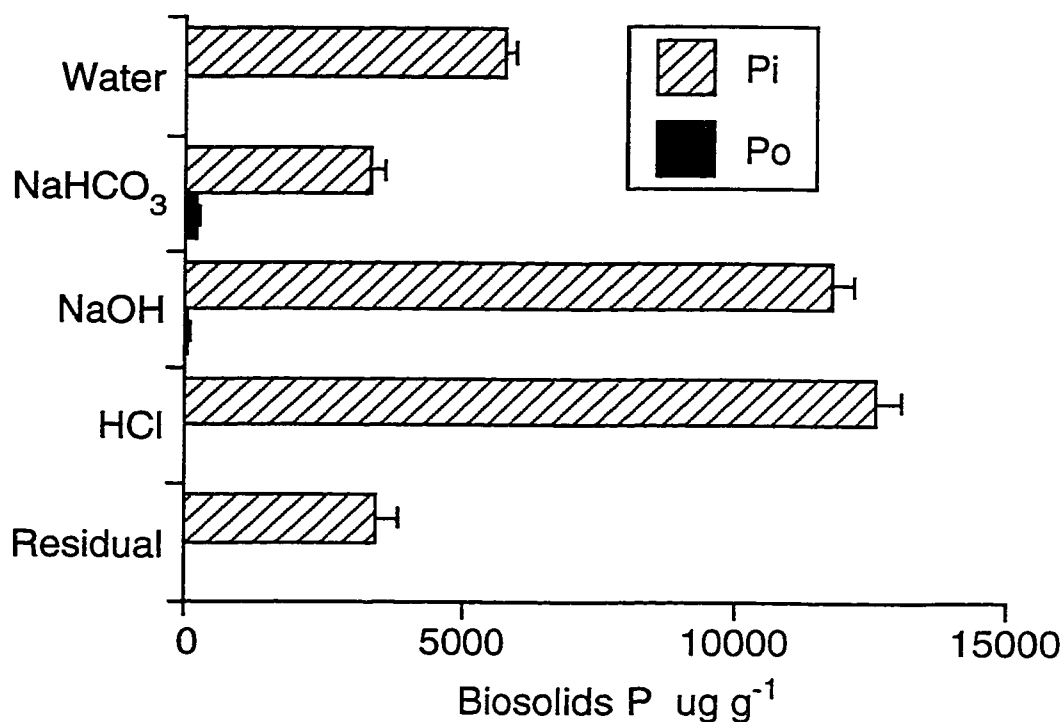


Figure 5.5. Concentration of phosphorus fractions in King County biosolids applied at Tiger Mountain State Forest. Pi =inorganic P; Po=organic P. (n=6). One standard deviation above the arithmetic mean shown.

### 5.3.2 Phosphate movement in interflow

Phosphate-P concentrations were below the detection limit of 0.01 mg L<sup>-1</sup> in nearly 90% of the samples analyzed. All individual water samples from horizon positions within the six interflow collectors with PO<sub>4</sub>-P concentrations above 0.01 mg L<sup>-1</sup> are shown in Table 5.4. The data suggest that PO<sub>4</sub>-P, when detected, is found primarily in near surface soil water. The detection of PO<sub>4</sub>-P as well as its concentration in interflow declines with

depth, probably because of strong inorganic and biotic retention near the soil surface and within the rooting zone. Phosphate-P was never detected in interflow below 60 cm, which at this site generally corresponds to the interface between the B or BC/CB horizons and indurated till layer. The absence of phosphate in interflow appears to be consistent with current theories on the affinity of the phosphate ion in forest soil solutions for positively charged oxide surfaces (Johnson et al., 1986) and on its limited mobility and conservation within forested ecosystems in the PNW (Edmonds and Blew, 1997; Edmonds, et al., 1995; Feller and Kimmons, 1979).

Table 5.4. Individual water sample PO<sub>4</sub>-P detected in interflow collector positions greater than 0.01 mg L<sup>-1</sup> from 11/96 to 6/98.

Position	Collectors					
	Biosolids-treated			Control		
	1	2	3	4	5	6
	----- mg L <sup>-1</sup> -----					
A/Bs	0.12	0.03b	0.03	0.01b	0.01b	0.01
		0.03b	0.04	0.03	0.01	0.02
		0.05	0.07	0.04	0.02b	0.04
		0.09		0.05	0.02	0.07
				0.05b	0.03	0.07
				0.07b	0.04	1.72
				0.44b	0.04	
					0.05	
					0.08b	
Bs	0.01	0.02		0.01		
	0.03			0.02		
	0.03			0.03		
	0.04b			0.07b		
	0.29					
Bw/BC	0.01			0.04		
				0.01		

Notes: Collectors 1-3 drain the biosolids treated plot; collectors 4-6 drain the control plot. Position 1 was located at the interface of the A/Bs horizons and positions 2 and 3 at the interface of the Bs/ Bw and Bw/BC interface, respectively. The letter b following a value denotes the sample was taken before biosolids application. Concentrations are sorted from low to high for each collector position.

Whenever possible measurement of interflow discharge was performed concurrently with water sampling. Interflow PO<sub>4</sub>-P concentrations are not related to changes in discharge (Figure 5.6). Thus, the evidence here suggests PO<sub>4</sub>-P in the soil solution may be limited to near surface horizons and that its mobility via interflow in this

zone is sporadic at best. As expected, the highest rates of interflow discharge were measured at the deepest collector positions and the lowest rates closer to the soil surface.

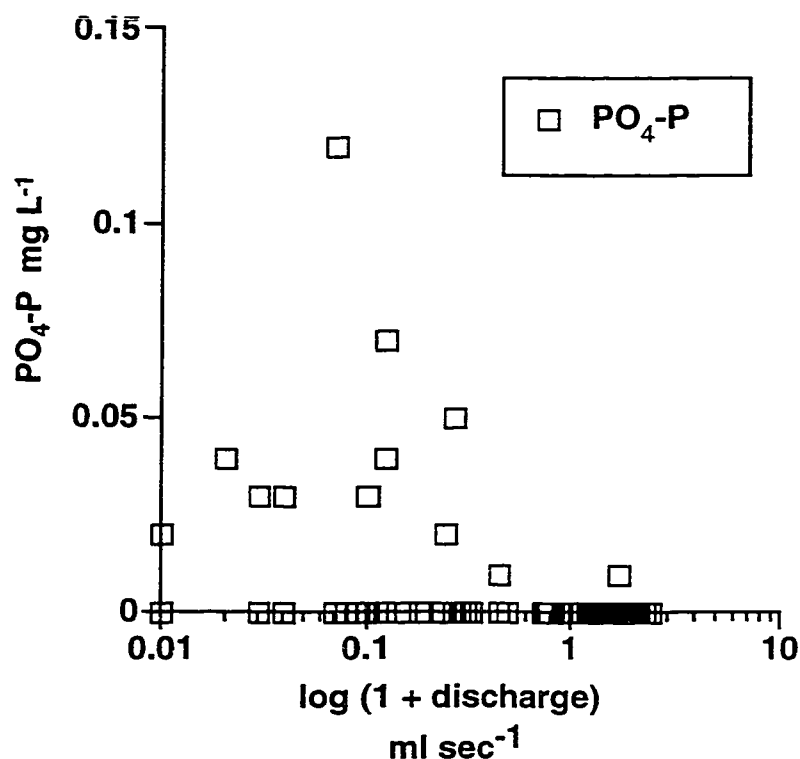


Figure 5.6. Phosphate-P concentration in interflow versus discharge at the time of sampling. Data points represent individual samples taken from soil horizon positions A/Bs or Bs/Bw within collectors draining both control and treated plots, November 1996-June 1998.

Despite the limited detection of PO<sub>4</sub>-P in interflow, it is believed that low concentrations of PO<sub>4</sub>-P exist in the soil solution. For example, Grey and Henry (1998) showed that surface water runoff near this site during heavy rainfall events contains trace amounts of dissolved PO<sub>4</sub>-P below 0.01 mg L<sup>-1</sup>, which is the detection limit for ion chromatography. Concentrations as low as 0.003 mg L<sup>-1</sup> have been consistently detected using the ascorbic acid procedure (Murphy and Riley, 1962). This method is more sensitive with respect to detecting PO<sub>4</sub>-P in natural waters than ion chromatography, with a

method detection limit of  $0.002 \text{ mg L}^{-1}$ . Stream water is an integration of water moving through the entire watershed, both over the surface and through the soil. Presumably this would include inputs of interflow during runoff event conditions in addition to other major sources such as groundwater baseflow and surface and subsurface stormflow.

To remove soil solution phosphate P concentrations during runoff event conditions, porous ceramic cup tension lysimeters were installed in control and treated plots in May 1997. Phosphate concentrations in soil water to a depth of 45 cm from November to June 1998 are shown in Table 5.5. The data, analyzed from samples collected during wet, rainy periods using ion chromatography, show that phosphate is present in the soil solution to a depth of 45 cm. This depth closely corresponds to the depth of horizon position A/Bs in each of the interflow collectors. However, these data are not comparable to water quality data from the interflow collectors due to differences in water collection method, i.e. zero tension saturated flow versus 0.01 MPa tension at the time of sampling using lysimeters. Tension lysimeters would tend to remove pore water and phosphate ions held more strongly within the soil matrix than would zero tension lysimeters sampling soil water that is in equilibrium with atmospheric pressure. Thus, using light tension, phosphate was consistently recovered from the soil solution while in interflow it was rarely detected. This suggests, as expected, that phosphate-P is held strongly via electrostatic forces near the soil surface. Thus, desorption or physical detachment into the soil solution is unlikely under saturated conditions given the large flux of low P concentration runoff waters moving via interflow.

Table 5.5. Phosphate-P concentration in lysimeters installed in control and biosolids treated plots, Tiger Mountain State Forest.

<u>Date</u>	<u>Control</u>	<u>Treated</u>
	-----mg L <sup>-1</sup> -----	
11/19/97	0.05±0.02	0.05±0.02
11/20/97	0.02±0.01	0.01±0.01
11/30/97	0.03±0.01	0.02±0.01
12/18/97	0.04±0.01	0.03±0.01
1/6/98	0.03±0.02	0.02±0.01
1/14/98	0.04±0.04	0.10±0.08
2/12/98	<0.01	<0.01
6/24/98	0.05±0.02	0.05±0.01

### 5.3.3 Effect of biosolids application on phosphate mobility in interflow

Lateral water moving through soil macropores and other large openings has been suspected as a pathway for some ions to bypass soil micropores before entering surface water (Jardine et al., 1990; Wilson et al., 1991; Luxmoore, 1981). Conceivably, precipitation contacting biosolids treated soils could be transported to surface waters via this pathway. Within the biosolids-water matrix, the three principal mechanisms for release of biosolids P would be displacement of soluble P held in pores during runoff events, desorption of labile P weakly held on particle surfaces, and dissolution of soluble P compounds.

Following biosolids application in July 1997, there is no clear evidence of biosolids increasing the concentration of interflow phosphate at any time (Figure 5.7). Phosphate was detected at times in near surface interflow before and after biosolids application, but the frequency of detection was sporadic and inconsistent. Even seasonal trends in

phosphate production and mobility were not noted. In most cases, phosphate concentrations were below  $0.01 \text{ mg L}^{-1}$  following biosolids application and in only nine cases during the entire study were sample concentrations from collectors at the A/Bs interface greater than  $0.05 \text{ mg L}^{-1}$  regardless of biosolids application (Table 5.4).

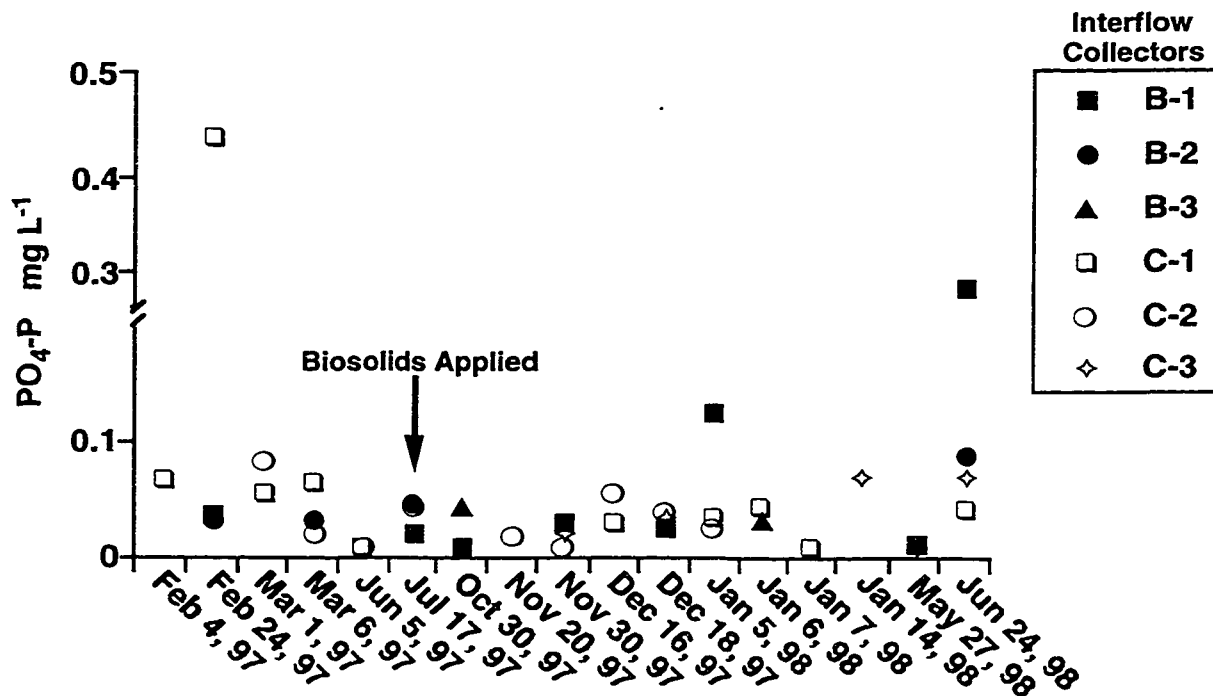


Figure 5.7. Phosphate-P detected in individual samples from soil horizon positions A/Bs and Bs/Bw in interflow collectors B,1-3 and C, 1-3, 2/97-6/98. Collectors B1-3 draining the biosolids treated area are represented by solid symbols; clear symbols represent control collectors C1-3.

During periods of elevated interflow discharge following biosolids application, the mobility of phosphate continued to be minor (Figure 5.8). It was expected that elevated concentrations of phosphate would be detected at low discharge rates because of the concentration of labile P in biosolids (~1%). However, a sharp increase in concentration at low discharge rates was only observed on one occasion (Figure 5.8).

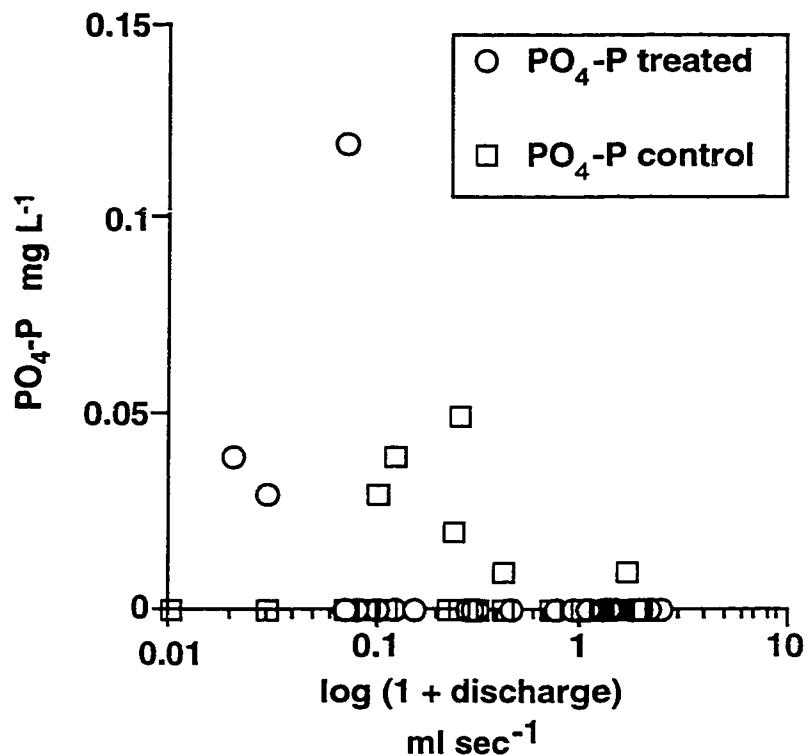


Figure 5.8. Phosphate-P concentration in interflow versus discharge at the time of sampling following biosolids application. Data points represent individual samples taken from soil horizon positions A/Bs or Bs/Bw within collectors draining either control or biosolids treated plots, July 1997-June 1998.

The data shown in Figures 5.7 and 5.8 suggest a single application of biosolids has done little to affect the equilibrium between solid phase P and P in the soil solution. In addition, the labile P fraction in biosolids (~1% of biosolids on a dry weight basis) apparently did not move far from the zone of application. The amount of P from biosolids that did move appears to be accounted for in moderate increases in P concentration in the O horizon material (Table 5.7) as well as in small, but statistically non significant increases in P fractions in the soil from the 0-15 cm sampling depth (Table 5.6). As little phosphate was detected in interflow after biosolids application, it is presumed that an equilibrium was rapidly attained between P released from biosolids and soil retention sites. The rate of phosphate adsorption has been reported to be relatively fast, on the order of hours and days, although some reactions can persist for months (Berkheiser et al., 1980).

It is also possible that P release from biosolids was slow and the mass released was insufficient to elevate mineral soil P pools, or that the mass of P released and measured in the O horizon material was equivalent to the mobile P fraction in biosolids. Phosphorus release rates from anaerobically digested biosolids have been reported to be between 20 and 40% of total P after 80 days under ideal laboratory conditions (Rydin and Ottabong, 1997; Rydin, 1996). A mass balance calculation using these release rates combined with study data and assumptions about O horizon bulk density is imprecise, yet instructive. Some assumptions are necessary: (1) total P range in biosolids shown in Table 5.3; (2) 0.1 ha area applied with biosolids; (3) assumed total P release rate (20-40%); (3) O horizon bulk density (0.25-0.5 g cm<sup>-3</sup>). Using, these assumptions, the concentration increase in total P in the biosolids treated plot could be accounted for using release rates between 20 and 30% across a range of bulk densities.

