

# Phosphorus forms and response to changes in pH in acid-sensitive soils on the Precambrian Shield

A Thesis submitted to the Committee of Graduate Studies in Partial Fulfillment of the requirements for the Degree of Master of Science in the Faculty of Arts and Science

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## **Abstract**

Phosphorus forms and response to changes in pH in acid-sensitive soils on the Precambrian Shield

Scott Robert Baker

Catchment soil acidification has been suggested as a possible mechanism for reducing phosphorus (P) loading to surface waters in North America and northern Europe, but much of the research that has been conducted regarding P immobilization in pH manipulated soils has been performed at high P concentrations ( $> 130 \mu\text{M}$ ). This study investigated how soil acidity was related to P fractionation and P sorption at environmentally relevant P concentrations to evaluate the potential influence of long term changes in soil pH on P release to surface waters. Total phosphorus (TP) concentrations declined between 1980 and 2000 in many lakes and streams in central Ontario; over the same time period forest soils in this region became more acidic. Soils were collected from 18 soil pits at three forested catchments with similar bedrock geology but varying TP export loads. The soil pH at the 18 study soil pits spanned the historic soil pH range, allowing for 'space for time' comparison of soil P fractions. Soils were analysed by horizon for P fractions via Hedley P fractionation. Batch P sorption experiments were performed on selected B-horizon soils at varied solution pH. Soil P fractions varied by horizon but were comparable among the three catchments, with only apatite ( $\text{P}_{\text{HCl}}$ ) differing significantly across catchments. Contrary to expectation, both soluble and labile P showed negative relationships with pH in some horizons. Mineral soils were able to sorb almost all ( $> 90 \%$ ) of the P in solution at environmentally relevant P concentrations ( $4.5 - 45.2 \mu\text{M}$ ). Phosphorus sorption at environmentally relevant P concentrations was unrelated to solution pH but at high P concentration there was a positive relationship between P sorption and solution pH, suggesting a P concentration dependant P sorption mechanism. Phosphorus budgets indicate that P is accumulating within catchments, suggesting that P is being immobilized in the terrestrial environment. An alternative hypothesis, which attempts to explain both the decline in stream TP export and terrestrial P accumulation, is discussed. The results from this study suggest that acidification

induced P sorption in upland soils are not a contributing factor to decreases in stream TP concentration in the study catchments.

**Keywords:** phosphorus, soil acidification, Hedley fractionation, sorption, podzols, central Ontario

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## LIST OF ABBREVIATIONS AND SYMBOLS

Aluminium (Al)  
Aluminum Extracted with 0.2M Ammonium Oxalate and 0.2 M Oxalic Acid ( $Al_{ox}$ )  
Amphibolite and Schist (AS)  
Bear Brook Watershed in Maine (BBWM)  
Biotite, Hornblende and Gneiss (BHG)  
Calcium (Ca)  
Calcium Chloride ( $CaCl_2$ )  
Carbon (C)  
Cation Exchange Capacity (CEC)  
Dorset Environmental Science Centre (DESC)  
Exchangeable Aluminium ( $Al_{exg}$ )  
Exchangeable Calcium ( $Ca_{exg}$ )  
Exchangeable Potassium ( $K_{exg}$ )  
Exchangeable Magnesium ( $Mg_{exg}$ )  
Harp 3 Catchment (HP3)  
Harp 3A Catchment (HP3A)  
Hydrochloric Acid (HCl)  
Inorganic 0.1M Sodium Hydroxide Extractable Phosphorus ( $P_{NaOH_i}$ )  
Inorganic 0.5 M Sodium Bicarbonate Extractable Phosphorus ( $P_{NaHCO_3_i}$ )  
Inorganic Water Extractable Phosphorus ( $P_{H_2O_i}$ )  
Iron (Fe)  
Iron Extracted with 0.2M Ammonium Oxalate and 0.2 M Oxalic Acid ( $Fe_{ox}$ )  
Litter, Fibric and Humic (LFH)  
Migmatite (MIG)  
Nitrate ( $NO_3$ )  
Nitrogen (N)  
Organic 0.1M Sodium Hydroxide Extractable Phosphorus ( $P_{NaOH_o}$ )  
Organic 0.5M Sodium Bicarbonate Extractable Phosphorus ( $P_{NaHCO_3_o}$ )  
Organic Water Extractable Phosphorus ( $P_{H_2O_o}$ )  
Phosphorus (P)  
Phosphate ( $PO_4$ )  
Phosphorus Extracted with 0.2M Ammonium Oxalate and 0.2 M Oxalic Acid ( $P_{ox}$ )  
Phosphorus Extracted with 1M Hydrochloric Acid ( $P_{HCl}$ )  
Phosphorus in Ashed Soil Extracted with 1M Sulphuric Acid ( $P_{H_2SO_4}$ )  
Plastic 1-08 Catchment (PC1-08)  
Sodium Bicarbonate ( $NaHCO_3$ )  
Sodium Hydroxide (NaOH)  
Sulphate ( $SO_4$ )  
Sulphur (S)  
Sum of Phosphorus Found in the Four Extractions of the Hedley Fractionation ( $P_{sum}$ )  
Total Phosphorus in Soil ( $TP_s$ )  
Total Phosphorus in Water ( $TP_w$ )

## 1.0 Introduction

Since the 1980s significant decreases in surface water total phosphorous ( $TP_w$ ) concentrations have been recorded in central Ontario lakes and streams and are largely unexplained (Eimers et al. 2009, Yan et al. 2008). At the same time, despite reductions in acid deposition, soils in the region have acidified (Watmough and Dillon 2004, Miller and Watmough 2009), which has delayed the chemical recovery of many lakes (Stoddard et al. 1999). As current  $TP_w$  concentrations in many lakes in the region are very low ( $<10 \mu\text{g L}^{-1}$ , Yan et al. 2008) it is important to understand the causes of the decline in  $TP_w$  export to lakes. Soil acidity affects indicators of soil phosphorus (P) mobility (Barrow 1983, Kaňa and Kopáček 2006) although contradicting results are reported in the literature (Hingston et al. 1971, Geelhoed et al. 1997). The goal of this research is to evaluate the influence of changing soil pH on P forms and mobility in acid sensitive soils in central Ontario to test the hypothesis that soils with lower pH are able to sorb more P at environmentally relevant [P], thereby potentially reducing  $TP_w$  export in streams.

### 1.1 Phosphorus as a Limiting Nutrient

Over geological time scales, P has been referred to as the “master regulator of biological activity” (Chadwick et al. 1999). Phosphorus is an essential nutrient for all life forms (Westheimer 1987) and is a component of deoxyribonucleic acid (Holley et al. 1965, Ghosh and Bansal 2003), adenosine triphosphate, the phospholipid bilayer of cell membranes, and other important biological molecules (Ruttenberg 2003). Phosphorus availability to terrestrial and aquatic organisms is generally limited by slow geochemical cycling (Ruttenberg 2003), accumulation of P in soil organic matter, and P occlusion in soil minerals (Walker and Syers 1976).

Surface waters can be described as eutrophic (nutrient rich), mesotrophic (moderate nutrient levels) or oligotrophic (nutrient poor), and these trophic levels correspond to surface water total phosphorus ( $TP_w$ ) concentrations of approximately 1.5, 0.4 and  $0.1 \mu\text{M}$  (or 48, 12, and  $3 \mu\text{g} \cdot \text{L}^{-1}$ ), respectively according to Carlson’s (1977) trophic index.

Due to high nutrient levels, eutrophic water bodies tend to be very productive with relatively high algal populations, whereas mesotrophic water bodies are moderately productive, and oligotrophic waters have very low productivity. Globally, P and nitrogen (N) are usually the limiting nutrients in fresh water lakes (Elser et al. 2007) although most Canadian Shield lakes tend to be P limited (Hecky and Kilham 1988). Various anthropogenic activities however, can alter P loadings to surface waters and affect the lake trophic status, which may lead to undesirable ecological consequences.

Excess P loading to lakes, often from agricultural P application, can cause cultural eutrophication (Delgado and Scalenghe 2008) and algal blooms, which result in hypolimnetic anoxia, toxin-producing species, and deep-water fish mortalities (Heisler et al. 2008). When nutrient loads to lakes have been reduced, positive responses such as an increase in zooplankton-to-phytoplankton biomass ratio tend to occur (Jeppesen et al. 2002), and the risk of algal blooms is reduced as a result. Declines in N and P concentrations in eutrophic aquatic ecosystems have also resulted in increases in species richness of zooplankton, crustacean, and macrophyte communities in European and North American lakes (Anderson et al. 2005).

Although the impacts of eutrophication have been well-studied (Anderson et al. 2002, Anderson et al. 2005, Delgado and Scalenghe 2008, Heisler et al. 2008), the opposite trajectory of oligotrophication has received less scientific attention, but can also have negative ecosystem impacts (Lindman 1942, Rieman and Myers 1992, Ney 1996, Urabe et al. 1997, Jeppesen et al. 2002, Patterson et al. 2008). Very low levels of nutrients (i.e. ultra-oligotrophy) can limit the growth of primary producers and therefore limit the supply of energy and nutrients to organisms in upper trophic levels (Lindman 1942). Some studies have shown that ultra-oligotrophication causes a decline in fish populations and food web instability (Rieman and Myers 1992, Ney 1996, Urabe et al. 1997, Jeppesen et al. 2002, Patterson et al. 2008). Acid rain induced oligotrophication has been seen in areas of northern Europe such as Sweden and Norway (Grahn et al. 1974, Jansson et al. 1986) and studies have suggested that changes in lake TP are dominated by terrestrial processes (Hultberg and Andersson 1982, Schindler et al. 1985, Jansson et al.

1986). Understanding the mechanisms of how this occurs could be valuable to future management of these acidified lakes.

In contrast to freshwaters, forest ecosystems are more often N-limited (LeBauer et al. 2008), but P limitation is observed in certain forests types (Tanner et al. 1998). Foliar N:P ratios are negatively related to latitude, implying a higher P use efficiency in tropical ecosystems and higher N use efficiency in temperate ecosystems (McGroddy et al. 2004). This geographical nutrient bias is likely related to soil age, as P is often a limiting nutrient in tropical, highly weathered soils (Attwill and Adams 1993, Crews et al. 1995). Geologically young soils, such as the recently de-glaciated soils found in central Ontario's temperate forests (Kirkwood and Nesbitt 1991), should theoretically have more available P (Walker and Syers 1976) and be N-limited rather than P-limited (Aber et al. 1989). However, high N deposition in this region relative to estimated pre-industrial levels (Galloway et al. 1984) and possibly other geochemical side effects from acid rain, could lead to Ontario's temperate forests becoming P limited (Gradowski and Thomas 2008, Casson et al. 2011).

Like surface water, the amount of P in soil that is readily available to biota is not well represented by total P (Richardson and Simpson 2011). This is because P in mineral soil forms strong chemical bonds with aluminium (Al), iron (Fe), and calcium (Ca) (Cole et al. 1953, Muljadi et al. 1966a, Bowden et al. 1980) or is occluded within precipitated secondary minerals (Smeck 1985) and inaccessible to plants (Richardson and Simpson 2011). Phosphorus in the form of phosphate ( $\text{PO}_4$ ) is also thought to be less mobile compared with other common soil solution anions such as chloride (Cl), sulphate ( $\text{SO}_4$ ) and nitrate ( $\text{NO}_3$ ), which do not bind to soil particles as strongly as  $\text{PO}_4$  (Hingston et al. 1972, Wood et al. 1984, Kaiser and Zech 1996). Although P solubility in lower mineral soil horizons (i.e. B-horizon) is primarily influenced by geochemistry, P mobility in upper organic horizons (i.e. Litter Fibric Humic and A, Soil Classification Working Group 1998) may also be influenced by biological activity (i.e. plant uptake; microbial immobilization and mineralization).

Phosphorus sorption is the dominant process governing P solubility in B-horizon soils (Li et al. 1999, Väänänen et al. 2008), and P ‘sorption’ includes both ‘adsorption’, which is P bonding to the surface of a sorbent and ‘absorption’, which is P that has penetrated in to the mineral matrix of a sorbent (Barrow 1983, Barrow 1984). This research will also include precipitation of P with dissolved metals (e.g. Al) as part of P ‘sorption’ since P that precipitates during sorption experiments has been removed from solution and is therefore measured as sorbed P (Haynes and Mokolobate 2001). Much of what is known about P sorption is based on the results of such sorption experiments (Muljadi et al. 1966a, Hingston et al. 1972, Bowden 1980, Barrow 1983, Bolan et al. 1988) and therefore the effect of P precipitation has been considered within current understanding of P sorption.

## **1.2 Phosphorus Biogeochemistry**

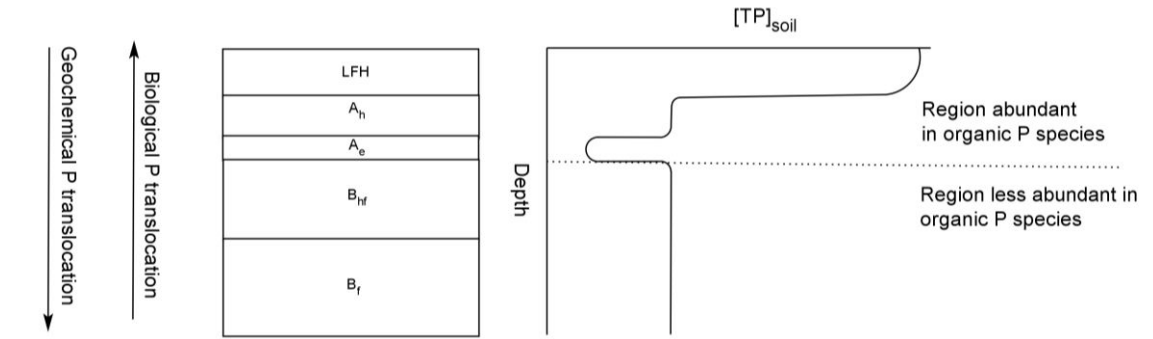
### *P movement through forest ecosystems*

Phosphorus in parent material is the primary biological P source in most regions of the world (Walker and Syers 1976), while dust deposition is only an important source of P in some (primarily arid) landscapes (Okin et al. 2004). Phosphorus released from weathered parent material is tightly recycled in most forest ecosystems and thus organic P is often the predominant form of P in surface soils (Bormann and Voigt 1984, Yanai 1992, Attiwill and Adams 1993, Campo et al. 2001). In a northern hardwood forest, Bormann and Voigt (1984) observed that more than 5 times as much P in the labile P pool came from the biological P pool, relative to the geochemical P pool. Yanai (1992) observed that 61% of P taken up by plants came from the forest floor. Plant P uptake is the dominant process that removes P from the mineral soil (Letskeman et al. 1996). Phosphorus also returns to the forest floor primarily through litter fall, which is dominated by leaf litter (Gosz et al. 1972). Decomposers such as bacteria and fungi mineralize the organic P stored in soil organic matter within the forest floor and mineral soil (Beara et al. 1992).