#### 5.3.4. Effect of biosolids application on nitrate mobility in interflow

Nitrate in interflow was observed following biosolids application (Figure 5.9) and the interflow collectors draining water from the biosolids treated plot appear to be efficient in detecting nitrate movement from this site under a range of discharge conditions. The data show that biosolids increased the production of nitrate and its application at this site changed the concentration-discharge relationship during periods of increased interflow discharge. Data from control collectors show a horizontal pattern of nitrate concentrations across the discharge range. Conversely, nitrate concentrations in soil water from biosolids treated collectors show a positive relationship, as high discharge was coincident with elevated nitrate concentrations. Thus, runoff events following biosolids application can be responsible for mobilizing nitrogen from biosolids via interflow at this site.

The nitrate data reported here agree well with those of the 27 Creek Watershed study presented in Chapter IV. On a watershed scale, the increase in  $\text{NO}_3\text{-N}$  concentrations in stream water was observed nine months after biosolids application and increases in concentration were coincident with increases in discharge. The results of both studies are similar and together suggest that runoff events are important in mobilizing nitrogen from biosolids application sites, both locally and on a watershed scale. However,  $\text{NO}_3\text{-N}$  concentrations in interflow and surface water runoff following a biosolids fertilization at agronomic rates meet water quality standards and are often at least an order of magnitude below the U.S. EPA drinking water standard of  $10 \text{ mg L}^{-1}$ .

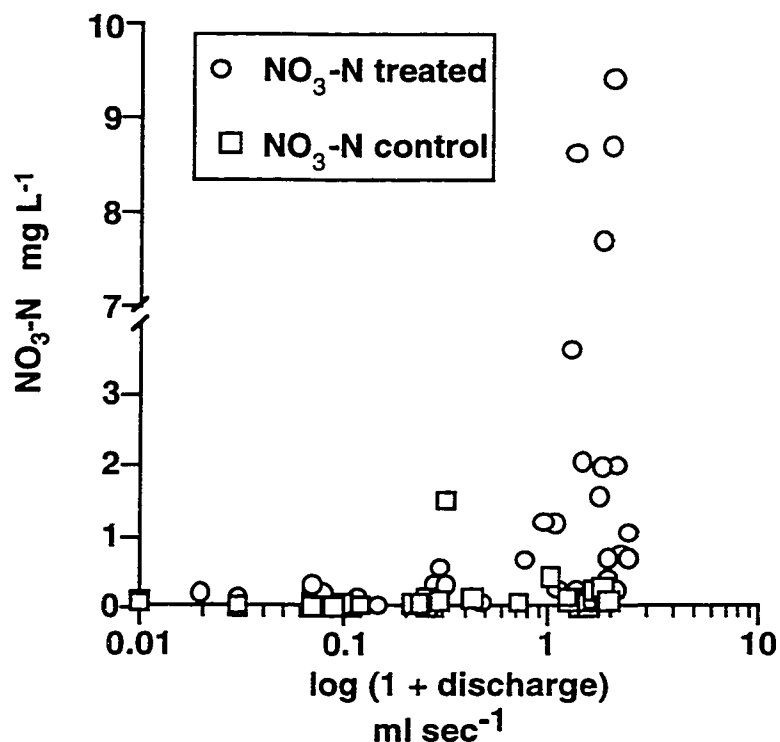


Figure 5.9. Nitrate-N concentration in interflow versus discharge at the time of sampling following biosolids application. Data points represent individual samples taken from all soil horizon positions within collectors draining either control or biosolids treated plots, July 1997-June 1998.

### 5.3.5 Vertical mobility of phosphorus applied in biosolids at Tiger Mountain

The vertical release of P into the soil was investigated 14 months after application of biosolids. Fractionation of soil P forms using a sequential extraction procedure revealed the limited effects of biosolids application on the concentration of P forms in the soil. There were no significant differences in the concentration of any P fraction comparing control and biosolids treated soils in the 0-15 cm sampling depth (Table 5.6). Slight mean concentration increases were noted in almost all P fractions, but this may simply reflect site variation in soil P rather than any effect of biosolids. There were no significant differences in the mean concentration of any P fraction in the 15-30 cm sampling depth as well (Table 5.6).

Microbial P in air-dried soil samples accounted for a minor portion of labile organic P at both sampling depths, and replicate sample concentrations were often less than 10 mg kg<sup>-1</sup> for both control and treated soils (data not shown). Such low microbial P concentrations were not expected, as Compton (1994) reported microbial P concentrations of 205 and 50 mg P kg<sup>-1</sup> in glacial soils that received 400 kg ha<sup>-1</sup> of triple super phosphate 16 months earlier.

Table 5.6 Mean soil P fraction concentrations in biosolids treated and control soils at two sampling depths 14 months after biosolids application. Microbial P data not shown. Significant differences between control and biosolids-treated soil were determined using a paired Student's *t*-test on log transformed data (\**p*<0.05) *n*=6.

<u>Fraction</u>	<u>Interpretation</u>	<u>Sampling Depth</u>			
		<u>0-15 cm</u>		<u>15-30 cm</u>	
		<u>Control</u>	<u>Treated</u>	<u>Control</u>	<u>Treated</u>
----- mg kg <sup>-1</sup> -----					
Resin Pi	exchangeable	14	20	7	8
Bicarb Pi	adsorbed labile Pi	4	9	3	1
Bicarb Po	organic labile P	50	60	40	30
NaOH Pi	Al/Fe-phosphates	280	300	240	250
NaOH Po	humic complexes	100	140	140	140
HCl Pi	Ca-phosphates	40	40	40	30
Residual P	recalcitrant P	200	200	180	160
Total P		700	600	800	600

The absence of any strong effect of biosolids in increasing soil P concentrations, especially the exchangeable and labile fractions, is unexpected. Hypothesis 1 states that the concentration of soil P fractions will be significantly increased by a single biosolids application to a Tokul series soil. Freshly applied biosolids contains nearly 1% labile P and of this, approximately half is water soluble. It is reasonable, therefore, to assume that much of this fraction would be mobilized after application. Conditions assumed to be ideal for P dissolution from biosolids existed at the study site: steady supply of slightly acidic precipitation; nitrogen transformations that decrease pH, which accelerates dissolution of Ca-phosphates (~1.2% of biosolids on a dry weight basis); and fluctuating water table that often results in reduced Eh which has been shown to increase the release of P from anaerobically digested biosolids (Rydin and Ottabong, 1997).

The soil fractionation data show that soil P concentrations were not significantly increased by biosolids application. Thus, hypothesis 1 was not supported. Biosolids did not significantly increase any soil P fraction identified using the Hedley et al., (1982) sequential extraction procedure. Even grouping the fractions into broad labile (Resin plus bicarb P), slowly available (NaOH-HCl), and resistant (residual) pools shows the limited effect, if any, of biosolids in elevating soil P concentrations and increasing P pool sizes in general.

O horizon material was also analyzed for changes in P concentration due to biosolids application. Labile and slowly available P were separated using a two-step NaHCO<sub>3</sub> and NaOH sequential extraction. Duplicate samples were digested in hot acid and total P determined colorimetrically. Statistically significant mean concentration increases ( $p < 0.05$ ) in the labile, slowly available, and total P fractions were observed in O horizon treated with biosolids compared to control soils (Table 5.7).

Table 5.7. Mean O horizon P fraction concentrations in biosolids treated and control plots 14 months after biosolids application. Significant differences between control and biosolids-treated O horizon were determined using a paired Student's *t*-test on log transformed data (\* $p < 0.05$ )  $n = 6$ .

<u>Fraction</u>	<u>O Horizon</u>	
	<u>Control</u>	<u>Treated</u>
	-----mg kg <sup>-1</sup> -----	
Labile P	56	200*
NaOH P	290	900*
Total P	900	2300*

It is important to recognize in interpreting the data that some undecomposed biosolids (<2 mm) probably remained on the surface of the O horizon material removed for

P fractionation. It is suspected these small particles account for the large differences in NaOH and total P concentrations and standard deviations in comparing control and treated soils. Regardless of the probable migration of biosolids particles into the O horizon, the data show the initial vertical migration of P from biosolids into the soil following a single biosolids application is primarily restricted to the biosolids-O horizon interface. Thus, vertical migration of biosolids particles may be a pathway for P movement lower into the soil profile in addition to the movement of P in the soil solution. However, it appears P release deeper into the soil may be a long-term process, because when O horizon data are contrasted with the mineral soil 0-15 cm and 15-30 cm fractionation data, the limited effect of biosolids on soil P status is apparent.

The P fractionation data in Tables 5.6 and 5.7 suggest that phosphate may not have been released in sufficient amounts to significantly increase soil P concentrations below the O horizon. Small, statistically non-significant increases were noted in the mineral soil horizons and the organic horizon was only moderately enriched with P relative to the amount originally contained in biosolids. Moreover, the soil water phosphate data presented in Section 5.3.3 shows the lack of any clear pattern of phosphate released from biosolids. Combined, the data suggest slow release of phosphate from biosolids could also limit P mobility. Unfortunately, release rates of phosphorus from biosolids were not determined explicitly in this study nor were mechanisms governing release rates identified.

## 5.4 Summary

The vertical and lateral mobility of phosphate in forest soil following a single biosolids application to a 12-year-old Douglas-fir stand located on a steep slope was examined. Emphasis was placed on assessing phosphate mobility during periods of heavy rainfall, which at the site selected for study induces interflow. Separate biosolids treated and control plots were established, with three separate interflow collection devices installed below each plot for a total of six collectors. The vertical migration of P into the soil was assessed 14 months after biosolids application using a paired sampling design and sequential phosphorus extraction procedure.

In nearly 90% of the interflow samples collected,  $\text{PO}_4\text{-P}$  concentrations were below detection limits. Segregation of the data into discrete soil horizon collection depths revealed that phosphate, when detected, was found only in near surface soils, generally corresponding to the A/Bs and Bs/Bw horizons at this site. In no case was phosphate ever detected in soil water moving laterally below 60 cm. During periods when water sampling was performed concurrently with interflow discharge measurements, a very weak trend of decreasing phosphate concentrations with increasing interflow discharge was observed. Applying biosolids to one-half of the study site at an approximate rate of  $500 \text{ kg P ha}^{-1}$  had no effect in elevating interflow phosphate concentrations nor did it alter the concentration-interflow discharge relationship. Thus, the pattern of P movement via interflow was not altered by biosolids application.

Nitrate concentrations were also measured in interflow coincident with phosphate measurements. A biosolids treatment of  $675\text{-}700 \text{ kg N ha}^{-1}$  increased interflow nitrate concentrations and this effect was observed approximately six months after application at the onset of autumn rain events. Nitrate-N concentrations in interflow from the control plot

ranged from 0.003 to 3.5 mg L<sup>-1</sup>, while the biosolids treated soil water ranged from 0.004 to 9.4 mg L<sup>-1</sup>. Without the application of biosolids, the interflow concentration-discharge relationship is generally linear over the discharge rates measured. Conversely, a biosolids application changes this relationship markedly, with high discharge rates resulting in elevated nitrate concentrations.

The contrasting patterns of phosphate and nitrate mobility following biosolids application have important consequences relative to the influence of rainfall induced runoff events on the mobility of P and N contained in biosolids. These events are suspected as being the principal pathway for nutrient export and possible loss from an application site. The data suggest runoff events are important in mobilizing N from biosolids application sites via interflow, yet relatively unimportant in mobilizing P. In addition, the data provide support for the theory that nitrogen mobility limits the application of biosolids to PNW forests, while P mobility is relatively minor.

Vertical migration of P from biosolids into the soil beyond the O horizon was relatively minor. No significant differences in P fractions were noted between biosolids treated and control soils at the 0-15 cm and 15-30 cm sampling depths. Slight increases were noted in most fractions in the biosolids treated soil (0-15 cm sampling depth) but this may be due more to soil variation than the effect of biosolids. Fractionation of O horizon material revealed that biosolids had certainly elevated P fraction concentrations in the labile, slowly available, and total P pools, but that further migration into the soil did not occur.

Hypothesis 1 states the concentration of soil P fractions will be significantly increased by a single biosolids application to a Tokul series soil. Study results do not support this hypothesis. There were no statistically significant differences in soil P

fractions comparing control and biosolids treated soils at either the 0-15 cm or 15-30 cm depths. However, O horizon material was enriched with P from the biosolids applied. Thus, the limited mobility of P may be due simply to the lack of release of P from biosolids in addition to attenuation of P within the O horizon and eventually mineral soil horizons.

## 5.5 Conclusions

1. Phosphate added in a single biosolids application to a steep slope is not mobile via interflow in soils with characteristics of the Tokul series.
2. In soils with characteristics of the Tokul soil series, biosolids application does not change the pattern of phosphate movement in interflow nor elevate the concentration of soil water phosphate.
3. The concentration of mineral soil phosphorus fractions to a depth of 30 cm are not significantly increased following biosolids application. This suggests the release of P from biosolids may also limit mobility in addition to soil P retention via sorption mechanisms.
4. Biosolids application increased the production of nitrate. A positive  $\text{NO}_3\text{-N}$  concentration-discharge relationship developed following biosolids application. Rainfall events that produce interflow appear to be an important pathway for the export of nitrogen from biosolids applied to this site.

## CHAPTER VI

VERTICAL MOBILITY AND FATE OF PHOSPHORUS  
IN BIOSOLIDS APPLIED AT PACK FOREST, WASHINGTON

This chapter examines the vertical mobility and fate of P in biosolids applied to forest soils at Pack Forest, Washington. Field soil sampling and laboratory analyses were used to assess the depth of P mobility and identify the dominant mechanisms for P retention following biosolids application. Four sites were evaluated for depth of P mobility and status, with two sites underlain by relatively unweathered glacial outwash soils and two sites underlain by more weathered residual soils formed in andesite and basalt. Within soil types, these sites also provide a contrast with respect to total biosolids P loading and method of application (direct incorporation versus surface application).

## 6.1 Experimental design

## 6.1.1 Hypotheses

- Hypothesis 2. The concentration of phosphorus in the soil following biosolids application at a P loading rate of 2 Mg ha<sup>-1</sup> will decline significantly with depth below the forest floor.
- Hypothesis 3. Biosolids application at a P loading rate of 2 Mg ha<sup>-1</sup> will significantly increase the concentration of sorbed P fractions in the top 15 cm of mineral soil.
- Hypothesis 4. Biosolids application at a P loading rate of 2 Mg ha<sup>-1</sup> will significantly increase soil P availability in the top 15 cm of mineral soil.

### 6.1.2 Choice of research sites

The University of Washington Charles Lathrop Pack Forest has been the site of numerous investigations examining the environmental effects and beneficial uses of biosolids for forest fertilization. Pack Forest is approximately 1720 ha and located at the base of the Cascade foothills about 110 km south of Seattle, WA. The climate is maritime, with relatively dry summers and wet winters. Moderate temperatures normally prevail, as the mean annual temperature is 10° C. Annual precipitation is about 120 cm, with approximately 50% falling between October and January. Summers months (July-September) can be extremely dry, often resulting in drought-like conditions on well drained soils. For normal temperatures and precipitation, evapotranspiration is estimated at 38 to 56 cm annually.

Four study sites were established at Pack Forest to investigate the vertical mobility and fate of P added in biosolids (Table 6.1). Two of the study sites were used to test hypotheses concerning the effect of surface biosolids application at a cumulative loading of 105 Mg ha<sup>-1</sup>. These sites are the Silvicultural Demonstration Site (SDS) and the Gessel site (Figure 6.1). Two other sites were also used to assess the fate of P following biosolids application: the Hugo Peak site and XA-5 site (Figure 6.1). However, because direct biosolids incorporation was used at these sites and the rates of application are much greater than those used at the SDS and Gessel sites, no hypotheses concerning the fate of P were tested. In addition, it was decided that uneven application coverage, especially at the Hugo Peak site, may introduce extreme variation into the data and could lead to erroneous conclusions concerning the fate of P. The XA-5 and Hugo Peak (Hugo) sites were included for study because they represent some of the heaviest biosolids P loadings possible on acidic forest soils. Both sites offer an opportunity to examine the long-term

(>20 years) effect of biosolids on P forms and availability where biosolids are incorporated directly.

A variable potentially influencing the vertical mobility and fate of P following biosolids application at Pack Forest is soil parent material. For this reason, sites were selected on either outwash or residual soils. Outwash soil has been formed in stratified sand and gravel deposits produced by glaciers. Material from receding glaciers is carried, sorted, and deposited by water that originated mainly from melting of glacial ice. Outwash is commonly found in valleys on landforms known as valley trains, outwash terraces, eskers, kame terraces, kames, outwash fans or deltas (SCS 1979). Residual soil material (or residuum) at Pack Forest is located primarily on ridgetops and slopes at elevations above 300 meters. The soil consists of unconsolidated, weathered, or partly weathered mineral material that accumulates over disintegrating rock (andesite and basalt).

Table 6.1. Study site characteristics.

<u>Site Name</u>	<u>Biosolids Applied Mg ha<sup>-1</sup></u>	<u>Total P Applied<sup>(1)</sup> kg ha<sup>-1</sup></u>	<u>Stand Age yr</u>	<u>Elev. meters</u>	<u>Soil Type</u>	<u>Soil series/texture</u>
SDS	105	1900	70	530	residual	Wilkeson Gravelly silt loam
Gessel	105	1900	70	275	outwash/ ash	Barneston Gravelly sandy loam
Hugo	188-376	3375- 6775	25	510	residual	Wilkeson Gravelly silt loam
XA-5	470	8460	30	275	outwash/ ash	Barneston Gravelly sandy loam

(1) Data sources: (Smith and Brallier, 1991; Harrison et al., 1994).

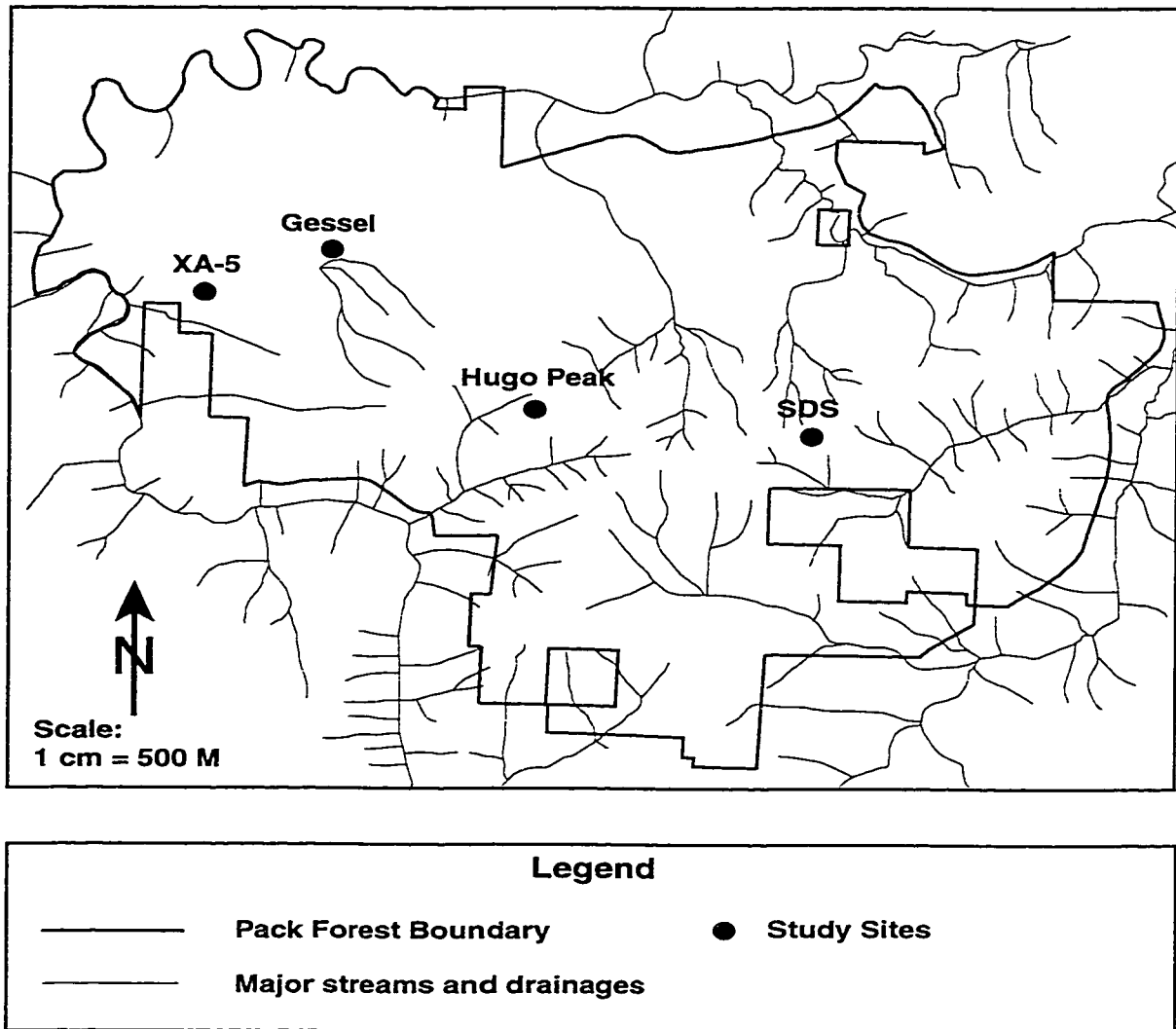


Figure 6.1. Study site locations, Pack Forest, Washington.

The Silvicultural Demonstration Site (SDS) is on residual soils and has received biosolids applied directly on top of understory vegetation and the forest floor. The biosolids loading at this site and at the Gessel site has been approximately  $105 \text{ Mg ha}^{-1}$  on a dry weight basis; dewatered biosolids were applied in 1985 ( $45 \text{ Mg ha}^{-1}$ ), 1990 ( $45 \text{ Mg ha}^{-1}$ ), and 1995 ( $15 \text{ Mg ha}^{-1}$ ) at both sites. The SDS is approximately 50 ha including control areas and supports a stand of 74 yr-old Douglas-fir planted in 1925. The Gessel site is approximately 6 ha including control areas; biosolids have been applied directly on top of understory vegetation and the forest floor. It is on outwash soil and supports 70-80 yr-old Douglas-fir.

The XA-5 site is approximately 1 ha and is on outwash soils. It currently supports a stand of 21 yr-old Douglas-fir with other conifer and hardwood species. In 1975, approximately  $470 \text{ Mg ha}^{-1}$  of liquid biosolids were applied to the site; in 1977 the biosolids were incorporated into the soil to approximately 30 cm using a construction disk. Various herbicides including Paraquat, Simazine, and Roundup have been used for weed control (Smith and Brallier, 1991). Paired, even-aged control and biosolids treated Douglas-fir sites have been maintained, with soil samples removed from multiple locations within both areas.

The Hugo Peak site (Hugo) is approximately 2.5 ha and is on residual soil. The biosolids treated site currently supports 22 yr-old Douglas-fir, while the control area supports Douglas-fir from 25 to 55 yrs-old. Douglas-fir within the biosolids-treated site were pruned in 1986. In 1977,  $188\text{-}376 \text{ Mg ha}^{-1}$  of liquid biosolids were applied to the site and incorporated directly into the soil using a construction disk. Because of the uneven application rate of liquid biosolids and sloping site which caused some biosolids

movement, soil nutrition data from the site over the years has been extremely variable (Smith and Brallier, 1991). Herbicides have been used periodically for weed control.

### 6.1.3 Testing of hypotheses

Biosolids application rates for Douglas-fir forests in the PNW are based primarily on the release and utilization of nitrogen. At this rate, P loading will be greater than plant uptake. Hypotheses 2 is developed around the concept that cumulative surface application of biosolids at a rate of 105 Mg ha<sup>-1</sup> (2 Mg P ha<sup>-1</sup>) will not result in significant vertical migration of phosphate-P into subsoils due to strong inorganic and organic retention of added P near the forest floor.

Hypothesis 2 was tested by removing soil samples from specific soil horizon depths--organic material, surface soil (0-15 cm, A and Bw horizons) and subsurface soil (15-30 cm, Bw horizon)--and chemically fractionating them using a sequential P extraction procedure. The chemical reagents used remove labile forms of P first, followed by moderately labile and resistant soil P forms. Comparisons of vertical P mobility were made between control and biosolids-treated soils separately at each of the four sites. Significant differences in the accumulation of P in separate soil P fractions at each sampling depth indicates the extent of P mobility as induced by biosolids application.

Unless biosolids is intimately mixed with the soil, the pathway for phosphate movement into mineral soil horizons is release of phosphate into the soil solution and movement via infiltrating rainwater. Once in the soil solution, any of a number of retention mechanisms can act to limit phosphate mobility. Separating soil P fractions using a sequential extraction procedure allows identification of "operationally defined" inorganic and organic P pools. This includes such definitions as labile, moderately labile, and

residual P according to ease of extraction; certain P retention mechanisms can be identified based on the relative strength and type of extractant used. Thus, P availability can be estimated, dominant retention mechanisms identified, and the influence of biosolids on soil P transformations determined by comparison with adjacent control soils at the same sampling depths.

With repeated biosolids applications (in this case a cumulative loading of 105 Mg ha<sup>-1</sup>), an increase in available P should be noted near the forest floor as the equilibrium phosphate concentration supported in the soil solution increases due to decomposition of biosolids P. Given an overall increase in P availability, it is expected that phosphate adsorption will be a dominant mechanism for the retention of P following repeated biosolids applications. Free Al and Fe are known to exist in relatively high concentrations within the soils studied and these cations are known to adsorb P (Khalid et al., 1977). Hypothesis 3 is based on the assumption that the release of phosphate from biosolids will result in significant increases in sorbed inorganic P relative to control soils. Hypothesis 4 was developed to test the idea that the addition of biosolids should result in a prolonged elevation of soil P availability near the forest floor.

## 6.2 Methods and materials

### 6.2.1 Soil sampling and sample preparation

Soil sampling was done at the SDS and Gessel sites in April 1998 and the Hugo Peak and XA-5 sites in August 1998. Six separate soil pits were excavated at all sites in control and treatment areas to a depth of 45 cm. Soil was removed from the O horizon (variable thickness), 0-15 cm (generally A horizon), and 15-30 cm (B horizon) depths in reverse order and placed in an unsealed plastic bag. All samples were stored aerobically at 4 C° for less than one week before air drying. In the laboratory, O horizon material was air-dried, living plants and roots removed, and sieved to <4 mm. Mineral soil was air dried, passed through a 2 mm sieve with gentle shaking, and placed in covered containers at room temperature until analysis.

At the SDS and the Gessel sites the A horizon was extremely thin (often <5 cm) and in some pits excavated, completely absent, so the 0-15 cm includes portions of the B horizon. At the SDS site, mottling was noted throughout the soil profile to a depth of 45 cm in both biosolids treated and control soils, thus it is probable that alternating oxidizing and reducing conditions occur at this site despite its position on a ridge top. Charcoal was also noted in the soil pits excavated. Organic horizons are strikingly different at the SDS and Gessel sites comparing biosolids treated and control areas. In biosolids treated areas, the O horizon thickness can be as much as 10 cm, while in control areas the O horizon thickness ranged between 2.5-5 cm. Organic horizons were also different comparing control and biosolids treated areas in the Hugo Peak and XA-5 sites. The O horizons in biosolids treated areas were generally 5 cm thick and contained primarily decomposing needles, while those in the control areas were less than 2 cm in most cases and were

composed primarily of decomposing needles, moss, and roots. Selected soil chemical characteristics in control and biosolids treated soil from 0-15 cm are given in Table 6.2.

## 6.2.2 Analytical methods used for soil and biosolids analysis

### 6.2.2.1 Sequential fractionation

The vertical mobility and fate of P from biosolids applied at the four study sites was assessed primarily using a modified P sequential extraction procedure (Hedley et al., 1982). The extractants and the resulting soil P fractions are shown in Figure 6.2. Resin inorganic P (denoted  $P_i$ ) was extracted by shaking (16 h) 0.5 g soil with 0.4 g resin (Dowex 1-X80-50 mesh) oversaturated with bicarbonate in nylon bags in 25 ml deionized  $H_2O$  (Sibbesen, 1978). Phosphate ions adsorbed on resin were extracted by shaking the bag containing resin with 20 ml of 0.5 M HCl for 1 h. The next steps of the fractionation were performed using the same samples and shaking 16 h with 25 ml of the appropriate extractant. For biosolids sequential P fractionation, a water extraction was performed instead of using anion exchange resin because of particle adherence to the resin bags, which can introduce error into subsequent sequential extractions due to sample mass loss. Separate biosolids samples were mixed with resin bags and exchangeable P determined.

The 0.1 M NaOH soil extracts were extremely dark due to solubilization of organic matter during the extraction and this adversely affects color development in the ascorbic acid method. Carbon black was used to absorb organic matter within the NaOH extracts and samples diluted either 2 or 3 times to reduce color.

Inorganic P was determined in all cases using the procedure of Murphy and Riley (1962), after neutralization when necessary. Total P (Pt) was determined in the 0.5 M  $NaHCO_3$  and 0.1 M NaOH extracts using a persulfate digestion procedure (APHA-

AWWA-WPCF, 1994) followed by colorimetric determination of liberated orthophosphate. Organic P (Po) was calculated as the difference between Pt and Pi in the bicarbonate and hydroxide extracts.

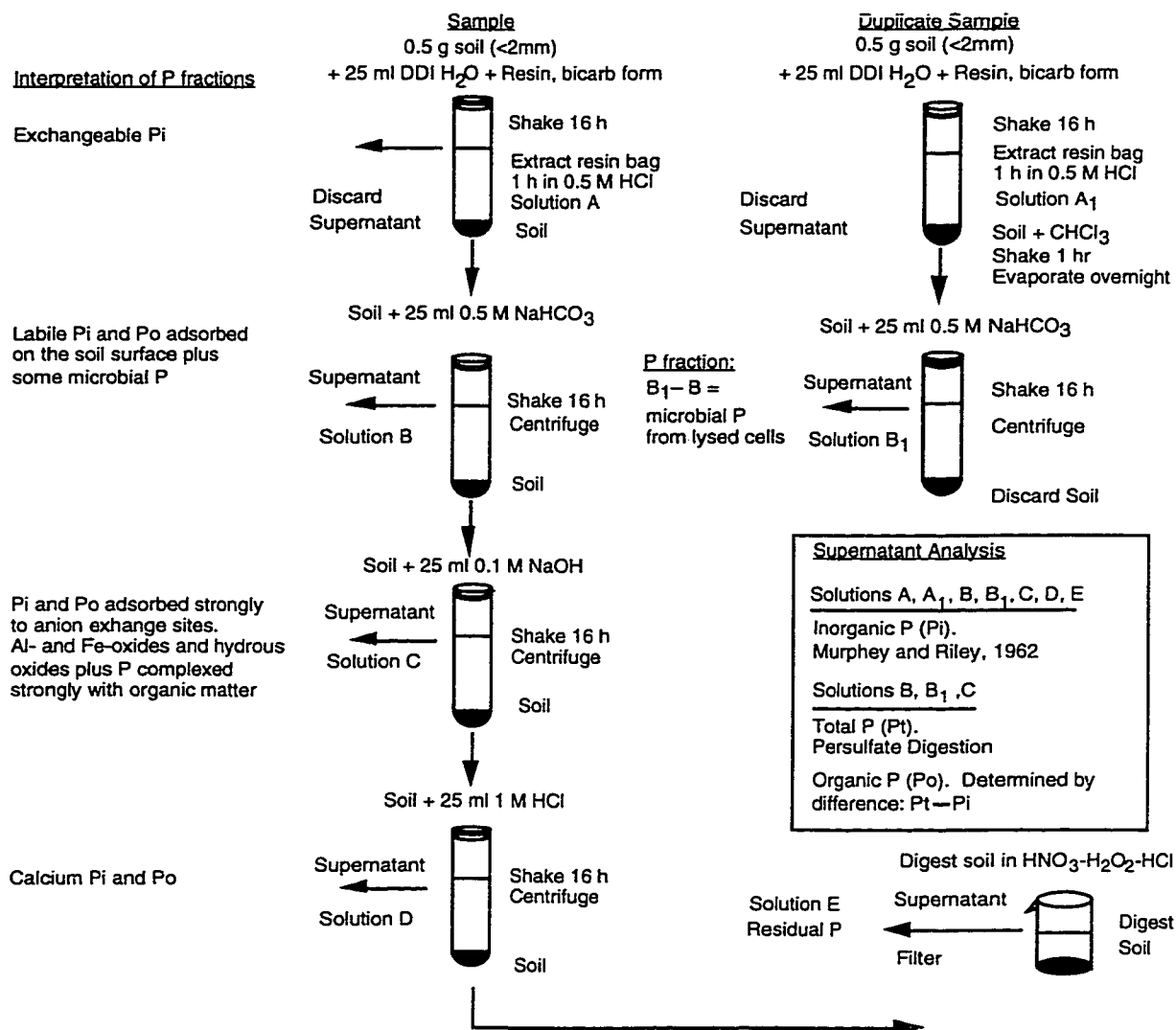


Figure 6.2. Sequential phosphorus extraction procedure.

#### 6.2.2.2 Microbial P determination

Microbial P was determined using the chloroform/bicarbonate technique (Hedley et al., 1982). Microbial P in this case is defined as the P released from lysed microbial cells

(Stevenson, 1986). Typically, in a sequential P extraction two pairs of duplicate soil samples are fractionated concurrently. However, because of the large number of soil samples analyzed, two samples from every treatment group (n=6) were duplicated at random for microbial P analysis. After resin extraction, two of the samples that had been duplicated were treated with 0.5 ml of  $\text{CHCl}_3$  and shaken for 1h. After shaking,  $\text{CHCl}_3$  was evaporated overnight in a fume hood. The following day, 25 ml of 0.5 M  $\text{NaHCO}_3$  was added and the sample shaken 16 h, centrifuged, and supernatant analyzed according to the procedures shown in Figure 6.1. The difference in the amount of Pt extracted by 0.5 M  $\text{NaHCO}_3$  from the  $\text{CHCl}_3$  sample versus the unfumigated sample was attributed to P released from lysed microbial cells and has been found to constitute up to 40% of total microbial P (Hedley et al., 1982); thus a correction factor of 0.4 was used in calculating the apparent recovery of microbial P.

#### 6.2.2.3 O horizon analysis

Air dried O horizon material was sieved to <2 mm and exchangeable phosphate determined using the method of Sibbesen, (1978). Separate 0.5 g samples were extracted sequentially with 0.5 M  $\text{NaHCO}_3$  and 0.1 M  $\text{NaOH}$ . The 0.1 M  $\text{NaOH}$  extracts were extremely dark due to solubilization of organic matter during the extraction and this adversely affects color development in the ascorbic acid method. Thus, only Pt was determined in O horizon extracts. Separate O horizon material samples were digested in hot acid (EPA Standard Method 3050) and liberated orthophosphate determined colorimetrically (Murphy and Riley, 1962).

#### 6.2.2.4 Additional chemical analyses

Biosolids and soil Pt in some samples were measured by using an  $\text{HNO}_3$ - $\text{H}_2\text{O}_2$ - $\text{HCl}$  acid digestion (EPA Standard Method 3050), followed by colorimetric determination

of liberated orthophosphate using the method of Murphy and Riley (1962). Total elements were determined using a  $\text{HNO}_3\text{-H}_2\text{O}_2\text{-HCl}$  acid digestion (EPA Standard Method 3050) and inductively coupled argon plasma spectroscopy (EPA Standard Method 6010. ICP; Thermo Jarrel Ash ICAP 61E, Thermo Jarrel Ash, Franklin, MA). Biosolids and soil total N and C in all samples were determined by dry combustion (Perkin-Elmer CHN Analyzer Model 2400). Soil and biosolids pH were determined using a VWF model 3000 pH meter. A 1:2 soil/biosolids-distilled deionized water ratio was used with an equilibration time of 30 minutes before pH measurement. Biosolids pH was determined on fresh samples prior to drying and homogenization.

#### 6.2.2.5 Determination of free Al and Fe

A preliminary study performed in August and September 1997 established the concentration of free Al and Fe at all four study sites using pyrophosphate, ammonium oxalate, and dithionite-citrate-bicarbonate extractions. For the preliminary investigation, six separate soil pits were excavated to 30 cm at each site and sample removed from the 0-15 cm depth. The six replicates were then composited into one bulk sample, with two individual samples removed from each composited sample for chemical analysis. Thus, data reported are grouped according to soil type (residual or outwash and control or biosolids treated) in order to increase replication,  $n=4$ . Free Al and Fe fractions were determined by separate extractions with (1) 0.1 M  $\text{Na}_4\text{P}_2\text{O}_7$ , (2) 0.2 M ammonium oxalate adjusted to pH 2, and (3) dithionite-citrate-bicarbonate reagent according to standard soil survey methods (USDA, 1972). Extract solutions were diluted up to 100 times with deionized water and analyzed using EPA Standard Method 6010 (ICP; Thermo Jarrel Ash ICAP 61E, Thermo Jarrel Ash, Franklin, MA).