Eluviation is an important P transport mechanism that moves dissolved material, including organic acids, dissolved metals, and dissolved nutrients downwards through the soil profile (Lundström et al. 2000). Chemical weathering reactions of primary minerals are driven by exposure of minerals to water, oxygen and dissolved carbon dioxide, as well as biologically produced organic acids (Lundström et al. 2000, Ruttenburg 2003). Subsequent illuviation of eluviated materials such as organic acids, Al, Fe, and P drives the formation of the ‘podzolic’ B-horizon that is diagnostic of this soil order (Soil Classification Working Group 1998; Lundström et al. 2000). The mobilized Al and Fe precipitate as they travel down through the profile and pH increases (Lundström et al. 2000). Eluviation ultimately creates a leached upper soil horizon ( $A_e$ ), and a metal (Al and Fe) and organic-rich lower soil horizon ( $B_f$  or  $B_{hf}$ ) in podzols (Giesler et al. 2002; Lundström et al. 2000). An organic-rich  $A_h$  horizon may also occur in podzols beneath the Litter Fibric Humic (LFH) layer (Soil Classification Working Group, 1998). High concentrations of sorbed P often co-occur with illuviated Al and Fe in the B-horizon (Huang and Schoenau 1996, Li et al. 1999, Väänänen et al. 2008).

These P translocation mechanisms should theoretically result in the idealized  $[TP_s]$  pattern in a podzol, shown in Figure 1.1. The highest  $[TP_s]$  is expected to occur in the LFH layer. Although trees are able to re-translocate much of the P present in leaves prior to senescence, a considerable amount of P remains in the discarded leaf tissue (Chapin and Moilanen 1991, Vergutz et al. 2012). For example, Vergutz et al. (2012) found that senescent leaves contain an average of 45% of the P content of active leaves across a large variety of plant types and climates. Very low  $[P]$  is expected in the  $A_e$  horizon, as soil in this horizon has been leached of P sorbing minerals and there is little organic P present (Soil Classification Working Group 1998). Phosphorus concentrations in the  $A_h$ ,  $B_{hf}$  and  $B_f$  are expected to exist between these two extremes and more organic forms of P are expected to accumulate in the upper soil horizons from decomposing litter fall.



**Figure 1.1.** Diagram showing the idealized  $[TP_s]$  distribution in a podzol. Geochemical P translocation refers to the eluviation of P-sorbing metals and clays from upper soil horizons and illuviation of those materials in the B-horizon leading to an increase in P sorption capacity. Biological P translocation refers to P that is taken up by plant roots and deposited on the forest floor by litter fall.

### *Forms of P in soils*

Inorganic P in soil generally exists in two forms: chemically bonded as relatively insoluble P compounds e.g. Ca or Al phosphates (Murrmann and Peech 1969, Smeck 1973), or as free orthophosphate, which can be immobilized to varying degrees via electrostatic attraction to soil particles (Barrow 1984, Zelazny et al. 1996). Phosphorus fractionation in soils is greatly influenced by Al and Fe levels in acidic B-horizons, as both Al and Fe oxides are strong sorbents for P (Väänänen et al. 2008). Aluminium has been shown to be more reactive with P than Fe per unit surface area (Cabrera et al. 1977), but dissolution of P from goethite ( $\text{FeO}(\text{OH})$ ) was observed to be slower than from gibbsite ( $\text{Al}(\text{OH})_3$ ) (Hingston et al. 1974). Aluminium solubility is more sensitive to pH (Norton 2006) whereas Fe solubility is more pE dependant (Miller et al. 2001). The sensitivity of P sorption on Fe and Al minerals to environmental conditions (i.e. pH, pe) likely explains why different studies have concluded that either Al or Fe is the main P sorbing material (SanClements 2009, Nair et al. 1999, Carreira and Lajtha 1997).

Soil organic P is formed as a result of biological uptake (by primary producers and microbial fixation) and decomposition processes (Wetzel 1992, Hinsinger 2001). Within biota, P undergoes intracellular bio-transformations to form organic P compounds including P monoesters, P diesters, polyphosphates, and phosphonates (Westheimer 1987, Barford 1996, Turner et al. 2005). However, the analysis of organic P fractions in soils often focuses on operationally defined P extractions (e.g. Crews et al. 1995, Cross and Schlesinger 1995, Beck and Elsenbeer 1999, Chen et al. 2000). Although P extractions do not provide information about the specific organic P species, they are thought to provide information about P fraction lability (Johnson et al. 2003). For example,  $\text{NaHCO}_3$ -extractable organic P is likely to be more readily mineralized and become available to plants whereas NaOH-extractable organic P is thought to be less readily mineralized (Johnson et al. 2003).

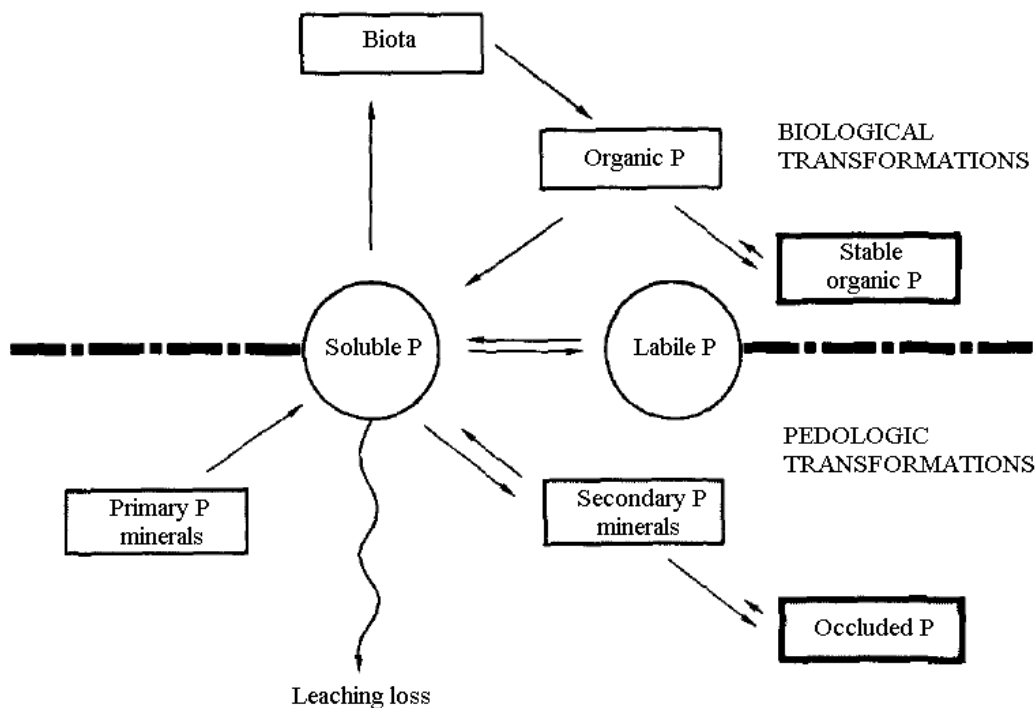
The availability of P in forests is strongly related to biological cycling (Attwill and Adams 1993) especially in P-limited forests (McGill and Cole 1981); however, “available

P” is difficult to define. Some have argued that trying to categorize soil P into biologically-available and unavailable forms is arbitrary (Frossard et al. 2000). Available P is often considered to be soluble inorganic P that is liberated from soil using water or weak salt solvents (Frossard et al. 2000, Devau et al. 2009, Casson et al. 2011). However, soil P pools are in constant dynamic equilibrium with one another (Smeck 1985) and mycorrhizal associations can allow plants to access P from less labile P pools (Bolan 1991).

This study will use the operational definitions of soil P pools described in Smeck (1985) (Figure 1.2) with some alterations, and P fractions will be measured using the Hedley fractionation process, such that:

1. Phosphorus extracted with H<sub>2</sub>O will be considered ‘soluble’
2. Phosphorus extracted with 0.5 M NaHCO<sub>3</sub> will be considered ‘labile’
3. Phosphorus extracted with 0.1M NaOH will be considered to contain labile P as well as P associated with secondary minerals and some stable organic P
4. Phosphorus extracted with 1M HCl will be considered to be associated with primary minerals (i.e. apatite).

In addition, extracts obtained from steps 1-3 were analyzed for both inorganic (i.e. ‘reactive P’) and total (i.e. PO<sub>4</sub> in solution produced after acid/autoclave digestion) solution P. Organic P obtained from each of these three extractions was determined by subtracting total solution P from inorganic solution P. Biota, and occluded P pools were not measured in this study.



**Figure 1.2.** Theoretical P pools and P transfer scheme described in Smeck (1985). Arrow length gives an indication of the magnitude of flow over time. The P pools are defined as follows: Soluble P is mobile and subject to leaching loss; Labile P is in equilibrium with soluble P; Secondary P minerals include Al and Fe phosphate minerals as well as phosphate sorbed to Al and Fe (hydr)oxides; Primary mineral P dissolves slowly (over geologic timescales) and mostly consists of apatite; Occluded P has been covered by precipitated Al and Fe or absorbed into the Al or Fe mineral lattice; Biota P includes the P within living organisms; Organic P and stable organic P are simple and complex carbon-based molecules respectively that exist within and on the soil. These organic P molecules likely exist in a solubility continuum rather than in discrete pools.

### *Phosphorus leaching to surface waters*

Atmospheric deposition and terrestrial export are the two main external sources of P to surface waters (Winter et al. 2002, Haygarth et al. 2005, Alvarez-Cobelas et al 2009, Eimers et al. 2009). A lake P budget of the of the present studies sites indicated that catchment  $TP_w$  export accounted for 38 % of total  $TP_w$  loading to Plastic Lake and 30 % of the total  $TP_w$  load to Harp Lake (Dillon et al. 1993). Catchment stream  $TP_w$  export was the second highest source of  $TP_w$  at both Plastic and Harp Lake with P inputs in deposition being the largest source of P at Plastic Lake (53 %) whereas potential anthropogenic P (i.e. septic system leachate) was the highest  $TP_w$  source at Harp Lake (58 %) (Dillon et al. 1993). Given that streams supply a substantial proportion of total TP input to lakes, changes in stream export over time may influence  $TP_w$  levels within these lakes (Eimers et al. 2009).

Water extractable P is related to the amount of soluble P present in the soil (Maguire and Sims 2002) and is the P fraction that is considered most susceptible to leaching (Nair et al 1999). Some of the factors that influence P solubility are presented in Table 1.1. Increased P solubility in upland soil does not necessarily equate to increased catchment P export. The P concentration of upland soil leachate is likely to be altered as it passes through organic soils located in wetland or riparian areas, which are well known biogeochemical hot spots (McClain et al. 2003). Biogeochemical hotspots are defined as areas that show disproportionately high reaction rates relative to their surroundings (McClain et al. 2003). Organic soils can be either a sink or a source of P depending on the concentration of dissolved oxygen in the soil solution (Carlyle and Hill 2001). Under anoxic conditions,  $Fe^{3+}$  is reduced to  $Fe^{2+}$  (Mortimer 1971). This change in oxidation state mobilizes Fe as well as any phosphate sorbed to it (Mortimer 1971); therefore water saturated anoxic soils can be P sources. Organic soils can also become P sinks when dissolved oxygen concentrations are higher in soil leading to less reduced  $Fe^{2+}$  and more iron oxides which are effective P sorbents (Carreira and Lajtha 1997; Väänänen et al. 2008). Although biogeochemical hot spots such as wetland or riparian areas have high rates of biogeochemical cycling they are still supplied with P from upland drainage and

many studies have found significant correlations between soluble P in soil and measures of P mobility such as, P exported from a catchment runoff simulator (Pote et al. 1996), soil column P leachate (Maguire and Sims 2002), and P measured in catchment runoff (Vadas et al. 2005). Therefore it is likely that soluble P in upland soils is a partial contributor to catchment P export and that changes in soluble P in upland soils could contribute to changes in catchment P export.

Several studies have shown total P export to be relatively low during base flow and relatively high during event flow conditions (Munn and Prepas 1986, Cooper and Thomsen 1988, O'Brien 2010). During small precipitation events water passes through the, soluble P rich, upper soil horizons and leaches P to the B-horizon. The Al and Fe (hydr)oxide rich B-horizon is able to sorb much of the P that percolates through it (Jansson et al. 1986), leaving deeper soil leachate/base flow water low in  $[TP_w]$ . During spring melt or large precipitation events, the B-horizon becomes saturated with water and flow paths become shallower (Scanlon et al. 2004). Water travelling along shallow flow paths mobilizes soluble and particulate P in shallow soil horizons and can export a disproportionately high percentage of P per unit volume of water (Prairie and Kalff 1988, O'Brien 2010). O'Brien (2010) showed that 6 high flow storm events at two of the catchments studied in the present research project, HP3 and HP3A, contributed 12.3 % and 9.8 % of the total annual P export despite representing only 3.3 % and 2.6 % of total annual runoff, respectively.

**Table 1.1.** Soil chemical and physical characteristics and their relationship with soluble P in soil.

Variable	Relationship to soluble P	Relationship description	Literature Source
Anoxia	+’ve	Fe is dissolved under reducing conditions, which mobilizes associated P.	Carlyle and Hill 2001, Miller et al. 2001
Particle size	+’ve	Larger particle size generally equates to a smaller surface area per unit volume and fewer binding sites.	Atalay 2001
pH	Variable	P sorption theory predicts that P solubility should decrease as pH declines below pH 5 due to adsorption on Al and Fe oxide surfaces. Highest soluble P should theoretically occur between pH 5 and 7.5. However there are several literature reports of increased P solubility at low soil pH.	Barrow 1984, Traina et al. 1986, Bolan et al. 1988, Devau et al. 2009 Kerr et al. 2011, McCray et al. 2012
Ionic strength	Variable	P sorption is more sensitive to changes in pH at low ionic strength and is less sensitive at high ionic strength below the point of zero charge (PZC). Ionic strength has the opposite effect above the PZC i.e. P sorption is more sensitive to changes in pH at <i>high</i> ionic strength and vice versa.	Barrow 1984, Bolan et al. 1988, Gustafsson 2001
Organic matter content	Variable	Organic matter bonded with Al and Fe results in less crystalline Al and Fe compounds with a higher surface area. These less crystalline Al and Fe compounds are able to sorb more P per mole of Al and Fe than highly crystalline compounds. Organic anions such as those from humic and fulvic acids can also compete with P for sorption sites.	Owusu-Bennoah and Acquaye 1989, Atalay 2001, Haynes and Mokolobata 2001



**Table 1.1. *cont***

<b>Variable</b>	<b>Relationship to soluble P</b>	<b>Relationship description</b>	<b>Literature Source</b>
Concentration of divalent cations	-‘ve	Ca and possibly other divalent cations may be involved in cation bridging or the formation of compact P-cation complexes which would allow for greater P sorption and reduced P solubility	Helyar et al. 1976a, Helyar et al. 1976b, Kerr and Eimers 2012
Concentration of Al and Fe (hydr)oxides	-‘ve	Al and Fe (hydr)oxides produce variable charged surfaces that provide strong binding sites for P molecules	Freese et al. 1992, Lookman et al. 1995, Daly et al. 2001, Giesler et al. 2002, Kaňa and Kopáček 2011

### 1.3 Phosphorus Sorption Theory

Phosphorus sorption is a spontaneous reaction that can occur without the input of energy at standard temperature and pressure (Juang and Chung 2004). Phosphorus sorption is strongly dependent on environmental conditions such as pH, abundance of sorption sites and ionic strength (Bowden et al. 1980, Bolan et al. 1988, Barrow 1994, Kaňa and Kopáček 2011). It has been demonstrated that adsorption occurs heterogeneously across sorption surfaces with the majority of sorption occurring at the charged edges and corners of the sorbent material and the least amount of sorption occurring on the smooth surfaces of the sorbent material (Kolthoff 1935).