#### 6.2.2.6 P adsorption procedure

The P sorption procedure used is similar to that developed and described in Nair et al., (1984). Phosphorus was added as  $\text{KH}_2\text{PO}_4$  to 0.5 g of the soils as collected in 6.2.2.5., to obtain 0 to 500  $\mu\text{g Pi g}^{-1}$  soil (0, 0.5, 1, 2.5, and 5 ml of 50  $\mu\text{g ml}^{-1}$   $\text{KH}_2\text{PO}_4$ ). All mixtures were prepared in duplicate and made up to 12.5 ml with deionized water. Following overnight shaking, suspensions were centrifuged and solution P was measured by the colorimetric procedure of Murphy and Riley (1962). Sorbed P was calculated as the difference between P added and P in solution.

#### 6.2.3 Biosolids chemical characteristics

A component of this study was the determination of phosphorus forms and concentrations found in biosolids produced by King County, Washington. This includes biosolids from the Renton and West Point wastewater treatment facilities, which both produce anaerobically digested, dewatered (20-22% solids) biosolids. Biosolids used for this study were collected from both treatment plants in June of 1998. In addition, biosolids used during applications at Pack Forest in the mid 1970s had been stored in an open lagoon. Samples were removed from six separate locations in June 1998 approximately 60 cm below the surface of the lagoon. All biosolids were stored aerobically at 4 C° before air-drying for at least one week in an enclosed fume hood. Biosolids were then lightly ground to pass a 5-mm opening, then sieved to less than 2 mm before analysis. All biosolids results are expressed on an oven-dry basis. Selected chemical characteristics are shown in Table 6.2.

Table 6.2. Selected biosolids and soil (0-15 cm) total elements and pH. Biosolids n=8; Soil n=6; . Standard deviations given. C=control; T=biosolids-treated

<u>Source</u>	pH	C	N	P	%	Al	Ca	Fe
Renton	8.4±0.3	31±1	5.3±0.1	3.6±0.1		1.5±0.1	2.8±0.2	2.6±0.2
W.Point	8.2±0.2	30.0±0.4	5.1±0.1	2.1±0.1		1.1±0.05	1.7±0.1	1.3±0.06
Stored	6.9±0.4	25.0±0.2	2.5±0.1	1.7±0.1		1.3±0.04	2.1±0.1	1.9±0.05
<u>Site</u>								
SDS-C	6.1±0.2	4±2	0.1±0.04	0.03±0.01		2.0±0.8	0.3±0.2	1.7±0.9
SDS-T	5.3±0.1	3±1	0.1±0.03	0.09±0.03		1.7±0.2	0.4±0.1	2.2±1.5
Gessel-C	6.3±0.5	6±3	0.3±0.1	0.2±0.07		2.6±0.8	0.3±0.0	2.4±0.5
Gessel-T	5.4±0.3	7±3	0.3±0.2	0.2±0.07		1.3±0.4	0.3±0.2	1.2±0.5
Hugo-C	6.4±0.2	3±1	0.1±0.03	0.02±0.01		0.5±0.07	0.2±0.03	0.5±0.2
Hugo-T	6.4±0.2	5±2	0.4±0.2	0.2±0.1		1.0±0.5	0.2±0.05	0.6±0.3
XA5-C	6.0±0.2	6±1	0.3±0.04	0.2±0.1		2.0±0.05	0.6±0.1	1.8±0.3
XA5-T	4.9±0.3	10±2	0.8±0.3	0.6±0.1		2.0±0.4	0.8±0.04	2.8±0.2

#### 6.2.4 Data and statistical analysis

All soil elemental concentration data were log transformed before performing statistical analyses. A paired Students *t*-test (StatView-SAS, 1998) was performed for each P fraction to establish the statistical significance of mean P concentration differences between biosolids treated and control soils at separate soil sampling depths. Alpha levels of 0.001, 0.01, and 0.05 were used for statistical testing of mean differences in P accumulation among fractions.

## 6.3 Results and Discussion

### 6.3.1 P fractionation of biosolids

The concentration of P fractions in current biosolids used at Pack Forest, compared to those stored for more than 25 years are shown in Table 6.3. Resin extractable P (data not shown) in Renton, West Point, and Stored biosolids averaged 4400, 3600, and 1200 mg kg<sup>-1</sup>, respectively. Renton biosolids contains nearly double the amount of P in all fractions as West Point, except for residual P. The Stored biosolids contains nearly the same amount of P compared to West Point, with the more resistant HCl (calcium P) and residual P fractions nearly equal in concentration. However, the Stored biosolids contains substantially less water soluble and bicarbonate extractable P than either Renton or West Point biosolids and the proportion of calcium P is substantially greater. The differences in concentration and relative accumulation are almost certainly due to long-term exposure to rainfall and leaching of P deeper into the lagoon below the point of sampling (>60 cm), uptake by grasses that cover the lagoon, and transformation of P to more resistant forms. The source of the Stored biosolids was the West Point wastewater treatment plant before secondary wastewater treatment.

Table. 6.3: Total phosphorus fractions in King County, Washington biosolids. Percent refers to percent of total of each fraction. n=8. Standard deviations given.

	<u>Water</u>	<u>Bicarb</u>	<u>Hydrox</u>	<u>HCl</u>	<u>Residual</u>	<u>Total</u>
<u>Biosolids Source</u>	-----mg kg <sup>-1</sup> -----					
Renton	5800±200 16%	3500±300 10%	11100±700 31%	12700±500 35%	3500±400 10%	36000±1300
West Point	2300±100 11%	1980±70 9%	6000±300 28%	7300±200 34%	3500±800 17%	21200±800
Stored	200±30 1%	940±40 5%	5700±400 32%	8700±400 48%	2100±200 12%	17900±700

Abbreviations: Bicarb=sodium bicarbonate (0.5 M); Hydrox=sodium hydroxide (0.1 M)  
HCl=hydrochloric acid (1 M).

### 6.3.2 Depth of vertical P mobility in the soil following biosolids application

#### 6.3.2.1 Surface application of biosolids

Surface application of biosolids significantly increased the mean concentration of all P fractions measured within the O horizon at the SDS and Gessel site. The mean concentration of resin, bicarbonate, and hydroxide extractable P within the O horizon was significantly greater in biosolids treated versus controls at both sites (Figures 6.3 and 6.4, respectively). The mean increase in P fraction concentrations in the biosolids treated O horizon were between 3 and 8 times greater than controls. Biosolids application also increased the ratio of bicarbonate Pi/Po, from 2 in controls to 5 and 6 in biosolids treated areas at the SDS and Gessel sites, respectively (Table 6.4). It is clear from these data that P contained in biosolids still remains on the forest floor four years after application (last application made December 1995), providing evidence that biosolids can serve as a long-term source of slowly available P in PNW Douglas-fir forests.

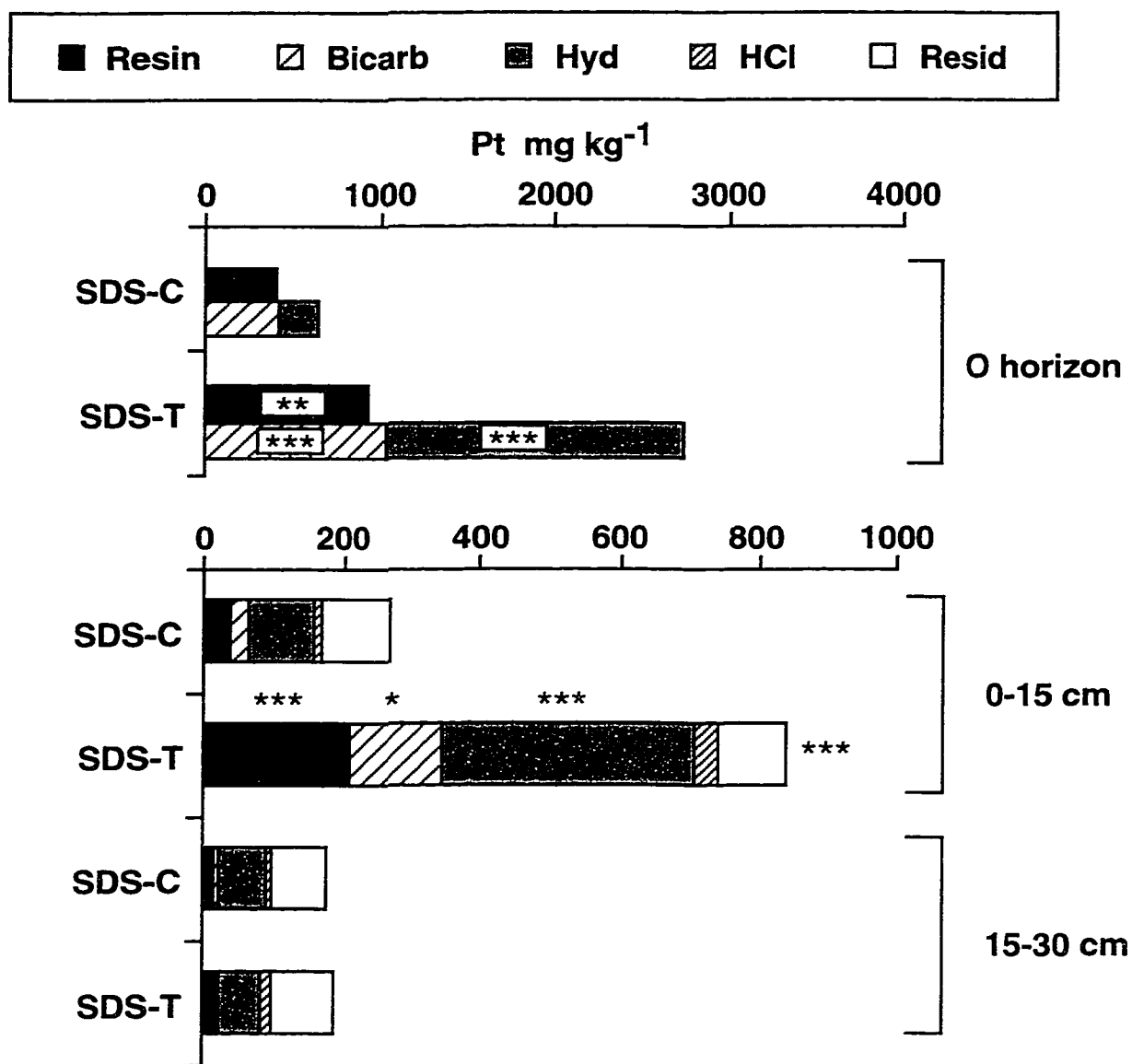


Figure 6.3. Soil P status and distribution of P fractions at the SDS. O horizon P fractionation was not sequential; resin P was determined on separate samples. Statistical comparisons are made in pairs, vertically, for each P fraction at each horizon depth. Significant differences in mineral soil total P between treatments are noted at the end of a bar, if applicable. Significant differences between control and biosolids treated O horizon or mineral soil were determined using a paired Student's *t*-test on log transformed data (\* $p < 0.05$ , \*\* $p < 0.01$ , \*\*\* $p < 0.001$ )  $n = 6$ .

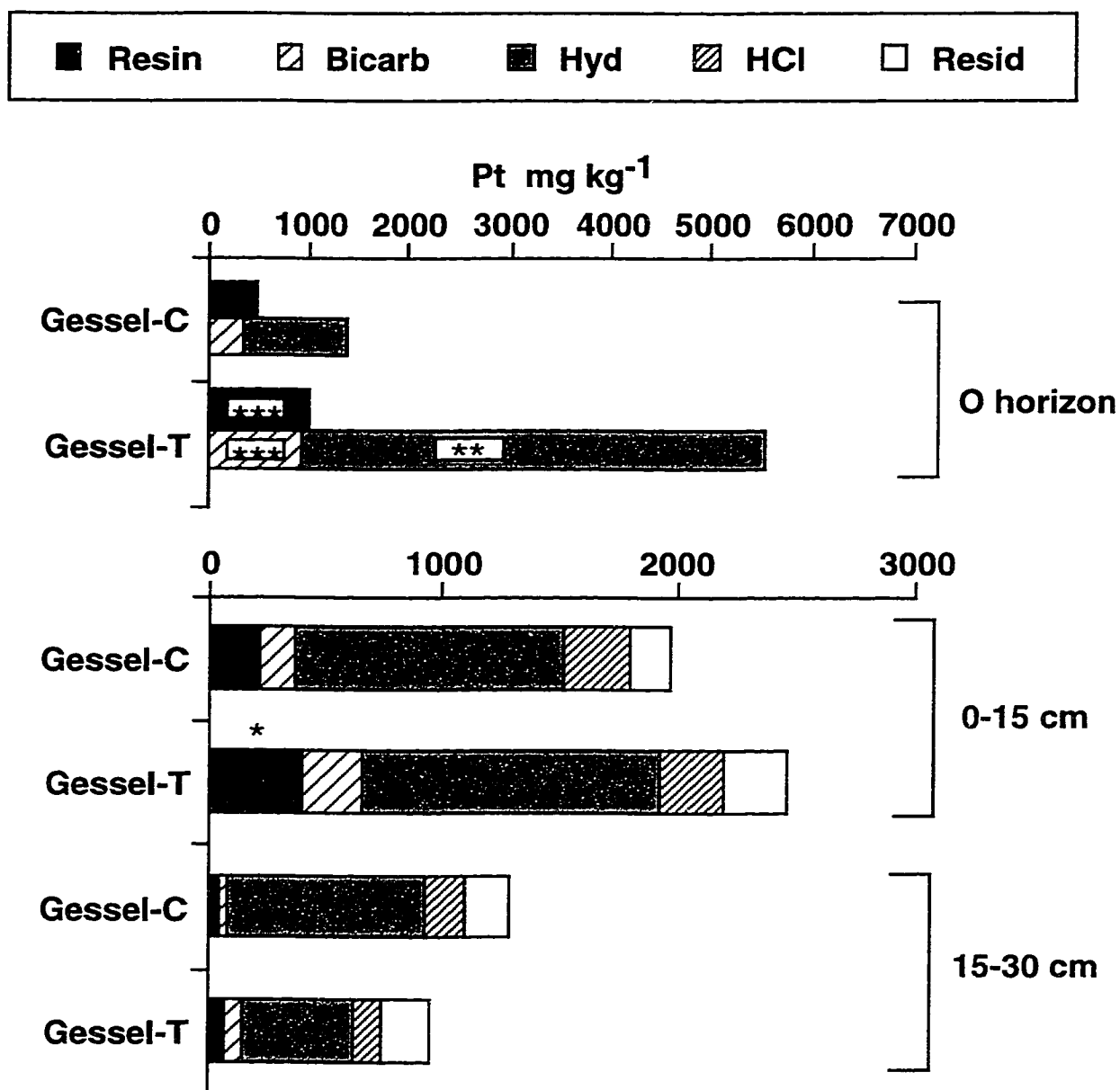


Figure 6.4. Soil P status and distribution of P fractions at the Gessel site. O horizon P fractionation was not sequential; resin P was determined on separate samples. Statistical comparisons are made in pairs, vertically, for each P fraction at each horizon depth. Significant differences between control and biosolids treated soil were determined using a paired Student's *t*-test on log transformed data (\* $p < 0.05$ , \*\* $p < 0.01$ , \*\*\* $p < 0.001$ )  $n = 6$ .

The mean P concentration in mineral soil (0-15 cm sampling depth) within the biosolids treated area at the SDS was significantly greater than controls for all fractions except calcium P and residual P (Figure 6.3). The ratio of inorganic P to organic P also increased at the SDS site due to biosolids application (Table 6.4). Conversely, the mineral soil from biosolids treated areas at the Gessel site (0-15 cm sampling depth) shows a slight but non-significant increase in mean P concentration for most fractions (Figure 6.4). The only statistically significant increase in mean soil P concentration due to biosolids application was in the resin extractable fraction. Thus, ratios of mineral soil Pi/Po were relatively unaffected by biosolids application at the Gessel site (Table 6.4). There were no significant differences in mean P fraction concentrations at the 15-30 cm sampling depth comparing biosolids treated and control soils at either site.

Hypothesis 2 states that the concentration of phosphorus in the soil following biosolids application at a P loading rate of 2 Mg ha<sup>-1</sup> will decline significantly with depth below the forest floor. The results shown in Figures 6.3 and 6.4 support this hypothesis. There is no evidence that shows cumulative application of biosolids at approximately 105 Mg ha<sup>-1</sup> (2 Mg P ha<sup>-1</sup>) has produced noticeable increases in the mean concentration of P fractions deeper than 15 cm below the forest floor at either site.

Table 6.4. Ratios of Pi/Po at the SDS and Gessel sites.

<u>Site/tmt.</u>	<u>Bicarb Pi/bicarb Po</u>			<u>Hyd Pi/hyd Po</u>		<u>Total Pi/total Po<sup>(1)</sup></u>	
	<u>O horz.</u>	<u>0-15 cm</u>	<u>15-30 cm</u>	<u>0-15 cm</u>	<u>15-30 cm</u>	<u>0-15 cm</u>	<u>15-30 cm</u>
SDS-C	2	3	>20	1	3	4	9
SDS-T	5	11	>20	7	3	14	>20
Gessel-C	2	2	>20	8	6	14	10
Gessel-T	6	4	>20	8	9	11	>20

(1): Total Pi = resin Pi + bicarb Pi + hyd Pi + HCl Pi + residual Pi; total Po = bicarb Po + hyd Po.

### 6.3.2.2 Direct incorporation of biosolids into the soil

It appears that a single heavy application of biosolids has a long-lasting effect on Douglas-fir litterfall Pt concentrations. Significant increases were noted within biosolids-treated O horizon material more than 20 years after application at the Hugo Peak and XA-5 sites (Figures 6.5 and 6.6, respectively). Data shown in each figure were derived from separate acid digestions (EPA 3050) of O horizon samples that were not subjected to resin extraction or to sequential extraction with bicarbonate and hydroxide before digestion and P determination. Mean resin, bicarbonate, and hydroxide extractable P concentrations were similar at the Hugo Peak site comparing biosolids treated and control O horizons (Figure 6.5). Conversely, the mean concentration of resin and bicarbonate extractable P was significantly greater in O horizon removed from the biosolids treated XA-5 area than from the control area (Figure 6.6). This difference in O horizon labile P concentrations between sites may be due simply to the higher application rate used at XA-5, in addition to greater native P supply and availability in outwash versus residual soils. For O horizon material, it appears the resin and bicarbonate extractions are removing the same pool of P, as separate extractions produced generally similar P values.

Mineral soil to a depth of 30 cm was generally enriched with P at both sites and the depth of enrichment corresponds closely to the depth of mixing at the time of biosolids application. The mean concentration of all P fractions in mineral soil removed from 0-15 cm within biosolids treated areas at both sites was significantly greater than controls (Figures 6.5 and 6.6). The mean concentration of all P fractions in soil from 0-15 cm at Hugo Peak were up to 10 times greater in biosolids treated soils and generally between 2 and 6 times greater at XA-5. Analysis of  $P_i/P_o$  ratios gave mixed results (Table 6.5). At the Hugo Peak site, bicarbonate and hydroxide  $P_i/P_o$  ratios were generally higher for

biosolids treated soils, especially near the soil surface. Conversely, ratios of bicarbonate  $P_i/P_o$  at XA-5 were lower in biosolids treated soils than in controls. Hydroxide and total  $P_i/P_o$  ratios were higher in biosolids treated soil compared to controls at XA-5, with the biggest differences observed in samples taken from 15-30 cm.

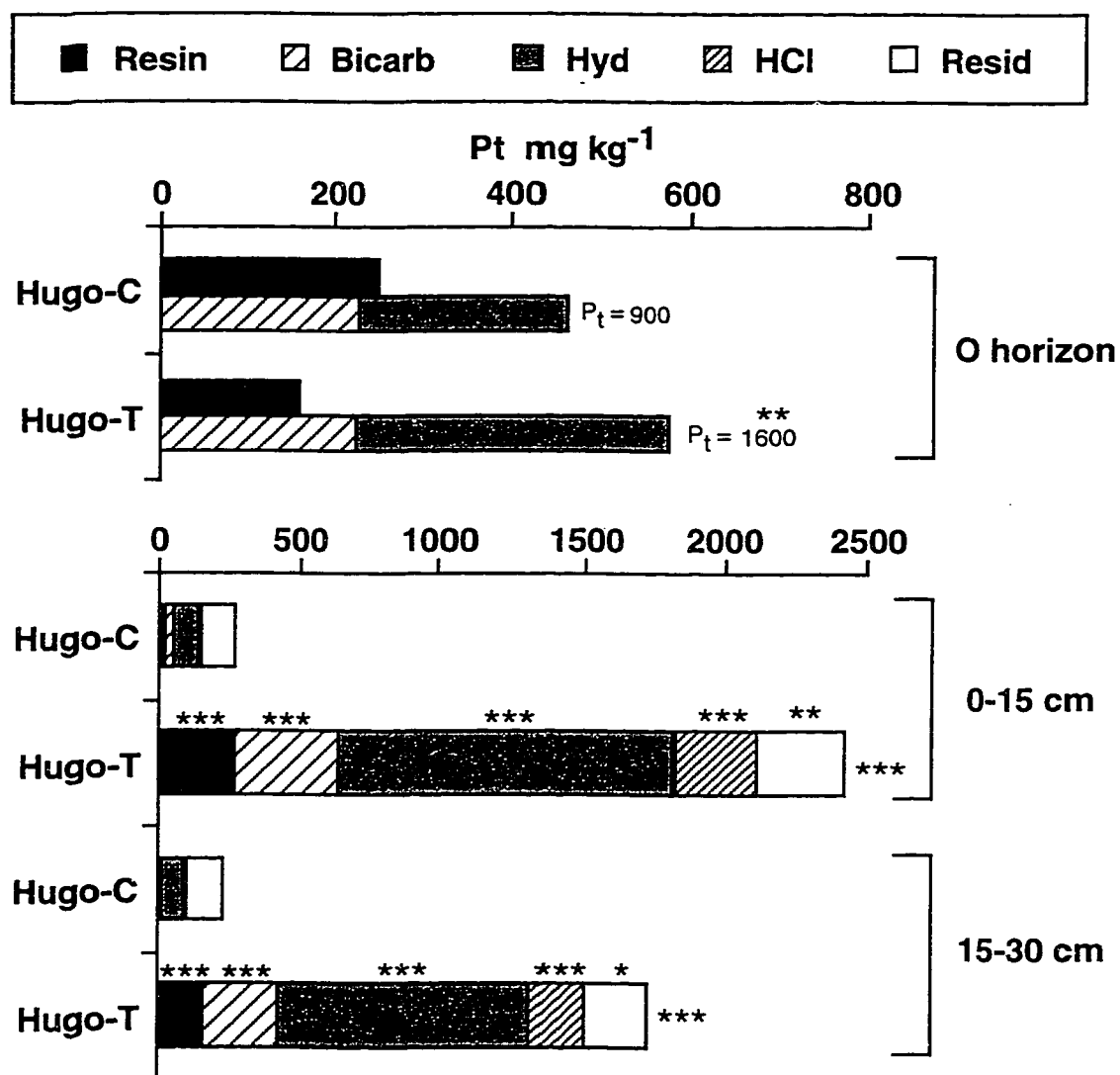


Figure 6.5. Soil P status and distribution of P fractions at the Hugo Peak site. O horizon P fractionation was not sequential; resin and total P were determined on separate samples. Statistical comparisons are made in pairs, vertically, for each P fraction at each horizon depth. Significant differences in total P between treatments are noted at the end of a bar, if applicable. Significant differences between control and biosolids treated soil were determined using a paired Student's *t*-test on log transformed data (\* $p < 0.05$ , \*\* $p < 0.01$ , \*\*\* $p < 0.001$ )  $n = 6$ .

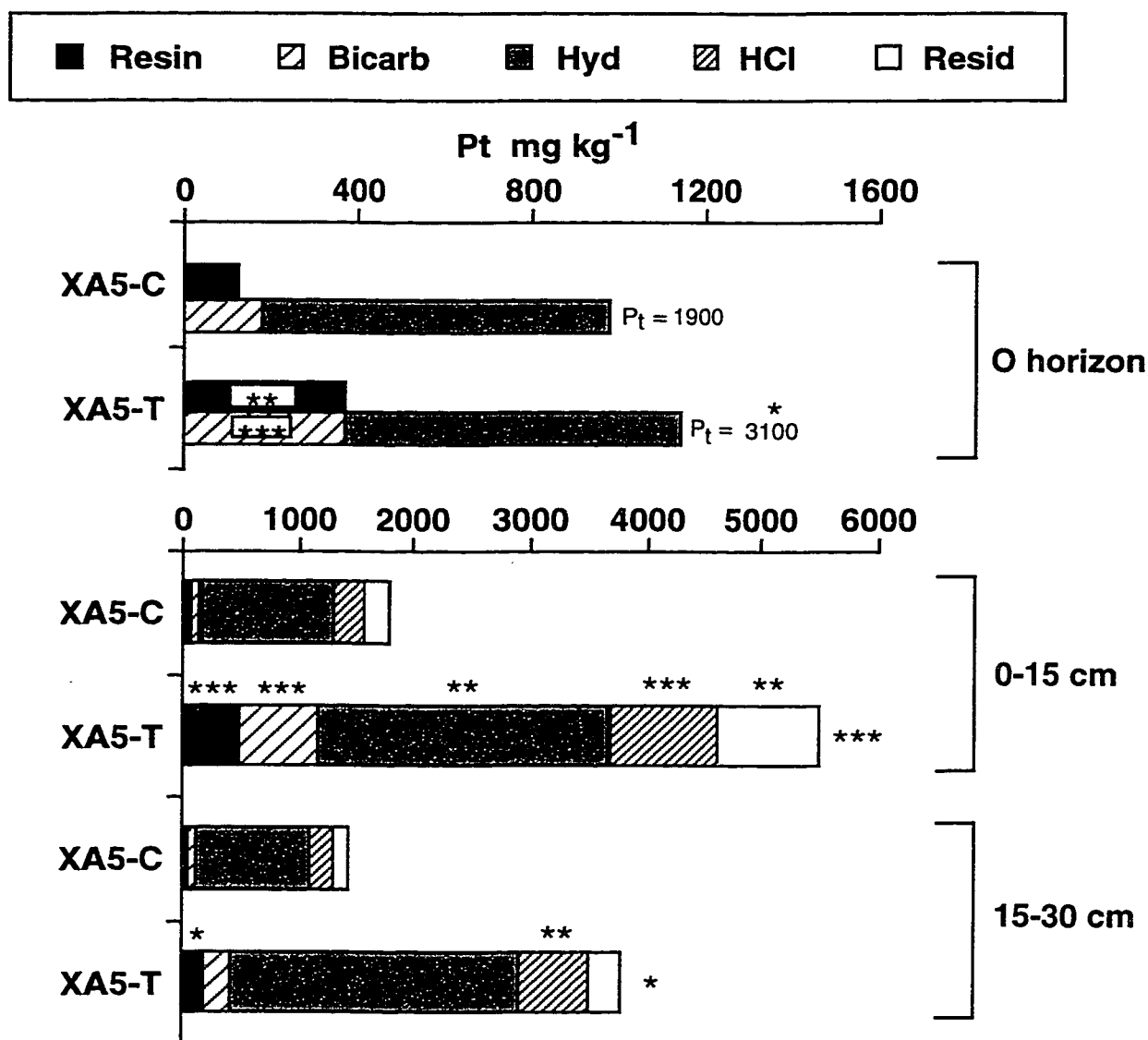


Figure 6.6. Soil P status and distribution of P fractions at the XA-5 site. O horizon P fractionation was not sequential; resin and total P were determined on separate samples. Statistical comparisons are made in pairs, vertically, for each P fraction at each horizon depth. Significant differences in total P between treatments are noted at the end of a bar, if applicable. Significant differences between control and biosolids treated soil were determined using a paired Student's *t*-test on log transformed data (\* $p < 0.05$ , \*\* $p < 0.01$ , \*\*\* $p < 0.001$ )  $n = 6$ .

Significantly higher mean P fraction concentrations in biosolids treated soil versus controls were measured at 15-30 cm at Hugo Peak. At XA-5 the enrichment of P fractions

to a depth of 30 cm is still evident in biosolids treated soil, but differences were not statistically significant in some cases because of high variation. The only significant differences in mean P fraction concentrations at XA-5 due to biosolids application were measured in the resin, calcium P, and Pt fractions.

Table 6.5. Ratios of Pi/Po at the Hugo Peak and XA-5 sites

<u>Site/tmt.</u>	<u>Bicarb Pi/bicarb Po</u>		<u>Hyd Pi/hyd Po</u>		<u>Total Pi/total Po<sup>(1)</sup></u>	
	<u>0-15 cm</u>	<u>15-30 cm</u>	<u>0-15 cm</u>	<u>15-30 cm</u>	<u>0-15 cm</u>	<u>15-30 cm</u>
Hugo-C	1	1	3	2	6	6
Hugo-T	3	3	7	6	9	8
XA-5-C	5	>20	7	6	11	10
XA-5-T	3	5	9	11	14	14

(1): Total Pi = AER Pi + bicarb Pi + hyd Pi + HCl Pi + residual Pi; Total Po = bicarb Po + hyd Po.

### 6.3.3 Release and retention of phosphorus applied in surface biosolids applications

Surface application of biosolids generally precludes contact between biosolids and mineral soil particles in mature Douglas-fir stands. Therefore, for phosphate from biosolids to reach subsoils it must first move downward through the O horizon in rainwater and infiltrate into mineral soil. The initial release of phosphate in biosolids is from the water soluble pool and the labile pool extracted by resin and bicarbonate. The release of additional P from biosolids would likely involve a complex set of interactions governed by the amount of water moving through the treated area, temperature, changes in pH induced by biosolids application, soil aeration, and nature of complexing metal cations in the biosolids-soil solution (Rydin, 1996; Hinedi and Chang, 1989; O'Connor, 1986; McLaughlin, 1983; Berkheiser et al., 1980). Under ideal laboratory conditions at 20° C the release of phosphate from Al and Fe in soil mixed with biosolids has been reported to be

relatively fast--on the order of weeks (Rydin and Ottabong, 1998), but may be much slower under field conditions where cooler temperatures and an uneven water flux prevail. Limited data exist concerning P release rates from anaerobically digested biosolids. In addition, biosolids nitrogen transformations promote acidification within biosolids (Henry, et al., 1999) and eventually within treated soils (Harrison et al., 1994). This would appear to encourage conditions ideal for dissolution of Ca-phosphates in biosolids, which comprises approximately 1% of biosolids on a dry weight basis (Table 6.4).

Data from the SDS and Gessel sites (Figures 6.3 and 6.4, respectively) show that the primary sinks within mineral soil for P added in a surface biosolids application are the exchangeable (resin), weakly adsorbed labile (bicarbonate), and moderately to strongly adsorbed (hydroxide) P fractions near the forest floor. In addition, applying biosolids caused a noticeable increase in the abundance of the resin and bicarbonate P fractions as a percent of Pt (Table 6.6). These effects were most pronounced at the SDS, with much more subtle responses at the Gessel site. Mean concentrations of both the calcium P and residual P fractions were unchanged due to biosolids application at either site, while the effect on their relative abundance as a percentage of Pt varied only for the residual P fraction at the SDS. The reactivity of the calcium P fraction in these soils would be minimal due to acidic soil pH conditions (Table 6.2) and results suggest that surface application of biosolids has done little to affect this pool. Applying biosolids over the forest floor at the SDS decreased the abundance of residual P as a percent of Pt in the 0-15 cm sampling depth (Table 6.6). Conversely, at the Gessel site biosolids application resulted in minor increases in residual P as percentage of Pt. This contrast in relative abundance of the residual P fraction is probably a result of initial differences in soil P concentrations between the two sites.

Table 6.6. Percent of total P (Pt) of each P fraction at the SDS and Gessel sites.

Rate Mg ha <sup>-1</sup>	Soil Type	Site	Tmt.	Depth (cm)	Resin	Bicarb	Hyd	HCl	Residual
					-----% of Pt-----				
0	R	SDS	C	0-15	14	10	34	5	38
105	R	SDS	T	0-15	24	16	42	4	11
0	R	SDS	C	15-30	9	5	36	5	45
105	R	SDS	T	15-30	10	5	31	8	47
0	OW	Gessel	C	0-15	11	8	58	14	9
105	OW	Gessel	T	0-15	16	11	51	11	11
0	OW	Gessel	C	15-30	4	3	67	13	15
105	OW	Gessel	T	15-30	7	9	51	14	22

Notes: Soil types: R=residual; OW=outwash. Tmt: C=control; T=biosolids-treated

No significant differences in P fraction concentrations exist below 15 cm at the SDS or Gessel site. In fact, results from the Gessel site suggest that equilibrium between phosphate released from biosolids and phosphate supported in the soil solution is attained within the forest floor and near the soil surface (Figure 6.4). Moreover, phosphate sorption data (Figure 6.7) suggest that the soils examined have a high capacity to retain added P; addition of biosolids at cumulative P loading rates from 1900 to 8500 kg total P ha<sup>-1</sup> has done little to affect the soil's capacity to adsorb additional P. At the Gessel site (outwash soil) substantial adsorption capacity likely remains in the near surface mineral soil despite relatively high native P concentrations. Assuming that leaching of P has been minimal in these outwash soils (Riekerk, 1978), it is possible that sampling from the entire 0-15 cm depth below the forest floor O horizon at the Gessel site did not isolate the effect of biosolids in elevating soil P concentrations and instead diluted it.

There is general agreement that equilibration times for phosphate adsorption onto soil particles can occur in several stages, usually a rapid first stage followed by much slower reactions (Barrow, 1979). Changes over time occur not only in the amount adsorbed but within the portion that has already been removed from the soil solution (Kurtz, 1981). Reactions continually occur that remove phosphate from the soil solution such as penetration of phosphate into soil particles or precipitation of secondary phosphate minerals.

In forest soils and especially in forest soils fertilized with biosolids, reaction of phosphate with soil components can be quite dynamic because of continual inputs of organic matter and products of biosolids decomposition. On one hand, biosolids contains large amounts of organic carbon. Biosolids decomposition (as well as soil organic matter decomposition) may lead to production of organic anions. While not explicitly determined in this study, the presence of organic anions in the soil solution has been shown to increase P solubility in some forest soils (Fox and Comerford, 1990). Organic anions, such as oxalate, form stable complexes with Al and Fe and thus compete with phosphate for adsorption sites. Conversely, biosolids contains high concentrations of Al and Fe as well as Ca (Table 6.2), which react with phosphate either through surface adsorption or precipitation reactions in the soil solution. In addition, it has been suggested that organic matter becomes stabilized by “free” iron and aluminum sesquioxides and the resulting gel complex is more effective than free iron and aluminum oxides alone in sorbing P from the soil solution (Sanyal and Da Datta, 1991). Thus, a paradox exists. Biosolids create a situation where decomposition is enhanced by nutrient availability. Decomposition products such as organic anions increase P solubility. However, biosolids add high concentrations of potentially reactive metal cations and these cations are known to form complexes with organic matter in addition to reacting directly with phosphate. The study

data suggest that a complex environment indeed exists in forest soils amended with biosolids. P availability was significantly increased near the forest floor, where decomposition is presumably quite active. Yet, it appears strong adsorption by free aluminum and iron oxides, which are abundant in the mineral soil horizons at Pack Forest, prevents P mobilization deeper than 15 cm using a cumulative loading of 2 Mg P ha<sup>-1</sup>.

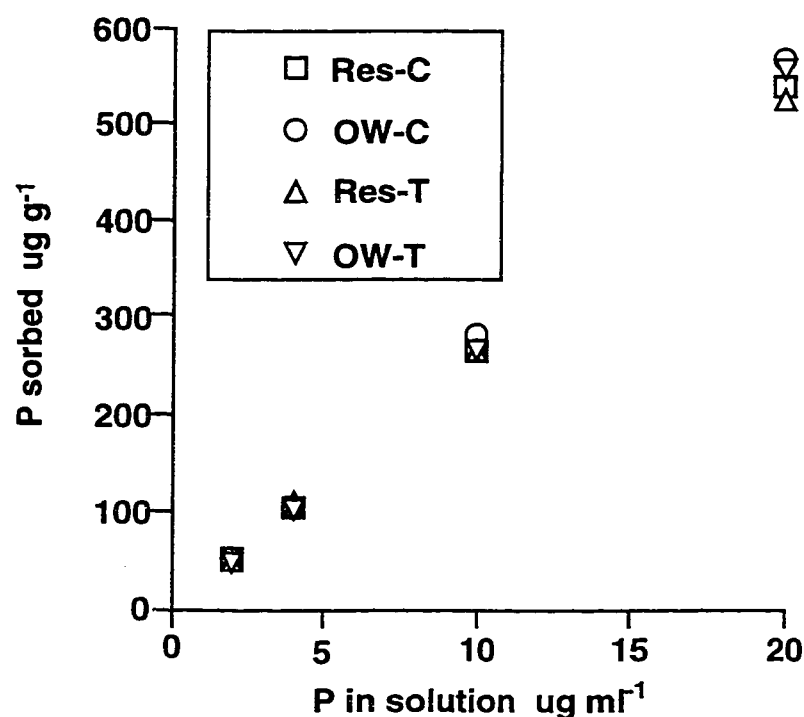


Figure 6.7. P sorption in control and biosolids treated residual and outwash soils at Pack Forest. Res=residual; OW=outwash; C=control; T=treated. n=4.