#### *Sorption regions*

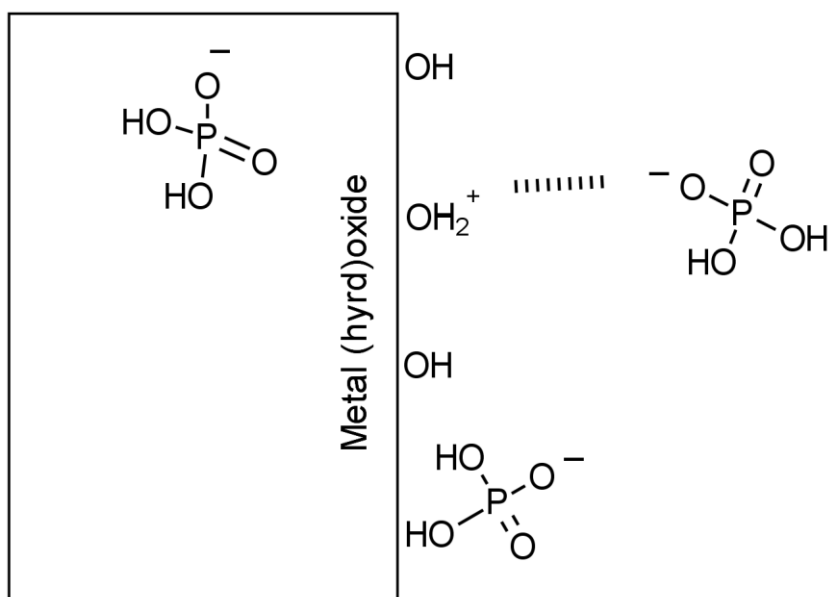
There are three distinct types of binding sites for P on variable-charged surfaces (i.e. Al and Fe (hydr)oxides) (Figure 1.3), although these regions are likely not homogeneous (Hingston et al. 1974). Different modes of sorption became apparent when Muljadi et al. (1966a) discovered that the phosphate ion was too big to account for all of the observed sorption on Al oxide surfaces during sorption experiments. It was concluded that some P must be electrostatically bound and/or absorbed into the mineral lattice (Muljadi et al. 1966a). It is now recognized that there are three general sorption regions including chemical adsorption sites, electrostatic adsorption sites, (Devau et al. 2009), and absorption sites (Muljadi et al. 1966b). Chemical adsorption sites are characterized by direct interaction between the anion and the material surface (Bowden 1977), the most important interaction being ligand exchange on Al and Fe (hydr)oxides (McLaughlin et al. 1981). Electrostatic adsorption sites are characterized by the electrostatic attraction of anions to positively charged sites on the sorbent material (Hingston et al. 1972).

Absorption sites are located within the mineral matrix (Muljadi et al. 1966b). Phosphorus absorption occurs very slowly, but is important over geologic timescales (Barrow 1983, McGechan 2002). Chemical adsorption sites are space limited (Bowden 1977) and are heavily influenced by the surface area of the sorbing material (i.e. ligand exchange sites) (Hingston et al. 1972). Electrostatic adsorption sites are charge limited (Bowden 1977),

and the charge density and strength of electrostatic adsorption sites decrease with distance from the particle surface (Zelazny et al. 1996). Electrostatic adsorption sites are heavily influenced by pH (Barrow 1984) and the composition of the electrolyte community (Ryden and Syers 1975).

Amorphous metals are thought to be the main P sorbing constituents in young podzolic soils (Carreira and Lajtha 1997, Väänänen et al. 2008). Older dryer soils, such as the found in the Mediterranean contain large amounts of crystalline Fe, which had been identified to be the main sorbing material in that region (Carreira and Lajtha 1997). Studies on soils, similar those in the present study, have found P sorption to be strongly related to the concentration of amorphous Al and Fe (Freese et al. 1992, Yuan and Lavkulich 1994, Lookman et al. 1995, Beauchemin and Simard 1999, Kaňa et al. 2011) and it will be assumed that amorphous Al and Fe are the main sorption materials in the study soils.

Sorption experiments are typically performed at high solution [P] ( $> 500 \mu\text{M}$ ) and for durations of  $\sim 24$  hours (Muljadi et al. 1966, Geelhoed et al. 1997, Kaňa and Kopáček 2006). Batch sorption experiments are more common than column sorption experiments as they allow for greater control over experimental conditions, which makes them well suited to investigating adsorption mechanisms (Bolan et al. 1988). Batch sorption experiments also avoid complications of preferential flow paths that cause contact heterogeneity between soil and solution. Sorption experiments are often used to measure the maximum sorption capacity of a soil, which is useful for defining limits of P fertilizer application in agricultural settings (Yuan and Lavkulich 1994, Nair et al. 1999, Dodor and Ova 2000, Vadas et al. 2005 Gichangi et al. 2008). Less experimental sorption work has been completed at P concentrations that are environmentally relevant, such as in unfertilized forest ecosystems.



**Figure 1.3.** Image depicting theoretical sorption regions. Electrostatic adsorption is shown at the far right, with a phosphate molecule being electrostatically attracted to a positive  $\text{OH}_2^+$  ligand. Chemical adsorption is shown in the centre with a phosphate molecule adsorbed by ligand exchange at the metal hydroxide surface. Absorption is shown on the far left with a phosphate molecule that has moved into the mineral lattice of the metal hydroxide.

## 1.4 Acidification of Soils and Phosphorus Behaviour

Acidification has the potential to alter the [P] of P fractions in soils and hence alter P mobility, although the ecosystem response to acidification is complex (Cosby et al. 1985, Gbondo-Tugbawa et al. 2001). The response of forest soils to acidification has been extensively studied and modeled; much of this work has focussed on soil and surface water pH decline, depletion of acid buffering capacity (especially Ca compounds), and Al toxicity (Cosby et al. 1985, Norton et al. 1994, Cronan and Grigal 1995, Gbondo-Tugbawa and Driscoll 2002). There is no ecosystem-scale acidification model available for evaluating P mobility; however, a considerable amount of research has been directed to understanding the relationship between acidification and P behaviour at the Bear Brook Watershed in Maine (BBWM) Whole Ecosystem Acidification Experiment. For example, Roy et al. (1999) and Reinhardt et al. (2004) observed increases in stream  $[TP_w]$  coincident with increases in [Al] and [Fe] during storm events. The authors of both studies concluded that  $(NH_4)_2SO_4$  additions caused increased dissolution of Al and Fe compounds in soil, which liberated associated P (Roy et al. 1999, Reinhardt et al. 2004). Other studies at the BBWM have also discussed the possibility that Al dissolution causes increased P transport (Norton 2006, Sherman et al. 2006, SanClements 2009). The results at BBWM seem to be in contrast to P sorption theory, which predicts more P sorption under increasingly acidic conditions (Bowden et al. 1980, Barrow 1984, Muljadi et al. 1966). However, since ecosystem acidification is a complex process, it is possible that acidification could yield multiple P mobility responses.

Historically high levels of acid deposition (Summer and Whelpdale 1976, Galloway et al. 1984, Aherne et al. 2003) have caused soil acidification in central Ontario between 1980 and 2001 (Watmough and Dillon 2004, Miller and Watmough 2009). The soils in this region are acidic (Watmough and Dillon 2002, Watmough and Dillon 2003), but the effect of soil acidification on P behaviour has not yet been assessed. Over the same period, Eimers et al. (2009) observed that terrestrial TP export from central Ontario forested catchments is declining and mass balance calculations indicate that the catchments are retaining P, despite having geologically young soils (Kirkwood and

Nesbitt 1991) which should theoretically be losing P (Walker and Syers 1976, Johnson et al. 2003). Also, despite the fact that P appears to be accumulating in catchments, there have been reports of potential biological P limitation in forests in this region (Gradowski and Thomas 2008, Casson et al. 2011). Increased P sorption in acidified soils could explain both P accumulation in these soils as well as biological P limitation, as P that is strongly sorbed to Al and Fe (hydr)oxides is not readily soluble (Smeck 1985) and is therefore less likely to be biologically available. This study will explore whether soil acidification is a plausible mechanism to explain observed declines in stream TP.

### **1.5 Thesis Objectives**

This study had three primary objectives:

- 1) To characterize soil P fractions and pools at three forested catchments in central Ontario that show varying levels of stream  $[TP_w]$  and P export.
- 2) To investigate the relationship between soil acidity and labile P through a combination of field and experimental studies.
- 3) To calculate P budgets for the three forested catchments.

### **1.6 Thesis Hypothesis and Predictions**

**H<sub>1</sub>:** Soil P fractionation and concentrations within fractions will differ significantly among the three study catchments and by soil depth.

**P<sub>1.1</sub>:** The largest differences in soil P fractions will occur between PC1-08 and HP3 as these catchments have the largest difference in stream  $[TP_w]$ .

**P<sub>1.2</sub>:** The highest  $[TP_s]$  will be found in the LFH-horizon and the lowest  $[TP_s]$  will be found in the A<sub>c</sub>-horizon.

**P<sub>1.3</sub>:** There will be a higher proportion of organic P to inorganic P in the LFH and A<sub>h</sub>-horizons relative to the lower mineral soil horizons.

**H<sub>2</sub>:** Soil pH affects P sorption and is related to P fractionation in central Ontario upland soils.

**P<sub>2.1</sub>:** Mobile and labile P pools will be positively related to soil pH in upland soils.

**P<sub>2.2</sub>:** P sorption, at environmentally relevant solution [P], will be negatively affected by changes solution pH.

**H<sub>3</sub>:** Phosphorus imports into the study catchments will be larger than P exports.

## 2.0 Methods

### 2.1 Site Description

PC1-08, HP3 and HP3A are forested catchments located on the Precambrian Shield (Figure 2.1) in south-central Ontario on the southern edge of the Boreal ecozone, which is a region considered to be sensitive to acid deposition (Watmough and Dillon 2003). Soils in this region are geologically young (~ 12 000 years old, Kirkwood and Nesbitt 1991) and have been classified as acidic poorly developed podzols and brunisols (Dillon et al. 1991, Trumbore et al. 1992). The three study catchments contain headwater nutrient poor streams (Eimers et al. 2009). PC1-08 drains into Plastic Lake while HP3 and HP3A drain into Harp Lake. The stream chemistry draining from these three catchments has been monitored since the 1970's as part of the Ontario Ministry of Environment's Dorset Environmental Science Centre (DESC) long-term monitoring program (Eimers et al. 2009).

Total P concentrations have declined in central Ontario lakes (Yan et al. 2008) and streams (Eimers et al. 2009) since the 1980's. Although more pronounced at the Dorset lakes, declining lake [TP] has been observed across south central Ontario (Palmer et al. 2011). In 2003, average [TP] was 0.15  $\mu\text{M}$  in Plastic Lake and 0.21  $\mu\text{M}$  in Harp Lake; these TP concentrations are comparable to other lakes in the central Ontario region, such as Blue Chalk and Heney Lakes (Yan et al. 2008). Population density has been shown to have a positive relationship with terrestrial P export (Alvarez-Cobelas et al 2009), and yet TP declines have been observed at lakes (Yan et al. 2008) both with and without shoreline development in the central Ontario region (Dillon et al. 1992).

Precipitation in the region is approximately  $1 \text{ m} \cdot \text{yr}^{-1}$  and average TP bulk deposition was  $0.50 \text{ mmol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  between 1980 and 2000 (Eimers et al. 2009). The average annual temperature at the study sites is about 4.8 °C (Creed et al. 2008). Although these catchments and catchment streams share many characteristics, they differ in some important physical and chemical properties.



### 2.11 PC1-08

PC1-08 drains only the upland portion of PC1, and is therefore not influenced by the large downstream wetland (Figure 2.1). PC1-08 has a bedrock geology consisting mainly of granitized biotite, hornblende, and gneiss (Jeffries and Snyder 1983). The topography of PC1-08 is the steepest of the three catchments at 13% slope (Buttle and Eimers 2009). The surface geology at PC1-08 is dominated by thin till and rock ridges, and is the only study catchment with bedrock outcroppings (Watmough and Aherne 2008). PC1-08 has the shallowest soils of the three catchments with a depth to bedrock of 0.46 m (Watmough and Aherne 2008). Forest cover at the Plastic lake catchment consists of mainly conifers, dominated by white pine (*Pinus strobus*) and eastern hemlock (*Tsuga canadensis*) (Watmough and Dillon 2003).