In attempting to explain the lack of vertical P migration in outwash soil, the abundance of adsorbing minerals in outwash and residual soil at Pack Forest was measured. A significant correlation has been reported between Al and Fe solubilized by acid oxalate and phosphate sorption capacity (Khalid et al., 1977). The mean concentration of oxalate extractable Al was nearly three times greater in unamended outwash versus residual soils (6400 vs. 1900 mg kg<sup>-1</sup>), while that of Fe was 2 times greater (4000 vs. 2000 mg kg<sup>-1</sup>). When these data are converted into mmol kg<sup>-1</sup> and plotted against the sum of

labile and moderately labile P (bicarbonate plus hydroxide extractions) concentrations in unamended soils (Figure 6.8), differences in the concentration of free Al and Fe between sites is clear. Outwash soils in this region have a large component of volcanic ash and pumice (SCS, 1986). These materials are fine-grained and porous and have large surface areas that enhance their weathering and subsequent interactions with soil components (Wada, 1985). Allophane, imogolite, and Al and Fe-humus complexes are believed to be the primary materials that react with phosphate. Thus, the greater abundance of reactive Al and Fe in outwash soils, likely due to volcanic inputs, provides some explanation as to why significant differences in P fraction concentrations were detected at the SDS and not at the Gessel site. Apparently, more of the P retention sites have been saturated at the SDS compared to the Gessel site. However, as the P adsorption data showed (Figure 6.7), both soils examined (biosolids-treated and untreated) have a large capacity to retain P, with the outwash soils having the potential to sorb substantially more P than residual soils.

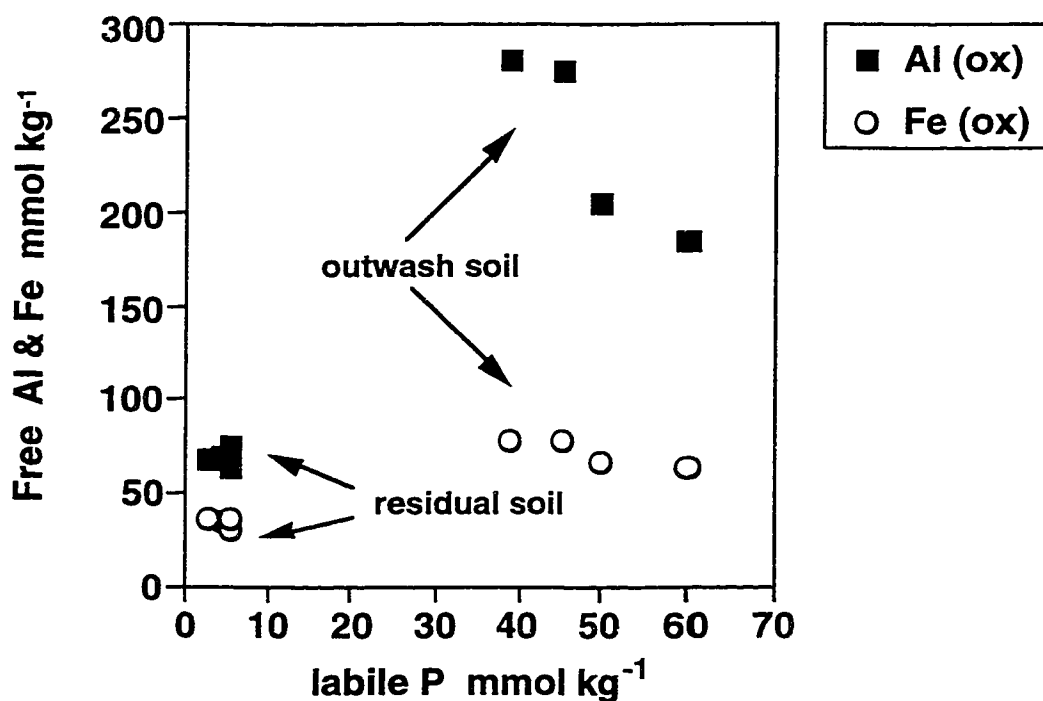


Figure 6.8. Relationship between labile and moderately labile P and free Al and Fe in mineral soil (0-15 cm) from Pack Forest. Labile P=(resin Pi + Bicarb Pt + Hyd Pt). n=4.

Hypothesis 3 states that biosolids application at a P loading rate of 2 Mg ha<sup>-1</sup> will significantly increase the concentration of sorbed P fractions in the top 15 cm of mineral soil. Based on results from the SDS, this hypothesis was supported. At the SDS, both exchangeable P and P adsorbed weakly and more strongly onto surfaces of Al and Fe oxides were significantly greater in biosolids amended soils compared to controls. This included both the O horizon and soil from the 0-15 cm sampling depth. At the SDS, adsorption appears to be a primary retention mechanism limiting mobility of biosolids P. At the Gessel site, all P fractions examined in the O horizon were significantly greater than controls. However, the mineral soil P concentrations were not significantly increased by biosolids application. The only statistically significant increase in P concentration due to biosolids application occurred in the resin extractable P fraction. Thus, Hypothesis 3 could not be supported based on results from the Gessel site.

Hypothesis 4 states that biosolids application at a P loading rate of 2 Mg ha<sup>-1</sup> will significantly increase soil P availability in the top 15 cm of mineral soil. The marked increase in resin (exchangeable) and bicarbonate extractable P in biosolids treated soil and the increase Pi/Po ratios in O horizon material and in soil removed from 0-15 cm suggests that biosolids has increased the pool of potentially labile and moderately labile Pi, supporting Hypothesis 4. The data also suggest biosolids provides a long-term supply of phosphate near the forest floor. Thus, given the high ratio of Pi/Po in most cases, desorption of Pi sorbed onto biosolids Al and Fe-compounds as well as dissolution of P from calcium phosphates in biosolids may, over the long-term, be more important than organic P mineralization in supplying P to the soil solution where biosolids has been applied. Results here confirm speculation that the application of biosolids to Douglas-fir forests induces long-term enhancement in P availability near the forest floor (Prescott et al., 1993).

Results of the field soil sampling and P fractionation suggest that biosolids has not had a significant effect in increasing soil organic P pools were moderate rates of biosolids are used. The only significant difference between treatments was found at the SDS comparing bicarbonate and hydroxide extractable Pi (Figures 6.9 and 6.10, respectively); no difference in bicarbonate or hydroxide extractable Po was noted at either site. Rather, it is possible that biosolids addition may have stimulated decomposition and thus mineralization of native organic P, which further reduced the pool of organic P relative to inorganic P sources (Compton, 1994). Carbon:P ratios are favorable for P mineralization at all sites regardless of biosolids application (Stevenson, 1986), although substantial decreases in C:P ratios were noted at the SDS in surface soils due to biosolids treatment, primarily because of increases in soil Pi (Table 6.7).

Table 6.7. Carbon, nitrogen and phosphorus ratios at the SDS and Gessel sites. n=6.

<u>Site-Tmt.</u>	<u>Sampling Depth</u>	<u>C/N</u>	<u>C/P</u>	<u>N/P</u>
		-----g g <sup>-1</sup> -----		
<u>SDS-C</u>	0-15	41	137	3
<u>SDS-T</u>	0-15	29	32	1
<u>SDS-C</u>	15-30	35	105	3
<u>SDS-T</u>	15-30	26	90	4
<u>Gessel-C</u>	0-15	24	31	1
<u>Gessel-T</u>	0-15	22	30	1
<u>Gessel-C</u>	15-30	20	17	1
<u>Gessel-T</u>	15-30	18	19	1

The lack of response in soil organic P to biosolids addition also includes the labile microbial P pool that is estimated using a chloroform-bicarbonate extraction of duplicate

soil samples during P fractionation. P extractions using this technique failed to give consistent results with respect to the effect of biosolids on soil microbial P and no differences between control and biosolids treated soils were noted. Microbial P to a depth of 30 cm ranged from undetectable in many cases to  $100 \text{ mg kg}^{-1}$  in both control and biosolids treated soils at the SDS and Gessel site. Other researchers have reported similar findings and high variation in microbial P using biosolids treated soils (Cline et al., 1985).

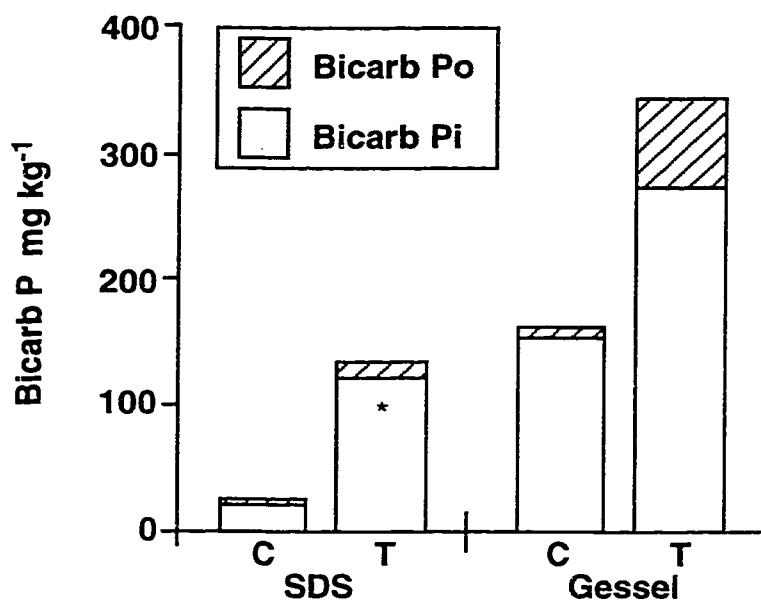


Figure 6.9. Concentration of bicarbonate extractable Pi and Po in soil removed from 0-15 cm at the SDS and Gessel site. Statistical comparisons are made between Po or between Pi in pairs at each site. Significant differences between control (C) and biosolids treated (T) soil at each site were determined using a paired Student's *t*-test on log transformed data (\* $p < 0.05$ )  $n = 6$ .

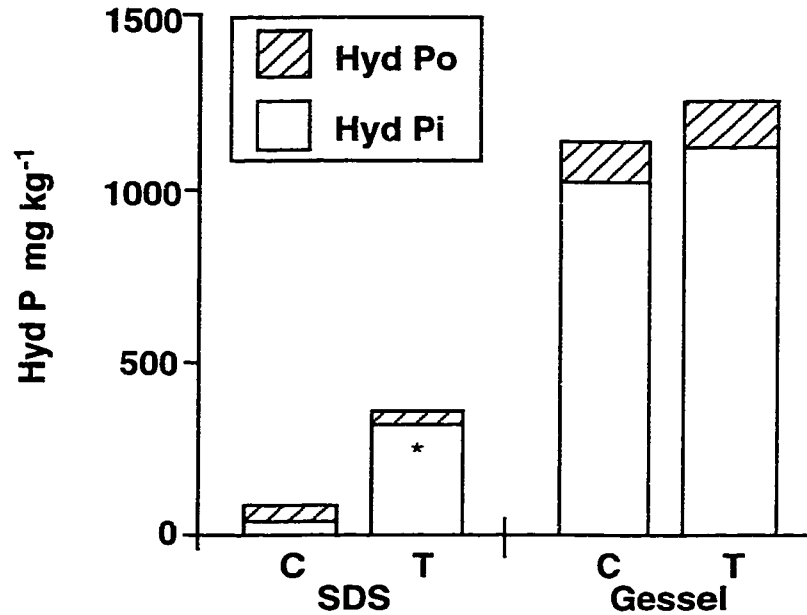


Figure 6.10. Concentration of hydroxide extractable Pi and Po from soil removed from 0-15 cm at the SDS and Gessel site. Statistical comparisons are made between Po or between Pi in pairs at each site. Significant differences between control (C) and biosolids treated (T) soil at each site were determined using a paired Student's *t*-test on log transformed data (\* $p < 0.05$ )  $n = 6$ .

#### 6.3.4 Phosphorus forms in the soil following heavy experimental applications

The effect of heavy application of biosolids and direct mixing into the soil on soil P transformations among pools is difficult to interpret because of the complex nature of P retention and release mechanisms. In addition, biosolids and soil P fractions are somewhat similar in terms of the distribution of P fractions as a percent of the total (Table 6.8) and direct mixing blurs the influence of biosolids on soil P transformations and vice versa.

Three primary observations can be made. First, the obvious change in soil P status produced by direct biosolids incorporation at Hugo Peak and XA-5 was the significant increase in labile P (resin + bicarbonate P) concentrations compared to control soils. This marked increase in labile P concentration is also reflected in differences in its relative abundance compared to control soils as a percent of total P (Table 6.8). At both sites,

biosolids application has elevated soil P availability and this effect appears to be long-lived. Presumably, a much higher equilibrium soil solution phosphate concentration has been established at these sites, as exchangeable P weakly held on soil surfaces is significantly greater to a depth of 30 cm.

Second, biosolids contains a much larger proportion of P in calcium phosphates than do the soils at Hugo Peak or XA-5 (Table 6.8). The naturally acidic soil conditions combined with biosolids nitrogen transformations which lower pH would encourage dissolution of these compounds rather than formation. Thus, significant increases at both sites in this fraction must certainly be the result of direct mixing and the continued presence of calcium phosphates derived from the biosolids application. The release of calcium phosphates would, therefore, presumably increase the supply of phosphate in the soil solution. As P adsorption is concentration dependent, an increase in P concentration results in an increase in adsorption.

Third, P adsorbed to Al and Fe is the dominant P fraction at either site regardless of biosolids application. Significant increases in this fraction were noted in almost all cases at Hugo Peak and XA-5. The increases are clearly due to biosolids application, but whether or not the increase is the result of P adsorbed from the soil solution following release of phosphate from biosolids or P derived from biosolids adsorption sites is unclear. It is likely that both factors contribute to the predominance of this fraction.

Table 6.8. Percent of total P (Pt) of each P fraction at the Hugo Peak and XA-5 sites.

Rate Mg ha <sup>-1</sup>	Soil Type	Site	Tmt.	Depth (cm)	Resin	Bicarb	Hyd	HCl	Residual
					-----% of Pt-----				
0	R	Hugo	C	0-15	12	10	35	4	46
>188	R	Hugo	T	0-15	11	15	49	12	13
0	R	Hugo	C	15-30	<1	7	35	4	53
>188	R	Hugo	T	15-30	9	15	52	11	13
0	OW	XA-5	C	0-15	3	5	64	15	13
470	OW	XA-5	T	0-15	9	13	46	17	16
0	OW	XA-5	C	15-30	3	5	71	15	10
470	OW	XA-5	T	15-30	5	6	65	16	7
W. Point Biosolids					11 <sup>(1)</sup>	9	28	34	17

(1) deionized water extraction

Heavy biosolids application and direct mixing into the soil generally resulted in a significant increase in the concentration of both Pi and Po 0-15 cm below the soil surface at the Hugo Peak and XA-5 sites (Figures 6.11 and 6.12). This increase in the abundance of Po contrasts with data from the SDS and Gessel sites (Figures 6.8 and 6.9), where no significant differences were detected at either sampling depth. Since stand age and biosolids rates and methods of application were different, direct comparison of soil Po amounts are not particularly meaningful. However, the difference suggests that heavy application rates and direct mixing affects the accumulation of organic P differently than surface applications.

One explanation for the differences in organic P accumulation could be that the long-term fertilizing power of biosolids results in an overall increase in available P supported in the soil solution which has in turn increased P uptake and cycling at these

sites. Carbon and N concentrations are noticeably higher in biosolids treated surface soils at both sites and especially evident at XA-5 (Table 6.2). Thus, C:N ratios (Table 6.9) remain favorable for N mineralization 20 years after application, which should presumably stimulate forest growth and increase nutrient uptake, P included. In addition, the significantly higher concentration of Pt within the O horizon at the Hugo Peak and XA-5 sites suggests biosolids application improved litter quality with respect to P within treated stands. Below the forest floor, soil organic P concentrations in mineral soil treated with biosolids are significantly greater than controls. Assuming P availability has been elevated for a number of years below the forest floor, this is probably the result of greater nutrient uptake and accumulation of P within the living and dead biomass in the rooting zone.

Table 6.9. Carbon, nitrogen and phosphorus ratios at the Hugo Peak and XA-5 sites. n=6.

<u>Site-Tmt.</u>	<u>Sampling Depth</u>	<u>C/N</u>	<u>C/P</u>	<u>N/P</u>
		-----g g <sup>-1</sup> -----		
<u>Hugo-C</u>	0-15	26	129	5
<u>Hugo-T</u>	0-15	13	22	2
<u>Hugo-C</u>	15-30	25	144	5
<u>Hugo-T</u>	15-30	15	23	2
<u>XA-5-C</u>	0-15	19	29	2
<u>XA-5-T</u>	0-15	12	16	1
<u>XA-5-C</u>	15-30	18	28	2
<u>XA-5-T</u>	15-30	19	9	0.5

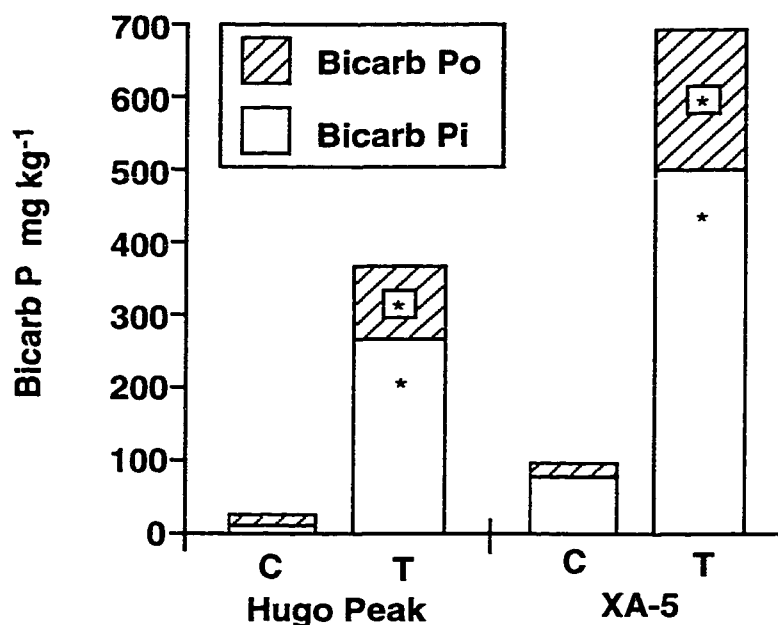


Figure 6.11. Concentration of bicarbonate (Bicarb) extractable Pi and Po in soil removed from 0-15 cm at the Hugo Peak and XA-5 sites. Statistical comparisons are made between Po or between Pi in pairs at each site. Significant differences between control (C) and biosolids treated (T) soil at each site were determined using a paired Student's *t*-test on log transformed data (\* $p < 0.05$ )  $n = 6$ .

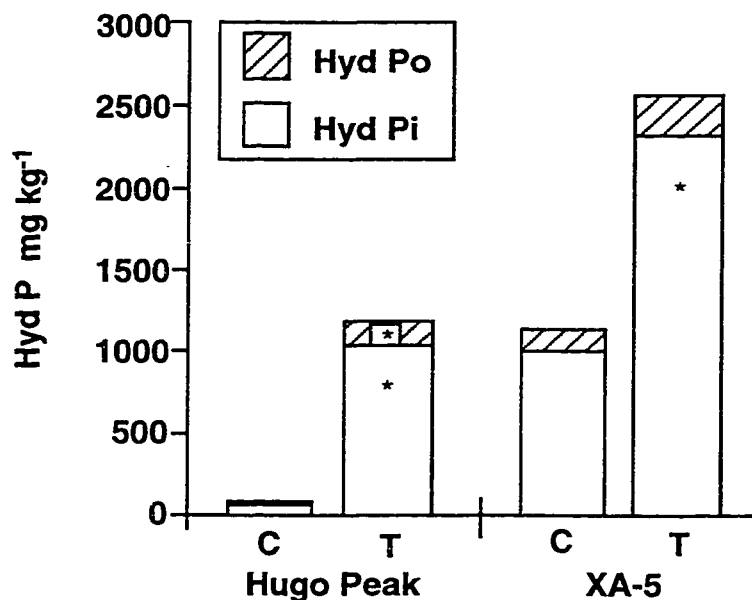


Figure 6.12. Concentration of hydroxide (Hyd) extractable Pi and Po in soil removed from 0-15 cm at the Hugo Peak and XA-5 sites. Statistical comparisons are made between Po or between Pi in pairs at each site. Significant differences between control (C) and biosolids treated (T) soil at each site were determined using a paired Student's *t*-test on log transformed data (\* $p < 0.05$ )  $n = 6$ .

## 6.4 Summary

The vertical mobility and fate of P applied in biosolids to two different forest soils were examined at Pack Forest, Washington. Two study sites were selected where the effect of surface application of 105 Mg ha<sup>-1</sup> of biosolids could be compared for effects on soil P status and mobility and on dominant P retention mechanisms. Two additional sites were selected for study, where the effect of directly incorporating biosolids into the soil on soil P status and dominant retention mechanisms was examined.

Study results demonstrate that surface application of biosolids at a cumulative loading rate of 105 Mg ha<sup>-1</sup> does not induce vertical movement of P. No significant differences were noted in any P fraction below 15 cm at the two study sites where surface applications were used. In surface applications, phosphate or soluble organic P must move downward through the soil before biological immobilization, uptake, adsorption or precipitation can occur. Phosphorus increases are noted in the most labile fractions while the refractory P pools remain relatively unaffected by surface biosolids application.

In contrast, direct incorporation of heavy rates of biosolids markedly changes both the concentration and relative abundance of P fractions, as biosolids particles contact mineral soil surfaces directly and presumably remain in the soil for a number of years after application. This contact and apparent slow release of biosolids P has led to statistically significant increases in all P fractions between 0-15 cm below the forest floor and substantial—but not always statistically significant—increases to a depth of 30 cm.

The primary soil inorganic P pools enriched by a surface biosolids application were those extracted by resin, bicarbonate, and hydroxide. These P fractions represent

exchangeable, labile, and moderately labile P pools, respectively. Biosolids contains high concentrations of all these fractions. The largest gains were noted in the P pool extracted by hydroxide. This pool is thought to consist primarily of P adsorbed onto hydrous oxides of Al and Fe. The abundance of these metal cations and their “free” forms in soils at Pack Forest were clearly demonstrated.

Hypothesis 2 states that the concentration of phosphorus in the soil following biosolids application at a P loading rate of 2 Mg ha<sup>-1</sup> will decline significantly with depth below the forest floor. This hypothesis was supported, as soil P fractionation data show that cumulative surface application of biosolids produced no noticeable increases in the mean concentration of P fractions deeper than 15 cm below the forest floor at sites where surface applications were used.

Hypothesis 3 states that biosolids application at a P loading rate of 2 Mg ha<sup>-1</sup> will significantly increase the concentration of sorbed P fractions in the top 15 cm of mineral soil. Based on results from the SDS, this hypothesis was supported. The concentration of sorbed labile and moderately labile P as extracted by bicarbonate and hydroxide was the largest sink for P in biosolids treated soils. At the Gessel site, this was true only in the O horizon, with mineral soil P concentrations generally unaffected by biosolids application. At this site, release of P from biosolids may also limit P mobility into subsoils in addition to soil sinks. In general, however, P sorption onto hydrous oxides of Al and Fe was identified as the primary retention mechanism in biosolids treated soils.

Hypothesis 4 states that biosolids application at a P loading rate of 2 Mg ha<sup>-1</sup> will significantly increase soil P availability in the top 15 cm of mineral soil. The marked increase in exchangeable and bicarbonate extractable P in biosolids treated soil and the

increase  $P_i/P_o$  ratios in O horizon material and in soil removed from 0-15 cm at the SDS suggests that biosolids has increased the pool of potentially labile and moderately labile  $P_i$  at all sites, supporting Hypothesis 4. In addition, resin extractable P was significantly greater in biosolids treated soil at the Gessel site and this fraction represents the most plant available P form identified. The data from the Hugo and XA-5 sites also show that biosolids provides a long-term supply of plant available phosphate near the forest floor.

## 6.5 Conclusions

1. There is strong phosphorus retention in the soil following surface application of biosolids. No statistically significant differences in P fraction concentrations were noted below 15 cm at two separate study sites on either residual or outwash soils.
2. Soil P availability is increased near the forest floor by either surface application or direct incorporation of biosolids using cumulative loading rates between 105 and 470 Mg ha<sup>-1</sup>.
3. Adsorption of P onto soil Al and Fe hydrous oxides and amorphous Al silicates and Al humates where volcanic ash is present is the predominant mechanism for soil P retention in soils treated with biosolids at Pack Forest.

## CHAPTER VII

## SUMMARY AND IMPLICATIONS

The studies described in this dissertation examine the mobility and fate of P applied in biosolids used for forest fertilization. The water quality effects of using biosolids within a steep, forested watershed were addressed by measuring P and N forms in 27 Creek, a small first-order stream draining a 21.4 ha headwater watershed at Pack Forest, Washington. Water quality and quantity measurements were made under a range of Creek discharge conditions before and after biosolids application.

Soil water interflow was also assessed as a pathway of P movement from hydrologically active biosolids application sites. A separate field study within the Tiger Mountain State Forest near Preston, Washington, addressed the effect of biosolids application on the concentration of phosphate in soil water interflow during runoff event conditions. Nitrogen was also included to provide a contrast with P regarding mobility following biosolids application.

Finally, the vertical mobility of P in acidic forest soil treated repeatedly or with a single heavy application of biosolids were assessed at Pack Forest, Washington. Four separate sites on two different soil types were sampled for soil P forms at three discrete depths: O horizon, 0-15 cm and 15-30 cm. Operationally defined P pools were identified using a P sequential extraction procedure. This procedure aided in identifying the dominant P retention mechanisms in the soil following biosolids application. It also provided information about the relative availability of P and the influence of biosolids on accumulation of inorganic versus organic P in biosolids treated and control soils.

## 7.1 Overall summary

The mobility of P following biosolids application to forest soils is strongly limited, by soil retention mechanisms and, in addition, possibly by slow release of P from biosolids. Field studies characterizing P mobility following a single biosolids application to soils never previously fertilized showed that runoff waters (surface or soil interflow) contacting biosolids treated areas carry little, if any, P from biosolids. Fractionation of mineral soil P forms to a depth of 30 cm following a single application revealed no statistically significant increases in mean P concentrations. Thus, it appears both the release of P from biosolids as well as the soil's retentive capacity for P limit mobility. In contrast, N as  $\text{NO}_3^-$ -N was detected in runoff waters and in soil water interflow during periods of elevated discharge. Thus, these pathways undoubtedly exist, and the impact of biosolids can be seen with some constituents, but not with P.

Repeated application of biosolids resulting in a cumulative P loading of  $2 \text{ Mg P ha}^{-1}$  over the forest floor elevated the concentration of certain P fractions in the forest soils studied. Significant mean concentration increases in the most labile P fractions in the 0-15 cm mineral soil sampling depth were noted; adsorption to mineral soil surfaces (presumably hydrous oxides of Al and Fe) was the primary pool enriched by surface biosolids application. The soils studied all have a large capacity to retain P. Repeated biosolids applications at rates designed to meet stand N demands do not appear to diminish the soil's ability to retain additional P. No statistically significant differences were observed in the concentration of any P fraction below 15 cm.

## 7.2 Phosphorus and N mobility from biosolids on a watershed scale

Biosolids application at a rate of  $13.5 \text{ Mg ha}^{-1}$  to 40% of a 21 ha steep, forested watershed at Pack Forest, Washington did not result in direct runoff of P or N forms to

surface waters. Phosphorus does not appear to move far from the zone of application, as equilibrium P concentrations are maintained between the soil water and runoff water that enters 27 Creek, probably because of slow release of biosolids P and strong soil retention of added P via sorption reactions.

Runoff events were suspected of inducing movement of labile P compounds from biosolids into surface water following biosolids application to forested slopes greater than 30%. No clear difference in 27 Creek labile P concentration was observed before or after biosolids application under any discharge conditions. Elevated concentrations of total P were noted after biosolids application, but its appearance was episodic and inconsistent. Moreover, increases in non-labile particulate P coinciding with seasonal runoff events suggest that the source of increase in total P after application may not be related to biosolids, but rather to near-stream detrital P sources.

Nitrogen, in the form of  $\text{NH}_3\text{-N}$ , appears to be retained within the soil immediately following biosolids application. Biosolids application had no effect on 27 Creek  $\text{NH}_3\text{-N}$  concentrations under any discharge condition. Conversely,  $\text{NO}_3^-\text{-N}$  concentrations in 27 Creek noticeably increased nine months after biosolids application. Increases in concentration were positively related to discharge; no relationship existed prior to biosolids application in the watershed. However, of the nearly 5900 kg total N applied in biosolids, less than 1% of this was removed from the watershed in surface water runoff as  $\text{NO}_3^-\text{-N}$ .

### 7.2.1 Implications

Experimental evidence collected during monitoring of the 27 Creek watershed before and after biosolids application suggests that dewatered biosolids can be used on steep slopes in excess of 30% without jeopardizing receiving water quality. Direct runoff of P or N forms from biosolids was not observed. A combination of factors likely produced this result, including limited release of P and N from biosolids, strong soil retention of added nutrients, and the use of physical buffers around stream and ephemeral drainages.

As biosolids decomposes it releases nutrients. However, the behavior of P and N provides a striking contrast with regard to mobility following their release from biosolids. Phosphorus is strongly conserved in the soil and it appears a single application of biosolids has done little to alter the pattern of P movement from the watershed. Conversely, after biosolids application elevated concentrations of  $\text{NO}_3^-$ -N were observed in stream water, especially during periods of high stream discharge. However, the mean  $\text{NO}_3^-$ -N concentrations in 27 Creek are an order of magnitude lower than the drinking water standard in Washington state of  $10 \text{ mg L}^{-1}$  and export losses of nitrate are a very small percentage of total N applied.

### 7.3 Phosphorus and N mobility from biosolids in soil water interflow

The vertical and lateral mobility of  $\text{PO}_4$ -P and  $\text{NO}_3^-$ -N in forest soil water following a single biosolids application to a 12-year-old Douglas-fir stand located on a steep slope was examined at a site near Tiger Mountain, Washington. Measuring interflow discharge under a range of hydrologic conditions and determining the concentrations of  $\text{PO}_4$ -P and  $\text{NO}_3^-$ -N in interflow gave contrasting results. In nearly 90% of the interflow samples collected,  $\text{PO}_4$ -P concentrations were below the detection limit of  $0.01 \text{ mg L}^{-1}$ . Segregation

of the data into discrete soil horizon collection depths revealed that  $\text{PO}_4\text{-P}$ , when detected, was found only in near surface soils, generally corresponding to the A and  $\text{B}_1$  horizons at the Tiger Mountain site. In no case was  $\text{PO}_4\text{-P}$  ever detected in soil water moving laterally below 60 cm. During periods when water sampling was performed concurrently with interflow discharge measurements, a weak trend of decreasing  $\text{PO}_4\text{-P}$  concentrations with increasing interflow discharge was observed.

Interflow was suspected as a potential pathway for the transfer of  $\text{PO}_4\text{-P}$  from biosolids to surface water. However, elevated concentrations of  $\text{PO}_4\text{-P}$  following biosolids application (total P loading rate of approximately  $500 \text{ kg ha}^{-1}$ ) were never observed during more than a one year period after biosolids application. The application of biosolids had no effect on the concentration of  $\text{PO}_4\text{-P}$  in interflow at any depth and did not change the  $\text{PO}_4\text{-P}$  concentration-discharge relationship.

Nitrate concentrations were also measured in interflow coincident with  $\text{PO}_4\text{-P}$  measurements. A biosolids treatment of  $675\text{-}700 \text{ kg N ha}^{-1}$  increased interflow  $\text{NO}_3\text{-N}$  concentrations and this effect was observed approximately six months after application at the onset of autumn rain events. Without the application of biosolids, the interflow  $\text{NO}_3\text{-N}$  concentration-discharge relationship is generally linear over the discharge rates measured. Conversely, a biosolids application changes this relationship markedly, with high discharge rates ( $>0.01 \text{ L sec}^{-1}$ ) resulting in elevated  $\text{NO}_3\text{-N}$  concentrations.

Vertical migration of P from biosolids into the soil beyond the O horizon was relatively minor. Hypothesis 1 states that the concentration of soil P fractions will be significantly increased by a single biosolids application to a Tokul series soil. Study results do not support this hypothesis. O horizon material was enriched with P from the biosolids

applied. However, there were no statistically significant differences in soil P fractions comparing control and biosolids treated soils at either the 0-15 cm or 15-30 cm depths. Thus, the limited mobility of P may be due simply to the lack of release of P from biosolids in addition to attenuation of P within the O horizon and eventually mineral soil horizons.

### 7.3.1 Implications

The contrasting patterns of  $\text{PO}_4\text{-P}$  and  $\text{NO}_3\text{-N}$  mobility following biosolids application have important consequences relative to the influence of rainfall induced runoff events on the mobility of P and N contained in biosolids. Runoff events are suspected as being the principal pathway for nutrient export and possible loss from an application site. The data suggest runoff events are important in mobilizing N from biosolids application sites via interflow, yet relatively unimportant in mobilizing P. In addition, the data provide support for the theory that N mobility limits the application of biosolids to PNW forests, while P mobility is relatively limited.

## 7.4 Vertical P mobility and fate of P in forest soils following biosolids application

The vertical mobility and fate of P in biosolids applied to two different forest soils were examined at Pack Forest, Washington. Four study sites were selected where the effect of surface versus direct incorporation and heavy versus lesser application rates could be compared and contrasted for effects on soil P status and mobility and on dominant P retention mechanisms.

Study results demonstrate that surface application of biosolids at a cumulative loading rate of  $105 \text{ Mg ha}^{-1}$  ( $2 \text{ Mg P ha}^{-1}$ ) did not induce vertical movement of P. Hypothesis 2 states that the concentration of phosphorus in the soil following biosolids

application at a P loading rate of  $2 \text{ Mg ha}^{-1}$  will decline significantly with depth below the forest floor. This hypothesis was supported, as soil P fractionation data show that cumulative surface application of biosolids produced no noticeable increases in the mean concentration of P fractions deeper than 15 cm below the forest floor. Phosphorus increases were noted in the most labile fractions while the refractory P pools remain relatively unaffected by surface biosolids application.

Hypothesis 3 states that biosolids application at a P loading rate of  $2 \text{ Mg ha}^{-1}$  will significantly increase the concentration of sorbed P fractions in the top 15 cm of mineral soil. Based on results from the SDS and Gessel sites, this hypothesis was supported. The concentration of sorbed labile and moderately labile P as extracted by bicarbonate and hydroxide were the largest pools of P in biosolids treated soils. At the Gessel site, this was true only in the O horizon, with mineral soil P concentrations generally unaffected by biosolids application. Thus, P adsorption onto hydrous oxides of Al and Fe, amorphous Al silicates, and Al humates appears to be the primary mechanism that limits deeper P movement into subsoils.

Hypothesis 4 states that biosolids application at a P loading rate of  $2 \text{ Mg ha}^{-1}$  will significantly increase soil P availability in the top 15 cm of mineral soil. The marked increase in resin and bicarbonate extractable P in biosolids treated soil and the increase  $P_i/P_o$  ratios in O horizon material and in soil removed from 0-15 cm at the SDS suggests that biosolids has increased the pool of potentially labile and moderately labile  $P_i$  at all sites, supporting Hypothesis 4. In addition, resin extractable P was significantly greater in biosolids treated soil at the Gessel site, as this fraction represents the most plant available P form identified. The data from the Hugo and XA-5 sites also show that biosolids provides a long-term supply of plant available phosphate near the forest floor.

In contrast, direct incorporation of heavy rates of biosolids markedly changes both the concentration and relative abundance of P fractions, as biosolids particles contact mineral soil surfaces directly and presumably remain in the soil for a number of years after application. This contact and apparent slow release of biosolids P has led to statistically significant increases in all P fractions between 0-15 cm below the forest floor and substantial--but not always statistically significant--increases to a depth of 30 cm. The absolute depth of effect of a single heavy application was not determined.