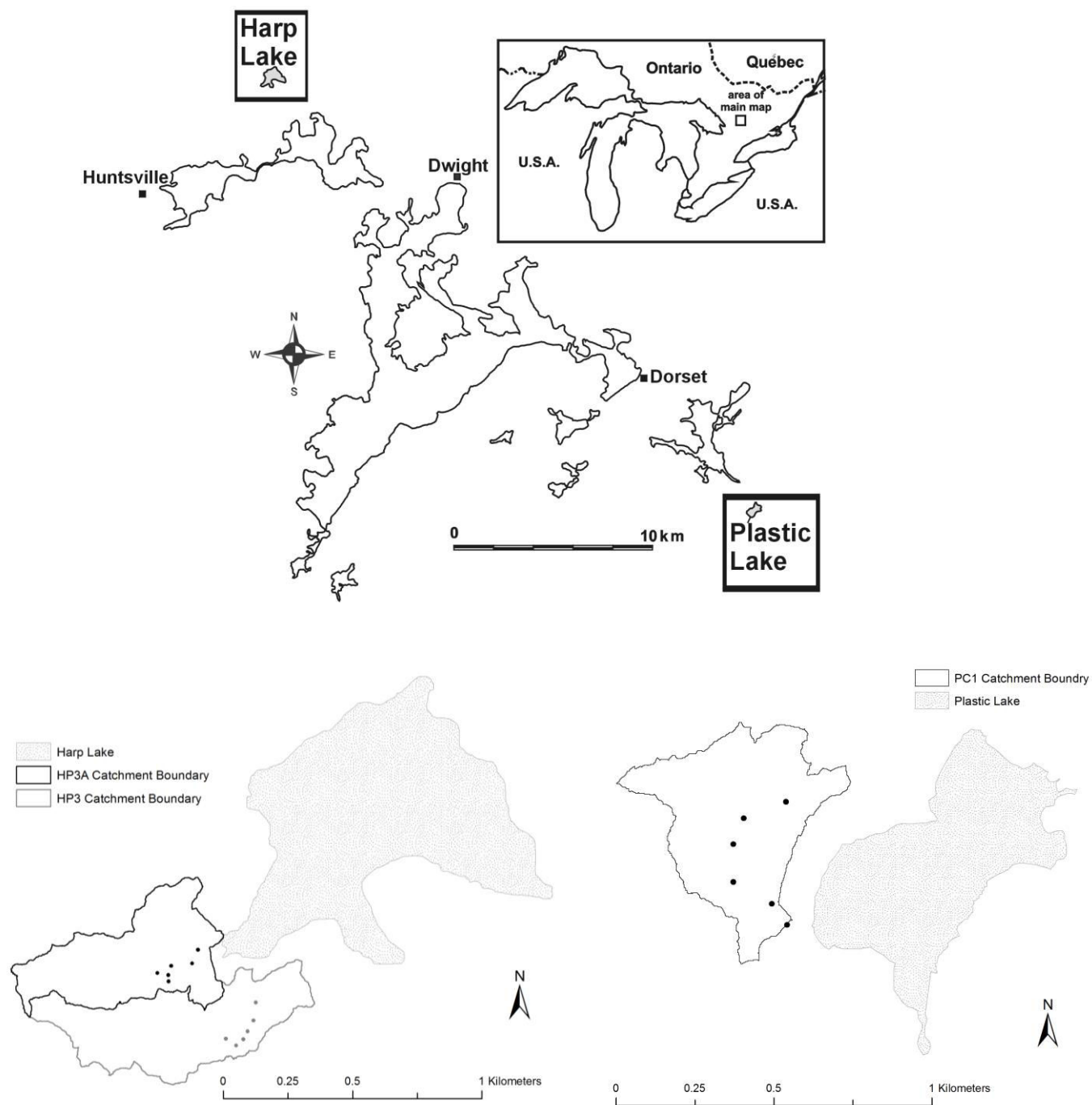
### 2.12 HP3

HP3 drains the entire catchment (Figure 2.1) and the bedrock geology of HP3 also consists mainly of granitized biotite, hornblende, and gneiss (Jeffries and Snyder 1983). The topography of HP3 is relatively flat, with a slope of 4%, and also contains the most peatland at 9.3% compared to the other study catchments (Buttle and Eimers 2009). The surface geology at HP3 is dominated by minor till and contains some thin till and rock ridges but no bedrock outcroppings (Dillon et al. 1991). The depth to bedrock for HP3 is estimated from catchment HP4 at 1.26m (Watmough and Aherne 2008). The forest cover at the HP3 catchment is mainly deciduous, dominated by sugar maple (*Acer saccharum*) and yellow birch (*Betula alleghaniensis*) (Watmough and Dillon 2003).

### 2.13 HP3A

HP3A drains the entire catchment (Figure 2.1) but the bedrock geology differs slightly from the other two catchments. The southern half of HP3A consists mainly of granitized biotite, hornblende, and gneiss, while the northern half of the catchment is amphibolite and schist (Jeffries and Snyder 1983). HP3A is steeper than HP3 but less steep than PC1-

08 with a slope of 8% (Buttle and Eimers 2009). The surface geology at HP3A dominated by minor till, contains no thin till, rock ridges or bedrock outcroppings, and has only 2.9% peat land (Dillon et al. 1991). The depth to bedrock for HP3A is estimated from catchment HP4 at 1.26m (Watmough and Aherne 2008). The forest cover at HP3A is similar to HP3 being dominated by sugar maple (*Acer saccharum*) and yellow birch (*Betula alleghaniensis*) (Watmough and Dillon 2003).



**Figure 2.1.** Map of study lakes with embedded map displaying the geographical area of study from Casson et al. (2012) (top) and maps of sampling locations within each of the studied catchments (bottom).

**Table 2.1.** Selected physiographic and climatic catchment characteristics. Data from (Dillon et al. 1991, Watmough and Dillon 2003, Watmough and Aherne 2008, Buttle and Eimers 2009).

Catchment	Area (m <sup>2</sup> )	Average Depth to Bedrock (m)	Mean slope (%)	BHG (%)	AS (%)	MIG (%)	Minor till (>1m deep, %)	Thin till, rock ridges (%)	Peat (%)	Bedrock Outcropping (%)	Precipitation (m • yr <sup>-1</sup> )
PC1-08	34500	0.46 <sup>†</sup>	13	99.4 <sup>‡</sup>	0.0 <sup>‡</sup>	0.6 <sup>‡</sup>	0	89	1.0	10	1.12 <sup>‡</sup>
HP3	259900	1.26 <sup>†</sup>	4	93.0	7.0	0.0	79.5	11.2	9.3	0	1.06
HP3A	196500	1.26 <sup>†</sup>	8	42.6	57.4	0.0	97.1	0	2.9	0	1.06

<sup>†</sup> Data from catchment HP4 (Watmough and Aherne 2008)

<sup>‡</sup> Data from whole PC1 catchment

BHG – biotite, hornblende and gneiss

AS – amphibolite and schist

MIG – migmatite

Peat – primarily *Sphagnum*

## **2.2 Sample Collection**

The Harp and Plastic Lake watersheds were chosen to represent catchments with large differences in TP export and differences soil pH. In October 2011, 6 randomly located soil pits were dug to approximately 30cm below the surface at each of the three study catchments (PC1-08, HP3, HP3A) for a total of 18 soil pits. Grab samples and bulk density cores were collected from the LFH, A and B-horizons. Soils were classified using criteria from the Canadian System of Soil Classification (Soil Classification Working Group 1998).



**Figure 2.2.** Photograph of the Plastic lake catchment. Photograph provided by Nora Casson.





**Figure 2.3.** Harp lake catchment and stream. Photograph provided by Nora Casson.

### 2.3 Soil Chemical and Physical Analyses

Mineral soils were air dried and sieved to 2mm. LFH samples were air dried and ground with a Wiley Mill. All samples were stored at room temperature in sealed polyethylene bags. Sub samples of each field-moist soil were oven dried at 105 °C for 24 hours to determine moisture content. Oven drying sub-samples allowed all chemical analyses to be expressed as oven-dried equivalents; however all chemical and physical analyses were preformed on air-dried soils. A Horiba Partica LA-950 was used to measure the sand, silt and clay contents of all mineral horizon soils after soils were first ashed at 375 °C for 16 hours in a muffle furnace to remove organic matter. An Elementar CNS analyser was used to measure the carbon (C), nitrogen (N) and sulphur (S) content of all soils. Soil pH was measured in 0.01 M CaCl<sub>2</sub> with a 4:1 solution-to-soil ratio using an Oakton pH 510 series pH meter. Total P was determined using an H<sub>2</sub>SO<sub>4</sub> extraction post loss on ignition method described by Walker and Adams (1958) with the following differences: 1) soils were heated to 375 °C for 16 hours in a muffle furnace and 2) ashed soils were extracted with a 1M H<sub>2</sub>SO<sub>4</sub> solution using a 1:50 soil to solution ratio. Ammonium oxalate extractable aluminium (Al) and iron (Fe) were extracted following the method described by McKeague and Day (1966) and measured using an Atomic Absorption Spectrometer. Ammonium oxalate extraction was used for Al and Fe analyses because this extraction is thought dissolve mostly amorphous Al and Fe, as appose to the citrate dithionite bicarbonate extraction, which is thought to remove both amorphous and crystalline Al and Fe, forms (McKeague and Day 1966). As amorphous Al and Fe are the main sorbing materials in young podzols (Carreira and Lajtha 1997, Väänänen et al. 2008), crystalline Al and Fe were not considered in this study. Exchangeable potassium (K<sub>exg</sub>), calcium (Ca<sub>exg</sub>), magnesium (Mg<sub>exg</sub>) and Al<sub>exg</sub> were determined by ammonium chloride extraction followed by a NaCl extraction to determine cation exchange capacity (CEC) similar to the method used by Miller and Watmough (2008).



**Table 2.2.** Definitions of Terms.

Term	Definition
$P_{H_2O_i}$	Inorganic water extractable P: P that is considered readily soluble and bioavailable; it can be mobilized or leached during a precipitation event.
$P_{H_2O_o}$	Organic water extractable P: P that is considered readily soluble and easily mineralized; can be mobilized or leached during a precipitation event.
$P_{NaHCO_3_i}$	Inorganic 0.5M Sodium bicarbonate extractable P: P that is considered labile; it can readily change chemical forms and replenish the soluble P pool when it is depleted.
$P_{NaHCO_3_o}$	Organic 0.5M Sodium bicarbonate extractable P: P that is considered easily mineralized; it can readily change chemical forms and replenish the soluble P pool when it is depleted.
$P_{NaOH_i}$	Inorganic 0.1M Sodium hydroxide extractable P: This pool contains both labile inorganic P and non-labile inorganic P that is strongly sorbed to Al and Fe (hydr)oxides.
$P_{NaOH_o}$	Organic 0.1M Sodium hydroxide extractable P: This pool contains easily mineralized organic P, non-labile organic P that is strongly sorbed to organic Al and Fe complexes, and other stable organic P compounds.
$P_{HCl}$	1M Hydrochloric acid extractable P: P that is considered to be from apatite; non labile.
$P_{sum}$	The sum of P found in the four extractions of the Hedley fractionation.
$P_{ox}$	P extracted with 0.2 M $(NH_4)_2C_2O_4$ + 0.2 M $H_2C_2O_4$ adjusted to a pH of 3. P from this extraction is considered soluble P + P sorbed onto all amorphous Al and Fe oxides. * <i>This was a separate extraction from the Hedley fractionation.</i>

**Table 2.2. cont**

Term	Definition
$P_{H_2SO_4}$	Sulphuric acid extractable P from ashed soil. * <i>This was a separate extraction from the Hedley fractionation.</i>
$Al_{ox}$ and $Fe_{ox}$	Al and Fe extracted with 0.2 M $(NH_4)_2C_2O_4$ + 0.2 M $H_2C_2O_4$ adjusted to a pH of 3. Al and Fe from the extraction are considered to have amorphous or poorly crystalline molecular structures.
$K_{exg}$ , $Ca_{exg}$ , $Mg_{exg}$ and $Al_{exg}$	K, Ca, Mg and Al extracted with 1M $NH_4Cl$ . Metals and cations dissolved by this extraction are considered to be exchangeable.
$TP_w$	Inorganic phosphorus measured in solution after a water sample has been digested with an acid and strong oxidizer to convert all phosphorus compounds to orthophosphate.
$TP_s$	Inorganic phosphorus measured in solution after attempting to remove all P from soil particles using a harsh extraction solution.

### *Hedley fractionation*

The Hedley fractionation (Hedley et al. 1982) modified by Tiessen and Moir (2008) was used to separate extractable soil P fractions. A mild extractant ( $\text{H}_2\text{O}$ ) followed by increasingly harsh extractants (0.5M  $\text{NaHCO}_3$ , 0.1M  $\text{NaOH}$ , 1M  $\text{HCl}$ ) were used to separate more labile P fractions from less labile P fractions (Turner et al. 2005) by sequentially adding these extraction solutions to a single soil sample.  $\text{H}_2\text{O}$ ,  $\text{NaHCO}_3$  and  $\text{NaOH}$  extractable fractions were then further divided into inorganic and organic sub fractions. Inorganic P was determined by taking an aliquot of the extraction solution, precipitating the organic matter out of solution by acidifying the solution to  $\text{pH} < 3$ , centrifuging the solution at 4500 rpm for 15min, and then measuring the reactive  $\text{PO}_4$  in the supernatant. Another aliquot of the extraction solution was analyzed for total P following autoclave persulphate acid digest, and organic P was calculated as total P – inorganic P. The sonicated  $\text{NaOH}$  and heated  $\text{HCl}$  extractions of the Hedley fractionation method were not performed. Solution [P] from all extractions was measured colorimetrically with a Lambda XLS+ photo spectrometer using the molybdate blue method of Murphy and Riley (1962) and modified by Tiessen and Moir (2008). The only exception was the 1M  $\text{HCl}$  extraction; P and Ca levels liberated using the 1M  $\text{HCl}$  extraction were measured on an ICP-OES.

## **2.4 Sorption Experiments**

In order to test the effect of changing pH on P sorption, a variety of sorption experiments were performed. Selected soils were equilibrated with a low solution [P] of 4.5 or 45.2  $\mu\text{M}$  for 3 hours; or a higher solution [P] of 452.1 or 6461.1  $\mu\text{M}$  for 24 hours, on an oscillating shaker table. Sorption experiments were performed at low solution [P] in an effort to simulate P sorption under realistic labile soil [P] levels. The soil [P] of the inorganic bicarbonate extraction was used to estimate a realistic soil labile [P]. The highest concentration of inorganic bicarbonate extractable P in 1 gram of B-horizon soil diluted to 25 ml of solution was 45.2  $\mu\text{M}$ . Therefore 45.2  $\mu\text{M}$  was used as an estimate of natural soil labile [P] for 1 gram of soil in 25ml of solution. P solutions were made with

B-Pure water and  $\text{KH}_2\text{PO}_4$ . All sorption experiments were conducted in 50ml conical tubes, with 1 gram of soil in 25ml of solution with a background electrolyte concentration of 0.002 M of  $\text{CaCl}_2$  (except one trial when a background electrolyte was intentionally not used) to give a consistent ionic strength. Solution pH was measured and then manipulated by adding drops of dilute HCl or KOH after 15, 30, 45 and 60 minutes of shaking. Initial kinetic experiments showed that at a  $[\text{P}]$  of 45.2  $\mu\text{M}$ , P sorption at 2 hours was equal to that at 24 hours. Helyar et al. (1976) also found that the vast majority of P sorption occurred within the first few hours of their sorption experiments. Sorbed P was calculated as the difference between initial and final solution  $[\text{P}]$ .

Sorption with and without a background electrolyte was compared to determine the effects of ionic strength on soil P sorption. In addition, a sorption experiment was conducted using ashed and un-ashed soil to determine the effects of organic matter on soil P sorption. The ashed samples were heated in a muffle furnace at 375° C for 16 hours. Several soil samples that varied naturally in  $\text{pH}_{\text{CaCl}_2}$  were analysed for P sorption at three different solution  $[\text{P}]$  concentrations (4.5, 45.2 and 452.1  $\mu\text{M}$ ). Sorption solution pH was maintained at each soil's measured  $\text{pH}_{\text{CaCl}_2}$  in the same manner that solution pH was manipulated. A sorption experiment with and without added chloroform was also performed to test whether microbial growth was occurring during sorption experiments. Samples with added chloroform sorbed slightly less P but the difference was negligible and not significant. All sorption experiments were conducted in a cold room (4°C) and in the dark; it is assumed that this temperature and absence of light were sufficient to inhibit microbial growth.

## 2.5 Phosphorus Budgets

P budgets were constructed using P stream export and bulk deposition data available from the Ontario Ministry of Environment's Dorset Environmental Science Centre (DESC) long-term monitoring program, as well as litter fall and biotic P pools from unpublished data collected by Eimers and Watmough (2012), and soil P pool data collected as part of

the present study. Terrestrial P accumulation was calculated as the difference between total P input from deposition and total P export in stream water.

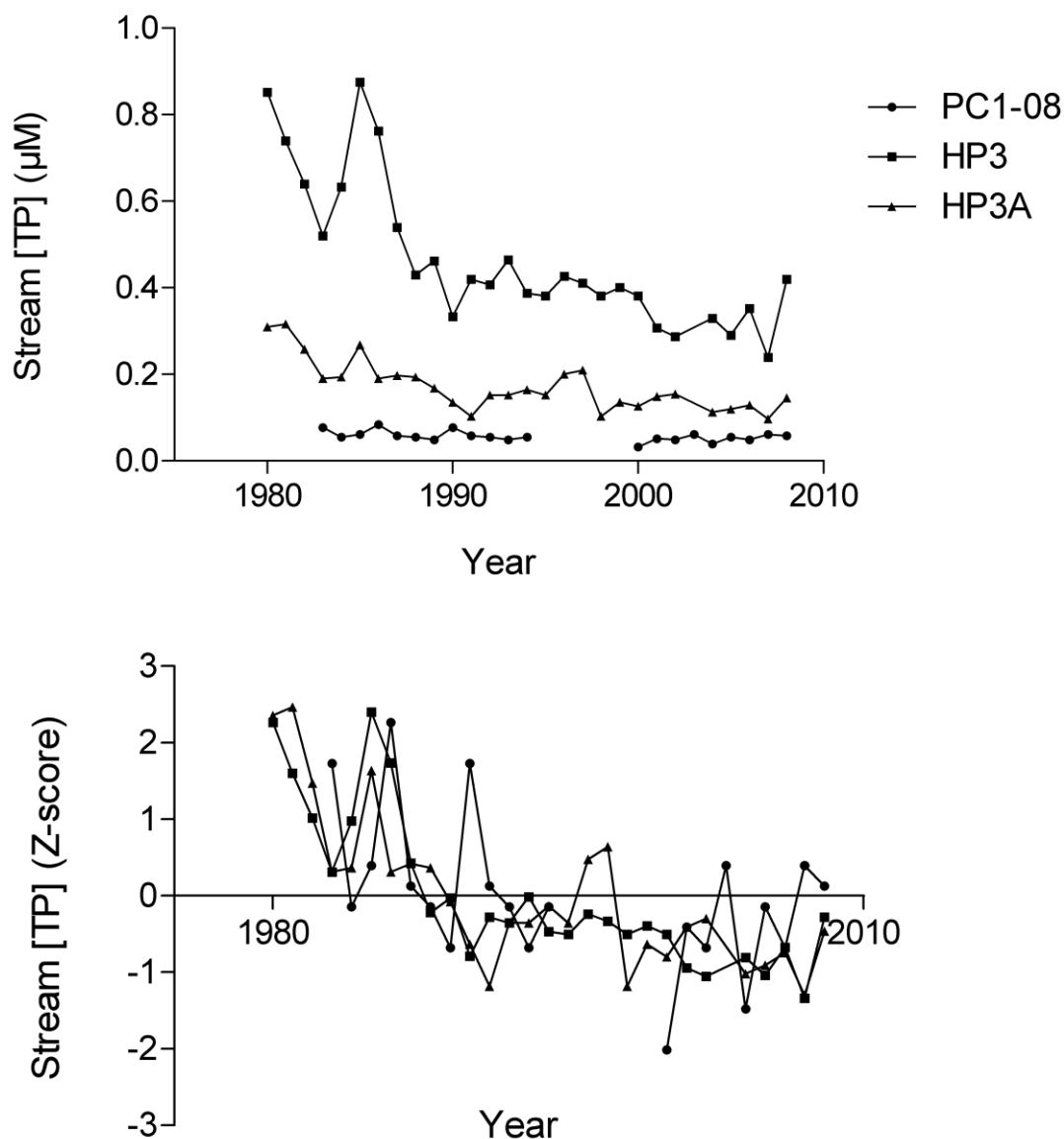
## 2.6 Statistics

All statistical tests were checked for assumptions of normality and homogeneity when applicable. Pearson's correlation tests were performed on various soil chemical parameters including concentration of soil labile P fractions and soil  $\text{pH}_{\text{CaCl}_2}$ . Spearman's correlation tests were used when data residuals were not normal. A Mann-Kendall test was performed on stream [TP] for all three study catchments. A one-way ANOVA followed by a Tukey test (given a significant ANOVA) was performed to identify differences in horizon P fractions between catchments. Statistical analysis was performed using Graph Pad Prism and the program R. All statistical tests involving the B-horizon did not include data from an AB horizon sample found at the HP3 catchment as it was considered to have distinct chemical characteristics. There were too few  $A_h$ -horizon or  $A_e$ -horizon soils at any particular catchment to perform any statistical analyses on the A-horizon.

### 3.0 Results

#### 3.1 Patterns in Stream Total Phosphorus Concentration at PC1-08, HP3 and HP3A

Total P concentrations were highest in streams at HP3 ( $0.2 - 0.9 \mu\text{M}$ ), followed by HP3A ( $0.1 - 0.3 \mu\text{M}$ ) and finally PC1-08 ( $< 0.1 \mu\text{M}$ ) (Figure 3.1). Volume weighted stream  $[\text{TP}_w]$  declined significantly ( $P < 0.001$ ) at both the Harp 3 and 3A subcatchments between 1980 and 2008 (Figure 3.1), whereas the decline in  $[\text{TP}_w]$  at PC1-08 was less pronounced ( $P = 0.097$ ). There is considerable year-to-year variation in  $[\text{TP}_w]$  at all sites, which is particularly evident when data are presented as Z-scores, nevertheless all catchments show a general decline in  $[\text{TP}_w]$  that was much more pronounced in the 1980s, with relatively little change during the 1990s (Figure 3.1).



**Figure 3.1.** Average annual volume weighted  $[TP_w]$  (top) and Z-scores of average annual volume weighted  $[TP_w]$  (bottom) in streams draining three long-term study catchments in south-central Ontario. Long-term data were provided by the Ontario Ministry of Environment Dorset Environmental Science Centre. The Mann-Kendall tau statistic and  $P$  values of total phosphorus for each subcatchment were as follows: PC108,  $\tau = -0.278$ ,  $P = 0.097$ ; HP3,  $\tau = -0.686$ ,  $P < 0.001$ , HP3A,  $\tau = -0.553$ ,  $P < 0.001$ .

### 3.2 Soil Physical and Chemical Properties

All 18 soil pits (6 in each catchment) were classified as podzols (Soil Classification Working Group, 1998), although there were differences in physical and chemical soil properties both within and among catchments. At all three subcatchments there were some soil pits in which an A-horizon was present. When an A-horizon was present, there was usually only an  $A_h$  or  $A_e$ , and not both (the one exception was HP3A pit 3 where both an  $A_h$  and  $A_e$  horizon were observed). B-horizons were found at all soil pits; there was usually only a  $B_{hf}$  or  $B_f$ , and not both (the one exception was HP3 pit 3 where both a  $B_{hf}$  and  $B_f$  horizon were observed).

All mineral soils collected in this study were dominated by sand and silt, and were low in clay (Table 3.1). The forest floor (LFH) horizon at the predominately coniferous site (PC1-08) was thicker and pH values in both the LFH and  $A_h$ -horizon were generally lower at PC1-08 (LHF - 3.2,  $A_h$  - 2.9) than at HP3 (LHF - 3.8,  $A_h$  - 3.4) and HP3A (LHF - 3.9,  $A_h$  - 3.4) (Table 3.1). In addition  $Al_{exg}$  ( $meq \cdot 100 g^{-1}$ ) in the LFH and  $A_h$  horizons was higher at PC1-08 (LHF - 2.47,  $A_h$  - 4.08) relative to HP3 (LHF - 0.22,  $A_h$  - 0.88) and HP3A (LHF - 0.61,  $A_h$  - 1.46) (Table 3.1). The pH (4.3 - 4.5) and  $Al_{exg}$  ( $1.0 - 2.6 meq \cdot 100 g^{-1}$ ) of the B-horizon was relatively similar among the three catchments (Table 3.1).  $Al_{ox}$ ,  $Fe_{ox}$  and  $P_{ox}$  were highest in the B-horizon and concentrations were similar within a horizon type across the 3 catchments.  $Al_{ox}$  ( $\mu mol \cdot g^{-1}$ ) was particularly high in  $B_{hf}$  relative to other horizons at both PC1-08 (807) and HP3 (816) (Table 3.1). Carbon and N concentrations decreased with soil depth, but were comparable among the three catchments (Table 3.1). As expected, CEC values generally decreased with soil depth reflecting the pattern in soil organic matter; similar values and patterns were observed at all sites (Table 3.1). There was little difference in  $K_{exg}$  among catchments, but the Harp subcatchments generally had higher average  $Ca_{exg}$  and  $Mg_{exg}$  in most horizons compared to PC1-08 (Table 3.1); this was especially apparent in the  $B_f$  where  $Ca_{exg}$  ( $meq \cdot 100 g^{-1}$ ) in PC1-08 (0.2) was less than a quarter of the  $Ca_{exg}$  in HP3 (0.9) or HP3A (1.4) (Table 3.1). Lower  $Ca_{exg}$  and  $Mg_{exg}$  concentrations in PC1-08 soil led to a lower % base saturation in all mineral horizons relative to HP3 and HP3A (Table 3.1).



**Table 3.1.** Mean soil physical and chemical characteristics (data range in parentheses) separated by catchment.

<b>PC1-08</b>					
	<b>LFH (n = 6)</b>	<b>A<sub>h</sub> (n = 2)</b>	<b>A<sub>e</sub> (n = 2)</b>	<b>B<sub>hf</sub> (n = 2)</b>	<b>B<sub>f</sub> (n = 4)</b>
<b>Horizon Depth (cm)</b>	6 (2 – 21)	7 (6 - 7)	3 (2 – 3)	26 (24 – 28)	19 (9 – 22)
<b>Bulk Density (g • cm<sup>-3</sup>)</b>	0.11 (0.10 – 0.14)	0.61 (0.51 – 0.70)	0.95 (0.88 – 1.01)	0.49 (0.48 – 0.50)	0.52 (0.39 – 0.71)
<b>pH<sub>CaCl2</sub></b>	3.2 (3.0 – 3.7)	2.9 (2.7 – 3.1)	3.2 (3.1 – 3.2)	4.5 (4.5 – 4.5)	4.3 (4.0 – 4.5)
<b>% clay</b>	N/A	2 (2 – 3)	3 (2 – 3)	2 (2 – 3)	3 (2 – 4)
<b>% silt</b>	N/A	62 (52 – 71)	60 (41 – 79)	37 (33 – 42)	54 (36 – 71)
<b>% sand</b>	N/A	38 (29 – 48)	40 (21 – 59)	62 (58 – 67)	46 (29 – 64)
<b>% C</b>	29.3 (11.9 – 48.9)	12.2 (7.2 – 17.3)	2.0 (1.1 – 2.9)	8.3 (7.8 – 8.9)	3.3 (1.5 – 4.3)
<b>% N</b>	1.0 (0.6 – 1.4)	0.5 (0.5 – 0.6)	0.3 (0.1 – 0.5)	0.3 (0.3 – 0.4)	0.2 (0.1 – 0.2)
<b>Al<sub>ox</sub> (μmol • g<sup>-1</sup>)</b>	100 (22 – 268)	102 (84 – 120)	51 (47 – 55)	807 (721 – 893)	415 (356 – 552)
<b>Fe<sub>ox</sub> (μmol • g<sup>-1</sup>)</b>	56 (10 – 201)	163 (153 – 172)	120 (120 – 121)	245 (230 – 261)	328 (249 – 462)
<b>P<sub>ox</sub> (μmol • g<sup>-1</sup>)</b>	3.4 (1.9 – 6.4)	3.3 (2.6 – 3.9)	1.2 (1.0 – 1.4)	14.8 (14.4 – 15.2)	9.0 (5.7 – 15.0)
<b>Al<sub>exg</sub> (meq • 100 g<sup>-1</sup>)</b>	2.5 (0.1 – 6.6)	4.1 (3.1 – 5.1)	2.0 (1.9 – 2.0)	1.0 (0.8 – 1.2)	2.5 (1.1 – 4.1)
<b>K<sub>exg</sub> (meq • 100 g<sup>-1</sup>)</b>	1.79 (1.22 – 2.69)	0.33 (0.31 – 0.35)	0.12 (0.09 – 0.16)	0.07 (0.06 – 0.09)	0.10 (0.07 – 0.14)
<b>Ca<sub>exg</sub> (meq • 100 g<sup>-1</sup>)</b>	18.4 (11.6 – 33.0)	1.7 (1.4 – 2.0)	0.3 (0.0 – 0.6)	0.7 (0.3 – 1.2)	0.2 (0.0 – 0.4)
<b>Mg<sub>exg</sub> (meq • 100 g<sup>-1</sup>)</b>	2.86 (1.82 – 4.98)	0.48 (0.46 – 0.51)	0.17 (0.08 – 0.26)	0.06 (0.04 – 0.09)	0.09 (0.05 – 0.13)
<b>CEC (meq • 100 g<sup>-1</sup>)</b>	43 (20 – 70)	12 (12 – 12)	4 (3 – 5)	11 (9 – 13)	6 (5 – 7)
<b>% Base Saturation</b>	58 (33 – 79)	21 (18 – 24)	13 (6 – 20)	7 (4 – 11)	6 (2 – 8)