#### 7.4.1 Implications

Biosolids are applied to Douglas-fir forests in the PNW based primarily on N release and subsequent transformations following application. Despite repeated application of biosolids over the forest floor, P movement into subsoils below 15 cm did not occur regardless of soil type: residual or outwash. Certainly, some differences exist between soil types. Outwash soils have a much higher native P status than do residual soils (2000 vs. 300 mg kg<sup>-1</sup> total P), and the abundance of free Al and Fe is 2 to 3 times greater in outwash soils, which can increase adsorption of P. However, study data showed that outwash and residual soils at Pack Forest, both untreated and those treated with 105 to 470 Mg ha<sup>-1</sup> of biosolids, have a similar capacity to retain P. In fact, soil retention of added P following surface biosolids application elevated soil P availability near the forest floor for a number of years since application. The lack of vertical mobility combined with the elevation of soil P availability suggests that the soils studied--certainly those receiving a cumulative loading of 2 Mg P ha<sup>-1</sup>--could support additional biosolids P loadings. Increased loadings would presumably continue to elevate the equilibrium phosphorus concentration supported in the soil solution. Thus, the decision to apply additional phosphorus via biosolids fertilization should be made based on the concentration of soil solution P to be supported, as the soils studied clearly demonstrate capacity to retain P.

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## APPENDIX A. TRACER EXAMINATION AT TIGER MOUNTAIN

## Part A. Rationale

Conservative tracers were used to better understand the pattern of soil water interflow movement through the Tiger Mountain site and to assess the likelihood of water contacting biosolids and moving to control interflow collector positions. The tracers used were bromide, fluoride, and chlorine, applied as dilute reagent grade salt mixtures. Ten L of 100 mg L<sup>-1</sup> solutions of NaBr, NaF, and KCl were applied to separate 80 m<sup>2</sup> areas above each collector in February 1997. Sampling began four months prior to tracer application to attempt to establish background concentrations and continued during the remainder of the study. Water samples were analyzed for Br, F, and Cl using ion chromatography. Fluoride analysis was suspended after 2 months. Detection limits in mg L<sup>-1</sup> are as follows: Br=0.01; Cl=0.01; Fl=0.002.

Results of the initial tracer application were mixed, with some indication that cross contamination could occur between certain plots. Sodium fluoride was applied above collector C-3, but was detected in collector C-2 on two occasions afterward that were above the background concentration of approximately 0.01 mg L<sup>-1</sup> (Table A.1). Fluoride was never detected in collector C-3 after tracer application. It was also applied above collector B-3, yet was only detected three times after application near the application area: once in collector B-2 (0.01 mg L<sup>-1</sup>) and twice in collector C-1 (0.009 and 0.086 mg L<sup>-1</sup>). Bromide generally did not appear in any of the collectors immediately following the February 1997 application; the exception was from collector B-2, where bromide was detected during an early summer rain event at 0.7 mg L<sup>-1</sup>. Background chloride concentrations appeared to mask any effect of the KCl tracer applied. Thus, potential for ion movement from plot C-3 to C-2 was identified and it was expected that ion movement could occur between plots B-3

and C-1. As plots B 1-3 are downslope of plots C 1-3, a decision was made to separate the site into separate control and biosolids-treated areas, with the control plots and interflow collectors located upslope of the treated plots and collectors.

Subsequent application of 30 L of 100 mg NaBr L<sup>-1</sup> during early October 1997 to a 720 m<sup>2</sup> area above collectors B 1-3 revealed that water moving through the biosolids-treated plots did not move to nearby control collectors. In fact, bromide was never detected in collector C-1 and, bromide detected in collector C-2 at 0.9 mg L<sup>-1</sup> in January 1998 was attributed to the original application of bromide to plot C-2. Bromide was detected on a number of occasions in collectors B1-3 draining biosolids-treated plots and ranged from 0.01 to 0.7 mg L<sup>-1</sup> (Table A.1).

Table A.1. Tracer Data Summary

Interflow collector C-3 FI applied 2/4/97										Interflow collector C-2 Br applied 2/4/97										Interflow collector C-1 CI applied 2/4/97										Interflow collector B-3 FI applied 2/4/97 Br applied 10/1/97										Interflow collector B-2 Br applied 2/4/97										Interflow collector B-1 No tracer check 2/4/97 Br applied 10/1/97									
Date	Col.	Pos.	Cl	Br	FI	detection limits (mg L <sup>-1</sup> )	Date	Col.	Pos.	Cl	Br	FI	detection limits (mg L <sup>-1</sup> )	Date	Col.	Pos.	Cl	Br	FI	detection limits (mg L <sup>-1</sup> )	Date	Col.	Pos.	Cl	Br	FI	detection limits (mg L <sup>-1</sup> )	Date	Col.	Pos.	Cl	Br	FI	detection limits (mg L <sup>-1</sup> )																									
10/1/96	3					0.27 0.00 0.000	10/1/96	4					0.31 0.00 0.000	10/1/96	3						0.18 0.00 0.000	10/1/96	4					0.13 0.00 0.000	10/1/96	4				0.19 0.00 0.000																									
12/31/96	1					0.55 0.00 0.010	12/31/96	1					0.50 0.00 0.010	1/2/97	3							0.38 0.00 0.010	1/2/97	4					1.02 0.00 0.026	1/2/97	3				0.75 0.00 0.010																								
1/2/97	4					0.41 0.00 0.010	12/31/96	2					0.63 0.00 0.010	2/4/97	3							1.04 0.00 0.000	1/2/97	4					0.19 0.00 0.000	1/2/97	2				0.31 0.00 0.000																								
2/4/97	1					1.68 0.00 0.000	1/2/97	4					0.14 0.00 0.010	2/19/97	1							1.17 0.00 0.000	2/4/97	2					0.80 0.02 0.000	2/4/97	1				0.54 0.00 0.000																								
2/19/97	1					1.98 0.00 0.000	2/4/97	1					1.34 0.00 0.000	2/19/97	2							1.37 0.00 0.000	2/19/97	2					0.26 0.00 0.000	2/19/97	2				1.55 0.00 0.000																								
2/24/97	1					2.53 0.00 0.000	2/19/97	1					1.08 0.00 0.000	2/19/97	3							1.62 0.00 0.000	2/19/97	2					4.09 0.00 0.000	2/19/97	2				0.51 0.00 0.000																								
3/1/97	1					2.21 0.00 0.000	2/24/97	1					1.74 0.00 0.013	2/24/97	1							1.71 0.00 0.009	2/19/97	1					4.09 0.00 0.000	2/19/97	3				1.50 0.00 0.000																								
3/6/97	2					0.00 0.00 0.000	3/1/97	1					0.50 0.00 0.009	3/1/97	2							1.54 0.00 0.000	3/1/97	3					0.53 0.00 0.000	3/1/97	2				1.50 0.00 0.000																								
3/6/97	2					0.00 0.00 0.000	3/6/97	1					0.00 0.00 0.020	3/6/97	1							1.67 0.00 0.000	2/19/97	3					0.48 0.00 0.000	3/1/97	2				1.63 0.00 0.004																								
6/5/97	2					2.14 0.00	3/6/97	2					0.00 0.00 0.045	3/1/97	1							1.67 0.00 0.000	2/24/97	1					5.28 0.00 0.000	3/1/97	2				2.07 0.00 0.000																								
7/17/97	1					0.81 0.00	3/6/97	3					0.00 0.00 0.000	3/3/97	2							1.81 0.00 0.000	2/28/97	2					0.26 0.00 0.000	3/6/97	2				1.71 0.00 0.000																								
10/1/97	1					1.21 0.10	6/5/97	1					0.53 0.00	3/1/97	2							1.62 0.00 0.000	3/1/97	1					3.39 0.00 0.000	3/6/97	3				0.00 0.00 0.000																								
10/30/97	1					1.99 0.00	7/17/97	1					1.36 0.00	3/1/97	1							0.00 0.00 0.000	3/1/97	3					2.84 0.00 0.000	6/5/97	2				1.47 0.00																								
10/30/97	3					0.45 0.00	10/1/97	1					3.80 0.00	3/6/97	2							1.16 0.00 0.000	3/6/97	2					0.00 0.00 0.000	6/5/97	3				0.24 0.00																								
11/30/97	1					1.93 0.00	10/1/97	1					3.80 0.00	10/1/97	3							1.15 0.02	3/6/97	3					0.00 0.00 0.000	7/17/97	2				0.70 0.00																								
11/30/97	4					0.52 0.00	10/30/97	1					0.35 0.00	6/5/97	2							0.73 0.02	6/5/97	1					0.00 0.00 0.000	10/1/97	1				5.97 0.00																								
12/18/97	1					2.47 0.00	10/30/97	2					1.02 0.00	6/5/97	2							0.14 0.00	6/5/97	2					0.20 0.00	10/30/97	2				6.00 0.02																								
12/18/97	4					0.58 0.00	10/30/97	2					4.06 0.00	7/17/97	1							0.36 0.00	6/5/97	2					0.24 0.00	10/30/97	2				8.00 0.02																								
1/5/98	1					2.34 0.00	10/30/97	4					3.44 0.00	10/1/97	1							2.40 0.00	7/17/97	1					0.11 0.00	10/30/97	3				2.11 0.04																								
1/5/98	4					0.75 0.00	11/30/97	1					3.10 0.00	10/1/97	2							0.60 0.00	1/5/98	1					6.84 0.00	11/30/97	2				6.92 0.00																								
1/6/98	1					1.68 0.00	11/30/97	4					0.48 0.00	10/30/97	4							1.16 0.00	10/1/97	1					0.69 0.00	11/30/97	3				8.85 0.00																								
1/6/98	4					0.75 0.00	12/16/97	1					1.68 0.00	10/30/97	1							2.82 0.00	10/30/97	1					8.89 0.00	12/16/97	2				4.98 0.00																								
1/7/98	1					1.44 0.00	12/18/97	1					2.15 0.00	10/30/97	2							1.68 0.01	10/30/97	2					2.22 0.04	12/16/97	3				0.95 0.00																								
1/7/98	4					0.75 0.00	12/18/97	2					0.85 0.00	10/30/97	3							3.38 0.00	1/7/98	4					0.90 0.02	1/5/98	1				0.18 0.19																								
1/14/98	1					1.65 0.00	12/18/97	4					0.63 0.00	11/30/97	1							3.27 0.00	11/30/97	4					2.74 0.00	1/5/98	1				3.55 0.00																								
1/14/98	3					0.62 0.00	1/5/98	1					1.33 0.00	12/18/97	4							3.03 0.00	12/18/97	1					9.25 0.00	1/5/98	3				6.27 0.00																								
1/23/98	1					1.50 0.00	1/6/98	4					0.86 0.00	12/18/97	1							1.59 0.00	12/18/97	2					1.64 0.01	1/6/98	3				6.27 0.00																								
3/15/98	1					1.09 0.00	1/6/98	2					1.13 0.00	12/18/97	2							2.27 0.00	1/5/98	1					1.25 0.00	1/6/98	2				2.83 0.00																								
3/15/98	4					0.82 0.00	1/6/98	4					0.87 0.00	1/6/98	3							0.89 0.00	1/5/98	2					1.53 0.01	1/6/98	3				1.27 0.00																								
5/27/98	1					0.46 0.00	1/7/98	1					1.12 0.00	1/5/98	2							1.62 0.00	1/6/98	1					7.18 0.00	1/7/98	2				1.45 0.00																								
6/24/98	1					0.00 0.00	1/7/98	2					0.87 0.00	1/5/98	3							2.14 0.00	1/6/98	2					2.18 0.01	1/7/98	3				1.25 0.00																								
							1/7/98	4					0.82 0.00	1/6/98	1							1.86 0.00	1/6/98	4					4.11 0.00	1/14/98	2				2.00 0.00																								
							1/14/98	1					0.82 0.00	1/6/98	2							0.66 0.00	1/7/98	1					1.11 0.00	1/14/98	3				2.00 0.00																								
							1/14/98	2					0.83 0.00	1/6/98	3							2.33 0.00	1/7/98	2					2.31 0.01	1/14/98	2				1.22 0.00																								
							1/14/98	3					0.85 0.00	1/6/98	4							1.41 0.00	1/14/98	1					2.78 0.00	1/23/98	3				2.44 0.00																								
							1/14/98	4					0.85 0.00	1/7/98	1							0.91 0.00	1/14/98	2					1.28 0.02	1/23/98	1				0.91 0.00																								
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							1/23/98	1					1.76 0.00	1/7/98	3							1.38 0.00	1/23/98	2					0.89 0.00	3/15/98	3				3.15 0.00																								
							1/23/98	2					0.77 0.00	1/14/98	1							0.57 0.00	1/14/98	1					4.20 0.00	3/15/98	1				0.84 0.00																								
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							3/15/98	2					0.62 0.00	1/14/98	4							0.96 0.00	1/14/98	4					0.39 0.00																														
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							5/27/98	1					1.30 0.00	3/15/98	1							1.25 0.00	3/15/98	2					1.86 0.00																														
							6/24/98	1					0.21 0.00	6/24/98	1							1.86 0.00	6/24/98	1					0.70 0.00																														
							6/24/98	2					0.51 0.00	6/24/98	2							0.19 0.00	6/24/98	2					1.11 0.00																														

Notes: D values denote anion concentrations below detection limit.

## VITA

Name: Mark Alan Grey

Date of Birth: November 9, 1961

Place of Birth: Longview, Washington, USA

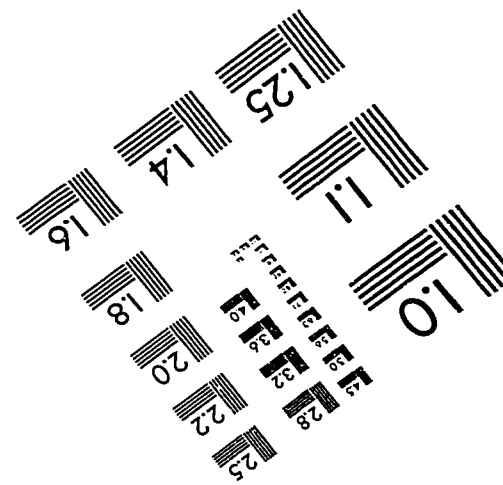
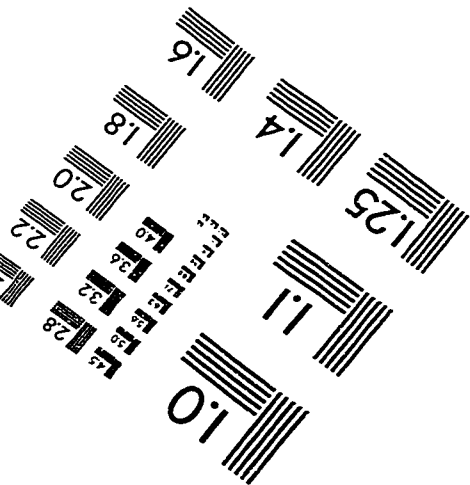
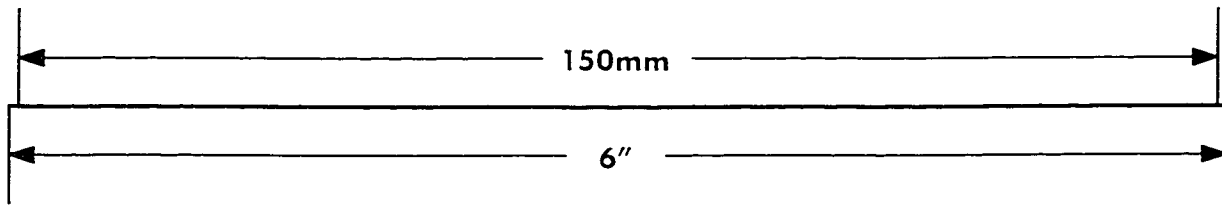
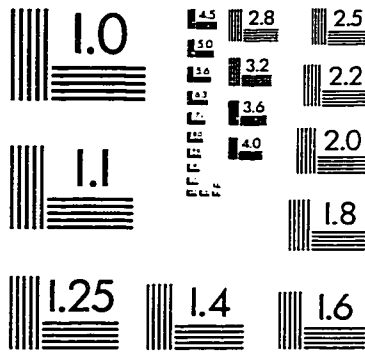
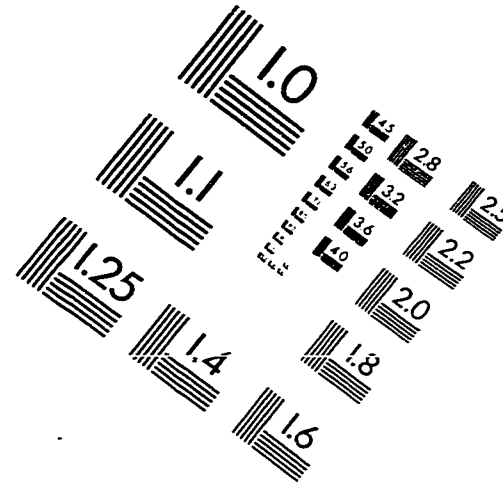
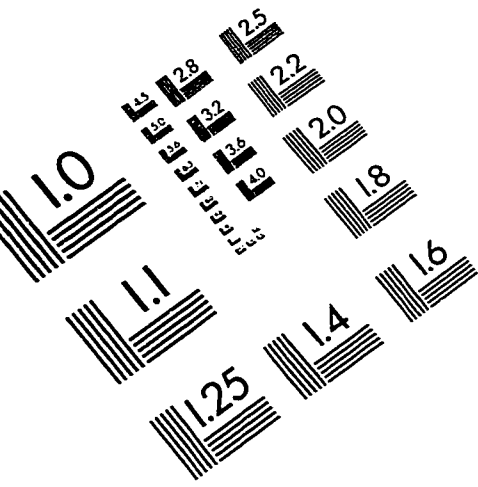
Education: Kalama High School, 1980

Bachelor of Arts (English), 1984  
Eastern Washington University, Cheney, Washington

Master of Science (Forest Ecosystem Analysis), 1995  
University of Washington, Seattle, Washington

Doctor of Philosophy (Forest Soils/Organic Waste Recycling), 1999  
University of Washington, Seattle, Washington

# IMAGE EVALUATION TEST TARGET (QA-3)



**APPLIED IMAGE, Inc**  
1653 East Main Street  
Rochester, NY 14609 USA  
Phone: 716/482-0300  
Fax: 716/288-5989

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