Table 3.1. *cont*

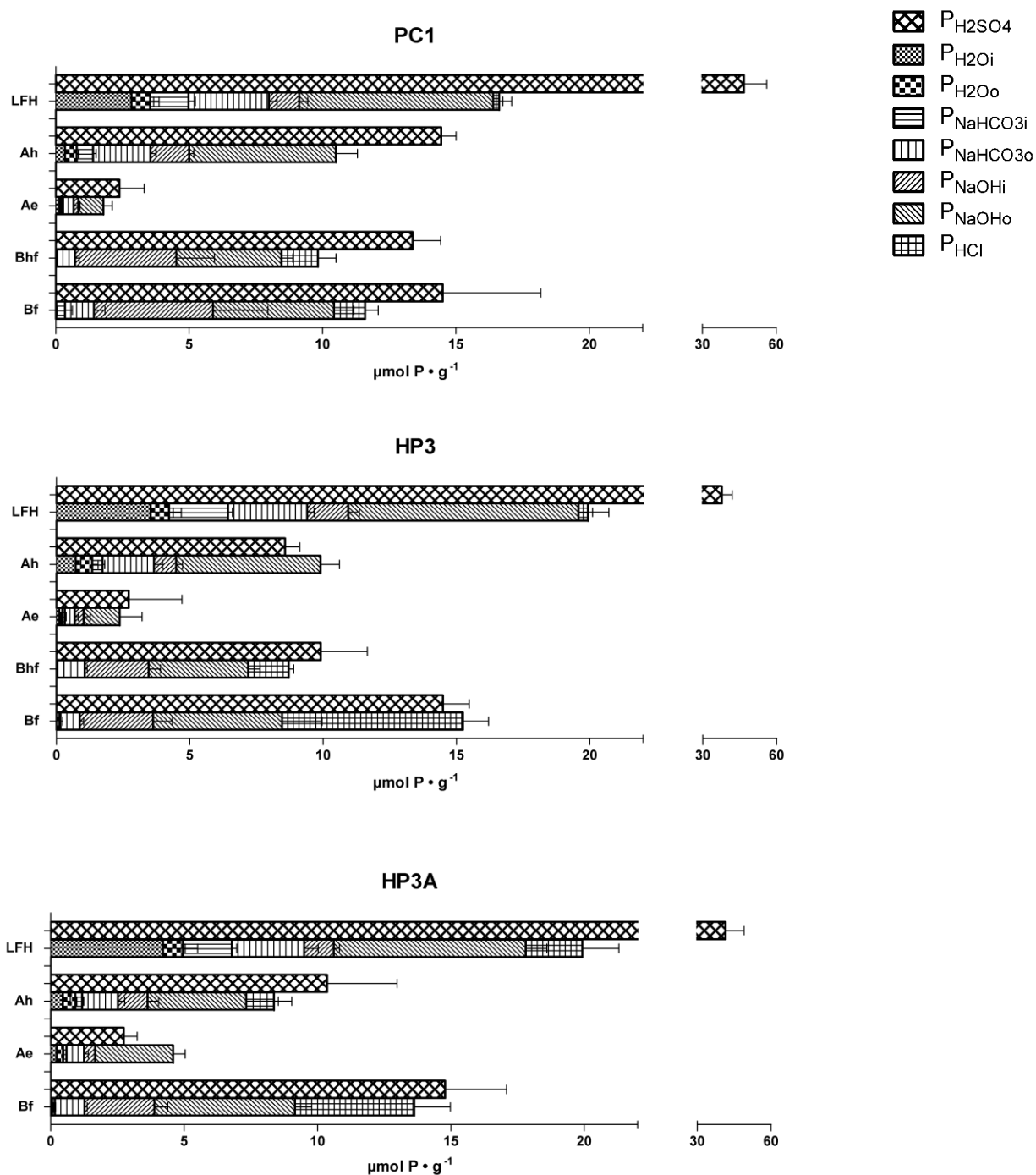
HP3					
	LFH (n = 6)	A <sub>h</sub> (n = 2)	A <sub>e</sub> (n = 2)	B <sub>hf</sub> (n = 3)	B <sub>f</sub> (n = 4)
<b>Horizon Depth (cm)</b>	3 (1 – 5)	7 (7 – 7)	8 (3 – 12)	14 (7 – 21)	22 (21 – 23)
<b>Bulk Density (g • cm<sup>-3</sup>)</b>	0.18 (0.15 – 0.21)	0.66 (0.61 – 0.71)	0.88 (0.62 – 1.13)	0.62 (0.57 – 0.66)	0.87 (0.73 – 1.09)
<b>pH<sub>CaCl2</sub></b>	3.8 (3.1 – 4.5)	3.4 (3.2 – 3.6)	3.0 (2.9 – 3.0)	4.3 (4.2 – 4.4)	4.4 (4.3 – 4.6)
<b>% clay</b>	N/A	1 (1 – 1)	2 (2 – 2)	2 (2 – 2)	3 (2 – 3)
<b>% silt</b>	N/A	34 (30 – 39)	36 (29 – 42)	28 (23 – 32)	35 (31 – 38)
<b>% sand</b>	N/A	66 (61 – 70)	64 (58 – 71)	72 (67 – 77)	65 (62 – 69)
<b>% C</b>	35.9 (26.1 – 46.4)	7.7 (7.0 – 8.3)	2.5 (2.0 – 3.0)	5.0 (5.0 – 5.1)	2.2 (1.8 – 2.7)
<b>% N</b>	1.7 (1.2 – 2.1)	0.4 (0.3 – 0.5)	0.1 (0.1 – 0.2)	0.3 (0.2 – 0.3)	0.1 (0.1 – 0.1)
<b>Al<sub>ox</sub> (μmol • g<sup>-1</sup>)</b>	84 (13 – 323)	32 (29 – 35)	53 (30 – 75)	816 (265 – 1396)	392 (288 – 601)
<b>Fe<sub>ox</sub> (μmol • g<sup>-1</sup>)</b>	73 (50 – 108)	113 (105 – 120)	109 (105 – 112)	227 (186 – 293)	208 (105 – 269)
<b>P<sub>ox</sub> (μmol • g<sup>-1</sup>)</b>	1.9 (1.2 – 2.6)	0.9 (0.9 – 0.9)	0.8 (0.2 – 1.3)	9.0 (2.2 – 13.0)	7.8 (6.5 – 9.0)
<b>Al<sub>exg</sub> (meq • 100 g<sup>-1</sup>)</b>	0.2 (0.0 – 1.3)	0.9 (0.1 – 1.6)	1.5 (0.8 – 2.3)	2.3 (1.7 – 3.4)	1.4 (0.9 – 1.9)
<b>K<sub>exg</sub> (meq • 100 g<sup>-1</sup>)</b>	2.31 (1.87 – 2.79)	0.29 (0.25 – 0.32)	0.07 (0.06 – 0.08)	0.05 (0.04 – 0.07)	0.05 (0.02 – 0.08)
<b>Ca<sub>exg</sub> (meq • 100 g<sup>-1</sup>)</b>	30.9 (25.2 – 34.9)	5.3 (3.4 – 7.3)	0.6 (0.3 – 0.9)	1.0 (0.2 – 2.1)	0.9 (0.3 – 1.5)
<b>Mg<sub>exg</sub> (meq • 100 g<sup>-1</sup>)</b>	5.59 (3.66 – 6.91)	0.97 (0.55 – 1.38)	0.11 (0.10-0.12)	0.10 (0.06 – 0.19)	0.14 (0.03 – 0.26)
<b>CEC (meq • 100 g<sup>-1</sup>)</b>	54 (26 – 80)	12 (9 – 15)	3 (1 – 5)	10 (8 – 13)	4 (3 – 5)
<b>% Base Saturation</b>	82 (43 – 149)	54 (46 – 62)	50 (25 – 77)	13 (3 – 28)	26 (12 – 46)

Table 3.1. *cont*

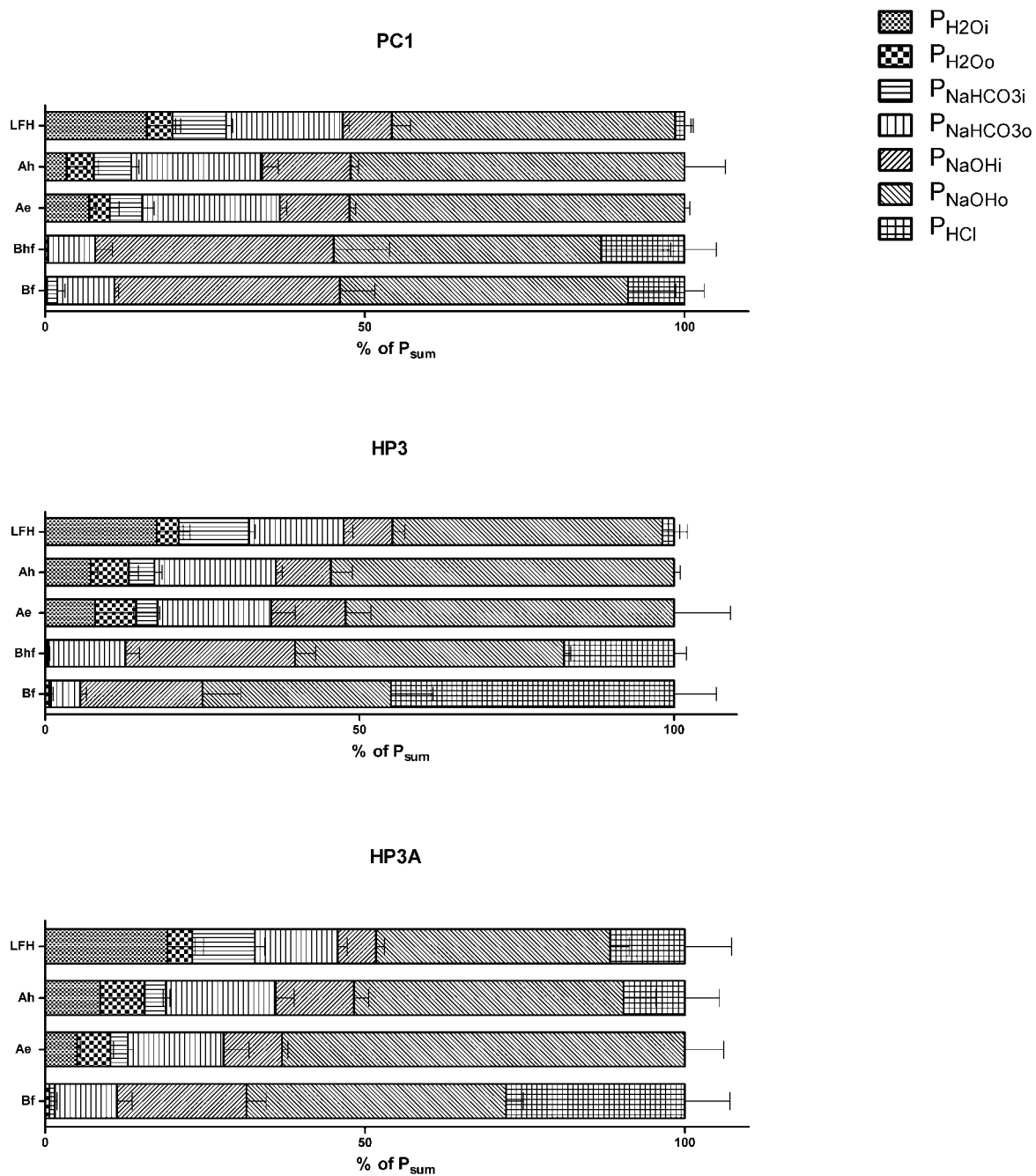
HP3A				
	LFH (n = 6)	A <sub>h</sub> (n = 3)	A <sub>e</sub> (n = 3)	B <sub>t</sub> (n = 6)
Horizon Depth (cm)	2 (1-5)	8 (5 – 11)	4 (3 – 5)	21 (15 – 28)
Bulk Density (g • cm <sup>-3</sup> )	0.08 (0.05 – 0.12)	0.62 (0.38 – 0.85)	0.83 (0.57 – 0.98)	0.71 (0.50 – 0.91)
pH <sub>CaCl2</sub>	3.9 (3.4 – 4.6)	3.4 (3.2 – 3.6)	3.3 (3.0 – 3.4)	4.3 (3.9 – 4.6)
% clay	N/A	2 (1 – 2)	2 (1 – 3)	2 (2 – 3)
% silt	N/A	39 (31 – 43)	38 (23 – 55)	33 (27 – 40)
% sand	N/A	61 (57 – 69)	62 (45 – 77)	67 (60 – 73)
% C	35.6 (20.0 – 49.2)	6.7 (6.2 – 7.1)	2.5 (1.8 – 3.3)	4.0 (2.5 – 4.5)
% N	1.6 (0.7 – 2.1)	0.4 (0.4 – 0.5)	0.2 (0.1 – 0.2)	0.2 (0.2 – 0.3)
Al <sub>ox</sub> (μmol • g <sup>-1</sup> )	63 (15 – 180)	77 (35 – 130)	44 (38 – 50)	342 (257 – 426)
Fe <sub>ox</sub> (μmol • g <sup>-1</sup> )	80 (14 – 238)	199 (136 – 305)	160 (128 – 195)	340 (160 – 580)
P <sub>ox</sub> (μmol • g <sup>-1</sup> )	4.0 (2.4 – 8.1)	3.2 (1.4 – 5.2)	1.5 (1.4 – 1.7)	8.2 (3.6 – 11.5)
Al <sub>exg</sub> (meq • 100 g <sup>-1</sup> )	0.6 (0.3 – 0.9)	1.5 (0.7 – 2.3)	1.4 (0.9 – 2.3)	2.6 (0.8 – 5.0)
K <sub>exg</sub> (meq • 100 g <sup>-1</sup> )	1.96 (1.20 – 2.98)	0.27 (0.21 – 0.31)	0.10 (0.08 – 0.11)	0.07 (0.04 – 0.15)
Ca <sub>exg</sub> (meq • 100 g <sup>-1</sup> )	29.9 (19.0 – 39.0)	3.8 (2.8 – 4.9)	1.2 (0.9 – 1.7)	1.4 (0.2 – 3.2)
Mg <sub>exg</sub> (meq • 100 g <sup>-1</sup> )	5.25 (3.18 – 8.57)	0.75 (0.59 – 1.01)	0.28 (0.22 – 0.34)	0.17 (0.08 – 0.34)
CEC (meq • 100 g <sup>-1</sup> )	54 (28 – 84)	10 (7 – 12)	3 (3 – 4)	6 (3 – 8)
% Base Saturation	71 (57 – 84)	51 (32 – 67)	53 (32 – 79)	30 (6 – 62)

### 3.3 Phosphorous Chemistry in Soils at HP3A, HP3 and PC1-08

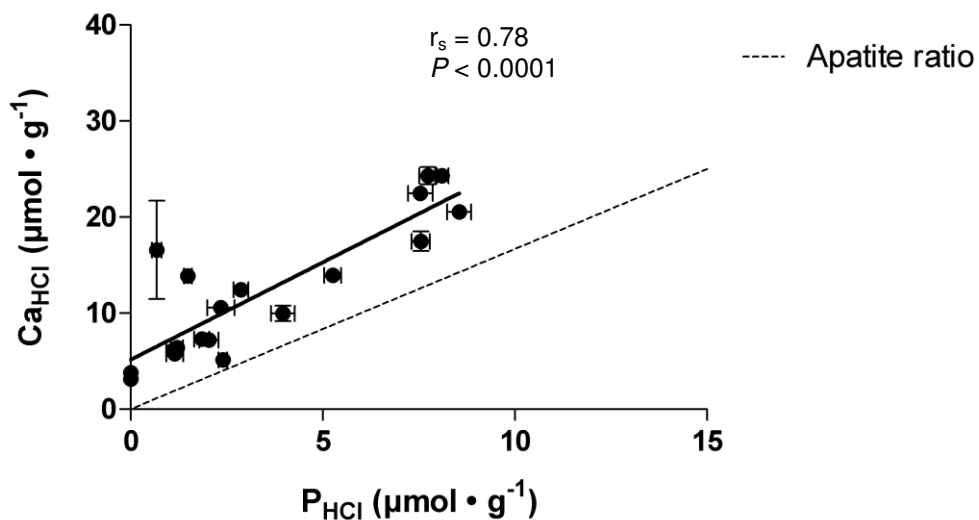
Despite very large differences in stream  $[TP_w]$ , the concentration and proportion of most P fractions was similar for each horizon among the three catchments (Figure 3.2, Figure 3.3). Total P concentrations in the mineral soil obtained using the  $H_2SO_4$  extraction were similar to concentrations obtained by summing the results of the four Hedley fractions ( $P_{sum}$ ). All 3 catchments showed similar trends in  $[TP_s]$ , with highest concentrations observed in the LFH horizon, decreasing in the  $A_h$ -horizon and reaching a minimum in the  $A_e$  horizon (Figure 3.2). The  $[TP_s]$  concentrations in the B-horizon were comparable to those observed in the  $A_h$  (Figure 3.2). The majority of the P in all horizons was  $P_{NaOH}$ , with the organic sub-fraction ( $P_{NaOHo}$ ) dominating in the upper soil horizons and relatively similar amounts of inorganic and organic P in the B-horizons (Figure 3.2, Figure 3.3). The LFH layer had the highest proportion of soluble P followed by the  $A_h$ -horizon and there was very little soluble P in the B-horizon (Figure 3.3). A one-way ANOVA followed by a Tukey test revealed that there was a significantly higher concentration of  $P_{HCl}$  in the Harp 3 subcatchment  $B_f$ -horizon soil relative to the Plastic  $B_f$ -horizon ( $q = 4.50$ ,  $P = 0.022$ ) (Figure 3.2). All other P fractions in the LFH and  $B_f$  horizons showed no significant difference between catchments; statistical tests were not performed on  $B_{hf}$ ,  $A_e$  or  $A_h$ -horizon soils as sample sizes within catchments were too small.  $P_{HCl}$  was measured in all LFH horizons, but not all A-horizons of the 3 catchments (Figure 3.2, Figure 3.3). Phosphorous measured in the 1M HCl extraction is thought to be mostly apatite (Hedley et al. 1982) and  $P_{HCl}$  was strongly correlated with  $Ca_{HCl}$  in the B-horizon (Figure 3.4). The Ca:P ratio in the extract was close to, but always greater than, the Ca:P ratio reported for apatite. The higher Ca:P ratio suggests that other Ca minerals (e.g. hornblende) were also dissolved in the extraction, but that this Ca source was relatively consistent among all soil samples.



**Figure 3.2.** Concentrations of P from the Hedley fractionation and total P extraction ( $P_{H_2SO_4}$ ) for each study catchment. Bars represent the mean of  $n$  (Table 3.3) observations  $\pm$  SE. One-way ANOVAs performed for each P fractions in the LFH,  $B_{hf}$ , and  $B_f$  horizons between catchments showed that there were no significant differences, between P fractions of each horizon among catchments, with the exception of  $P_{HCl}$  in the  $B_f$  horizon. A Tukey test confirmed that there was a significant difference in  $[P_{HCl}]$  in the  $B_f$  horizon between the HP3 and PC1-08 catchments.



**Figure 3.3.** Proportions of [P] from the Hedley fractionation for each study catchment. Bars represent the mean of  $n$  (Table 3.3) observations  $\pm$  SE.



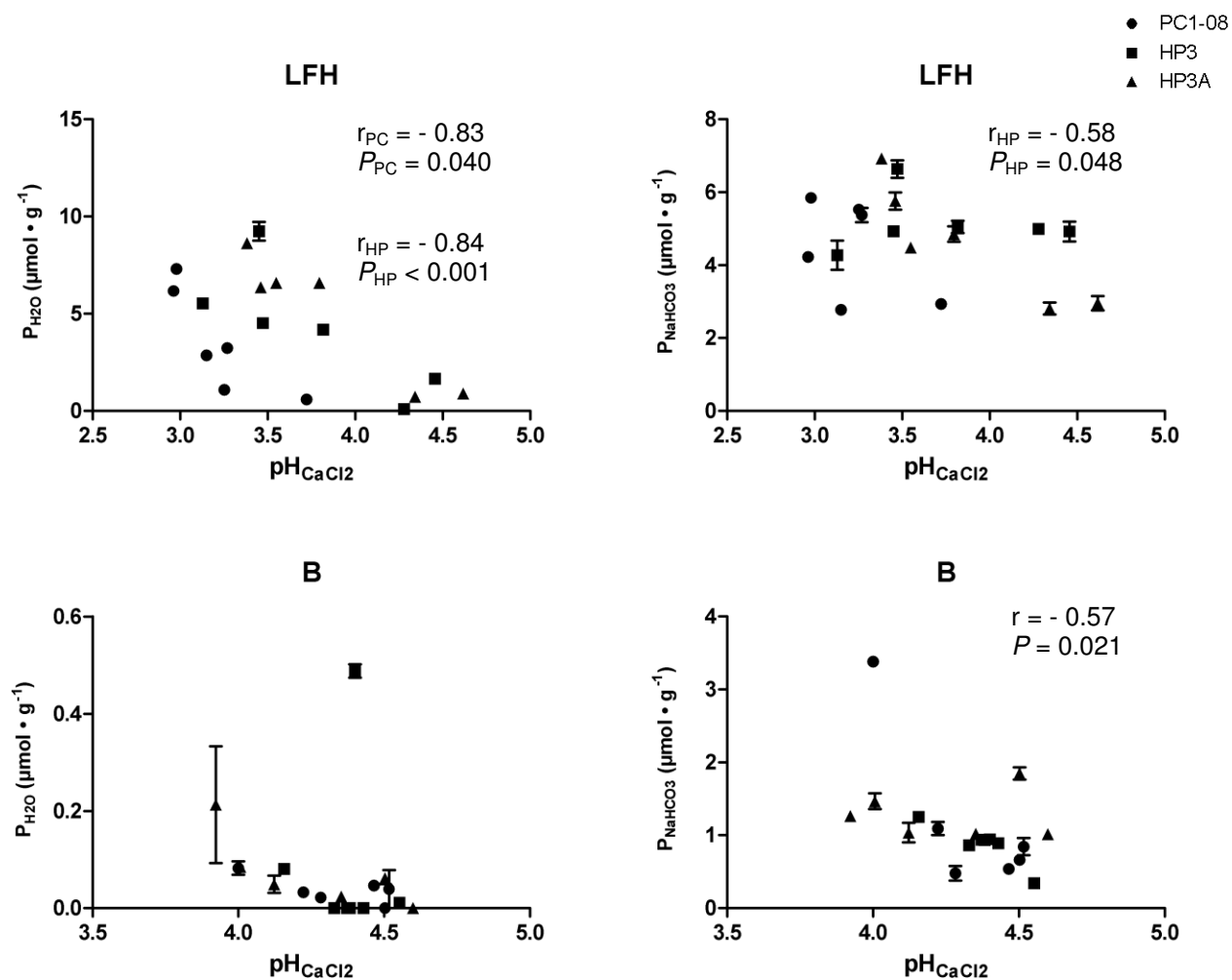
**Figure 3.4.** Scatter plot of  $[\text{P}_{\text{HCl}}]$  against  $[\text{Ca}_{\text{HCl}}]$  in B-horizon soils of the three study catchments. The dashed line represents the 1.67 Ca:P molar ratio of apatite (Ibrahim et al. 2011). The solid line represents the linear regression of the data points and has a slope of  $2.0 \pm 0.4$  (95% CI). Data residuals did not meet normality assumptions; therefore a Spearman correlation test was performed. Points represent means of analytical triplicates  $\pm$  SE.

### 3.4 Relationship Between Soluble Phosphorus, Labile Phosphorus, Extractable Metals and Soil $\text{pH}_{\text{CaCl}_2}$

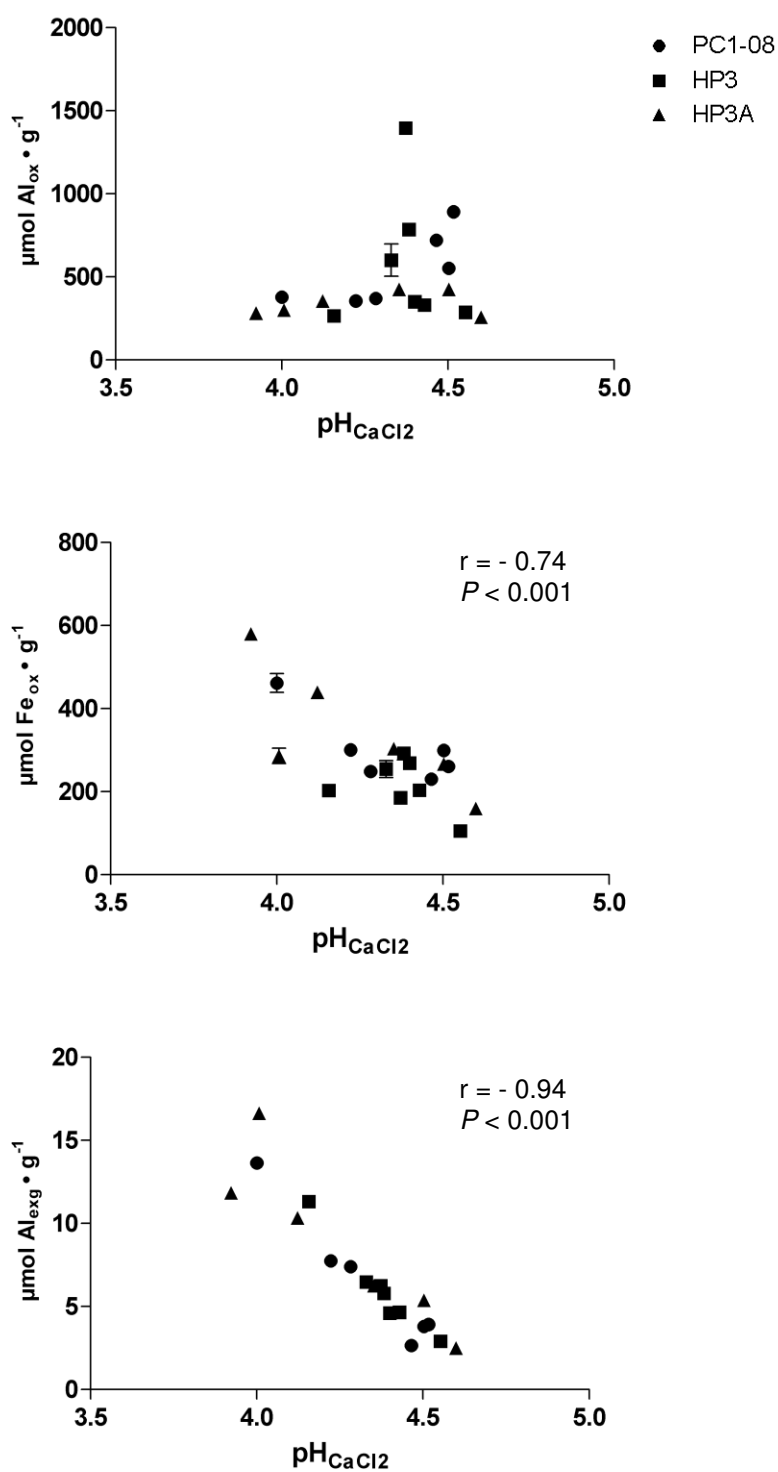
There was a significant negative linear relationship between  $\text{P}_{\text{H}_2\text{O}}$  and  $\text{pH}_{\text{CaCl}_2}$  of the LFH horizon in both the Harp (3 and 3A combined) and Plastic catchments (Figure 3.5). In contrast, there was no relationship between LFH  $\text{P}_{\text{NaHCO}_3}$  and pH at Plastic and a very weak negative linear relationship between LFH  $\text{P}_{\text{NaHCO}_3}$  and  $\text{pH}_{\text{CaCl}_2}$  using the combined Harp data (Figure 3.5). There was also a weak negative linear relationship between  $\text{P}_{\text{NaHCO}_3}$  and  $\text{pH}_{\text{CaCl}_2}$  of the combined B-horizon soil data from all three catchments (Figure 3.5).  $\text{P}_{\text{H}_2\text{O}}$  concentrations in the B-horizon at both catchments were very low ( $< 0.5 \mu\text{mol} \cdot \text{g}^{-1}$ ).

There was a strong negative linear relationship between  $\text{Al}_{\text{exg}}$  and the  $\text{pH}_{\text{CaCl}_2}$  of the B-horizon that was independent of site (Figure 3.6). Similarly, there was a strong negative linear relationship between  $\text{Fe}_{\text{ox}}$  and B-horizon pH, but there was no significant relationship between  $\text{Al}_{\text{ox}}$  and  $\text{pH}_{\text{CaCl}_2}$  (Figure 3.6).  $\text{Al}_{\text{exg}}$  is an order of magnitude lower in concentration than  $\text{Al}_{\text{ox}}$  (Figure 3.6); it can therefore be assumed that the dissolution of  $\text{Al}_{\text{ox}}$  to form  $\text{Al}_{\text{exg}}$  under more acidic conditions has not significantly changed  $[\text{Al}_{\text{ox}}]$  at the observed pH range (Figure 3.6).  $\text{Fe}_{\text{exg}}$  was below the detection limit for all collected B-horizon soils (data not shown).





**Figure 3.5.** Scatter plots of  $[P_{H_2O}]$  or  $[P_{\text{NaHCO}_3}]$  against  $\text{pH}_{\text{CaCl}_2}$  of LFH (top), or B-horizon (bottom) soil. Pearson's coefficient and level of significance are only shown for significant relationships. Correlation analyses on data from the LFH horizon were separated by catchment ( $n_{\text{PC}} = 6$ ,  $n_{\text{HP}} = 12$ ) because of the strong effect of the dominant tree fractions (i.e. coniferous vs. deciduous) on LFH chemistry. Points represent means of analytical triplicates  $\pm$  SE.



**Figure 3.6.** Scatter plots of soil extractable metals in the B-horizon against soil pH<sub>CaCl2</sub>. Pearson's coefficient and level of significance are only shown for significant relationships. Points represent means of analytical triplicates  $\pm$  SE.

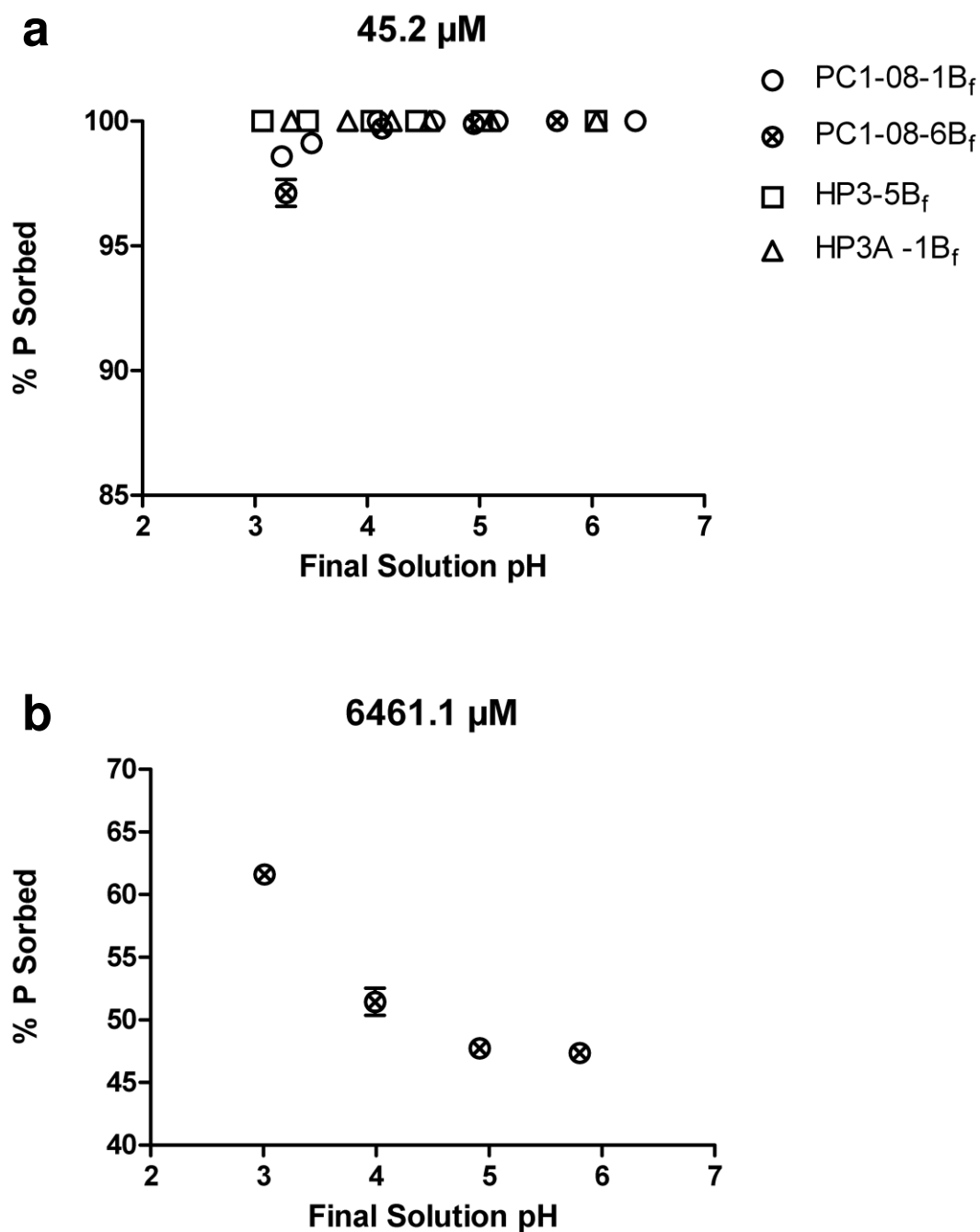
### 3.5 Experimental Phosphorus Sorption Studies

Lysimeter data from PC1-08 show that  $[TP_w]$  concentrations in the LFH soil solution are typically between  $0.18 - 11.72 \mu\text{M}$ , whereas in the B-horizon soil solution  $[TP]$  are  $0.09 - 3.04 \mu\text{M}$  (Table 3.2). Experimental studies conducted at solution  $[P]$  much higher than lysimeter solution  $[P]$  (i.e. experimental solution  $[P] = 45.2 - 452.0 \mu\text{M}$ ) demonstrated that soils were able to sorb almost all ( $>95\%$ ) of the P in solution (Figure 3.7, Figure 3.8, Figure 3.9, Table 3.3). Only at very low solution pH values (3 - 4) did soils not exhibit 100% sorption (Figure 7a). In contrast, when the experiment was conducted at  $6461.1 \mu\text{M}$ , sorption values decreased from around 60% at pH3 to  $<50\%$  at pH values  $> 5.0$  (Figure 3.7b).

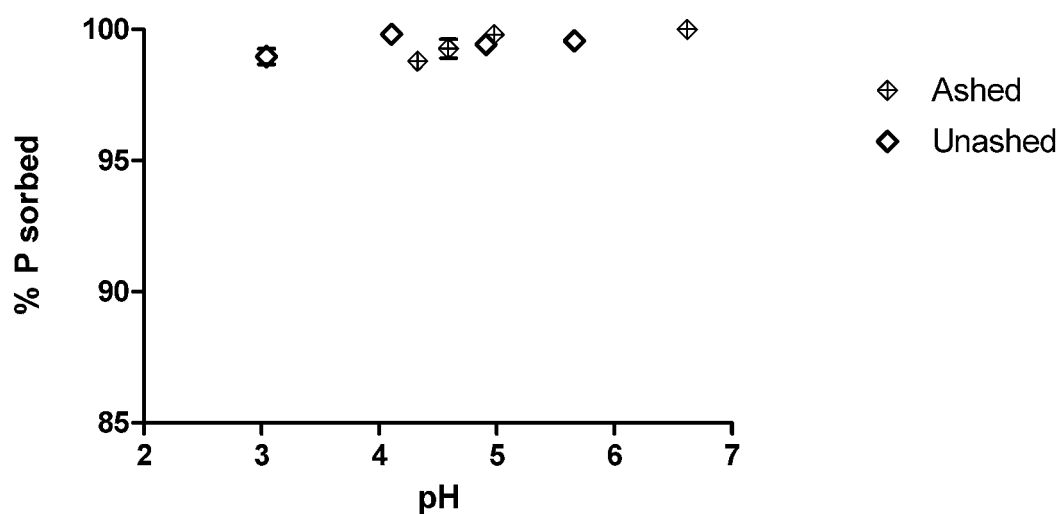
Sorption results using ashed and unashed soil samples were very similar indicating that removal of organic matter had no observable effect on P sorption at  $[P]$  of  $45.2 \mu\text{M}$  (Figure 3.8). There was a decrease in P sorption at a pH of 6 in the absence of a background electrolyte (Figure 3.9). Phosphorus sorption at natural soil  $\text{pH}_{\text{CaCl}_2}$  showed no clear trend but sorption was  $> 91\%$  in all cases (Table 3.3).

**Table 3.2.** Average lysimeter solution pH and total P concentrations (data range in parenthesis) at PC1-08. Lysimeter percolate samples were collected between 2003 and 2009 (n = 32).

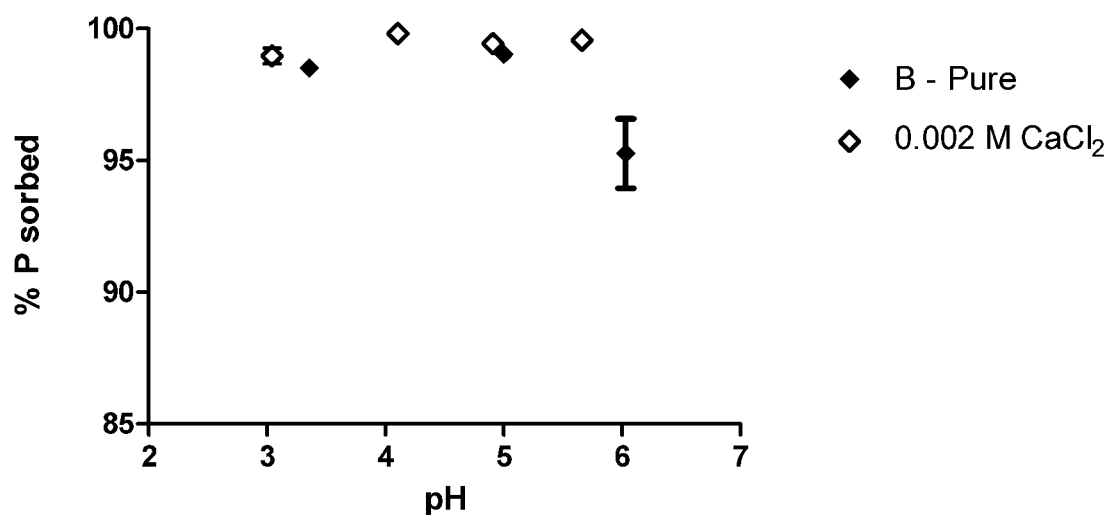
Horizon	Solution pH	Solution [TP] ( $\mu\text{M}$ )
LHF	4.4 (3.8 – 5.25)	2.11 (0.18 – 11.72)
B <sub>HF</sub>	4.7 (4.0 – 5.3)	0.36 (0.09 – 3.04)



**Figure 3.7.** Scatter plots of % P sorbed by soil in batch sorption experiments at various solution pH values. The % P sorbed was calculated by dividing (initial solution [P] - final solution [P]) by the initial solution [P] multiplied by 100. Final solution P was measured after a 3-hour and 24-hour equilibration period in a 45.2  $\mu\text{M}$  P solution (top) and 6461.1  $\mu\text{M}$  P solution (bottom), respectively. Points represent means of analytical triplicates  $\pm$  SE.



**Figure 3.8.** Scatter plot of the % P sorbed by a soil sample (HP3- 3B<sub>hf</sub>) in batch sorption experiments at various solution pH values. Ashed samples were heated in a muffle furnace at 375° C for 16 hours. The % P sorbed was calculated by dividing (initial solution [P] - final solution [P]) by the initial solution [P] multiplied by 100. Final solution P was measured after a 3-hour equilibration period in a 45.2  $\mu$ M P solution. Points represent means of analytical triplicates  $\pm$  SE.



**Figure 3.9.** Scatter plot of the % P sorbed by a soil sample (HP3- 3B<sub>hf</sub>) in batch sorption experiments at various solution pH values. Sorption experiments were performed in the presence (0.002 M CaCl<sub>2</sub>) and the absence (B – Pure) of a background electrolyte. The % P sorbed was calculated by dividing (initial solution [P] - final solution [P]) by the initial solution [P] multiplied by 100. Final solution P was measured after a 3-hour equilibration period in a 45.2  $\mu$ M P solution. Points represent means of analytical triplicates  $\pm$  SE.

**Table 3.3.** Percent P sorbed by 7 different soil samples at their natural soil pH in three different solution [P]. The % P sorbed was calculated by dividing (initial solution [P] - final solution [P]) by the initial solution [P] multiplied by 100. Final solution P was measured after a 3-hour equilibration period in a 4.5  $\mu\text{M}$  or 45.2  $\mu\text{M}$  P solution or a 24 - hour equilibration period in a 452.0  $\mu\text{M}$  P solution. % P sorbed values are means of analytical triplicates (standard error in parentheses).

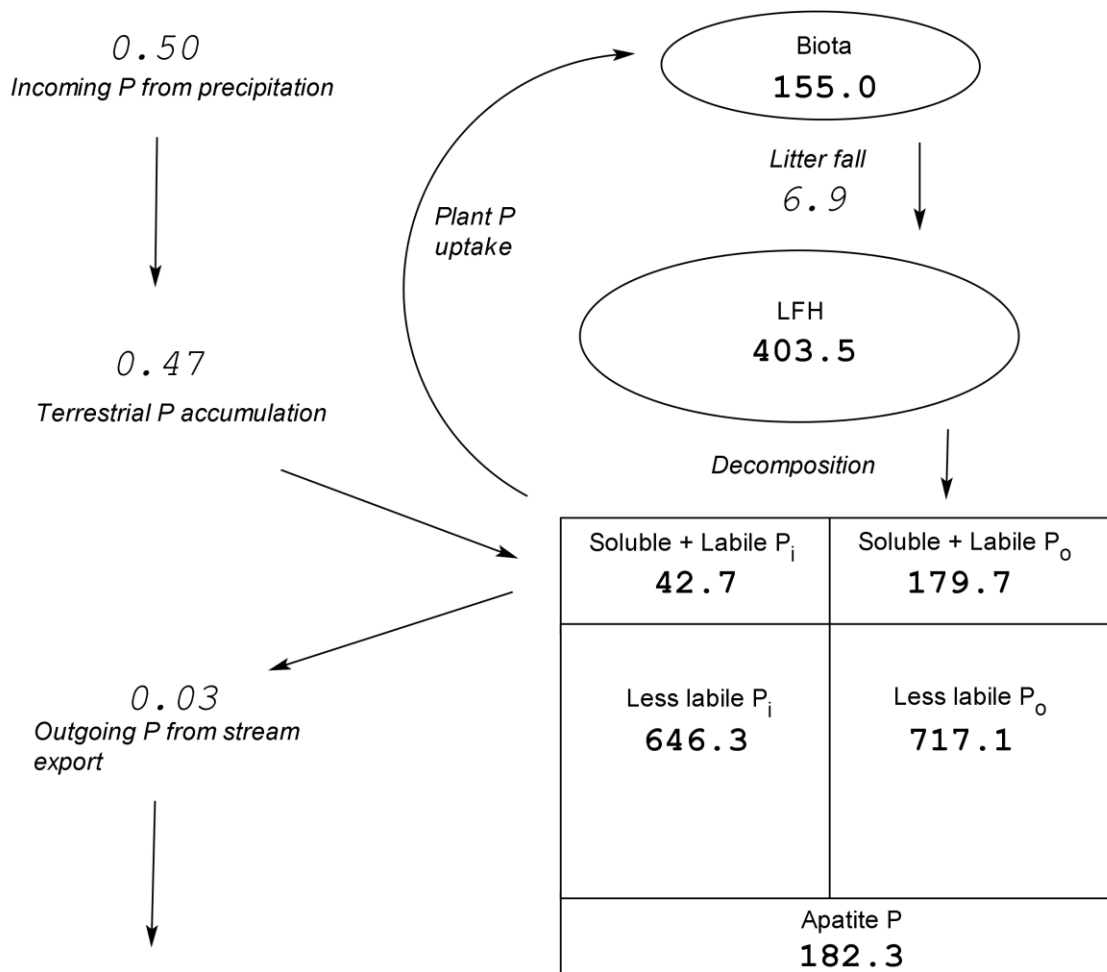
	$\text{pH}_{\text{CaCl}_2}$	% P sorbed		
		4.5 $\mu\text{M}$	45.2 $\mu\text{M}$	452.0 $\mu\text{M}$
<b>HP3A-2B<sub>f</sub></b>	3.9	92 (5)	100 (0)	98 (0)
<b>HPA-3B<sub>f</sub></b>	4.1	100 (0)	100 (0)	98 (0)
<b>PC1-08-2B<sub>f</sub></b>	4.3	92 (2)	99 (0)	99 (0)
<b>HP3-4B<sub>f</sub></b>	4.3	90 (7)	99 (0)	99 (0)
<b>HP3-5B<sub>hf</sub></b>	4.4	92 (2)	98 (0)	99 (0)
<b>HPA3-4B<sub>f</sub></b>	4.4	100 (0)	100 (0)	99 (0)
<b>HP3A-1B<sub>f</sub></b>	4.6	91 (5)	99 (0)	95 (0)



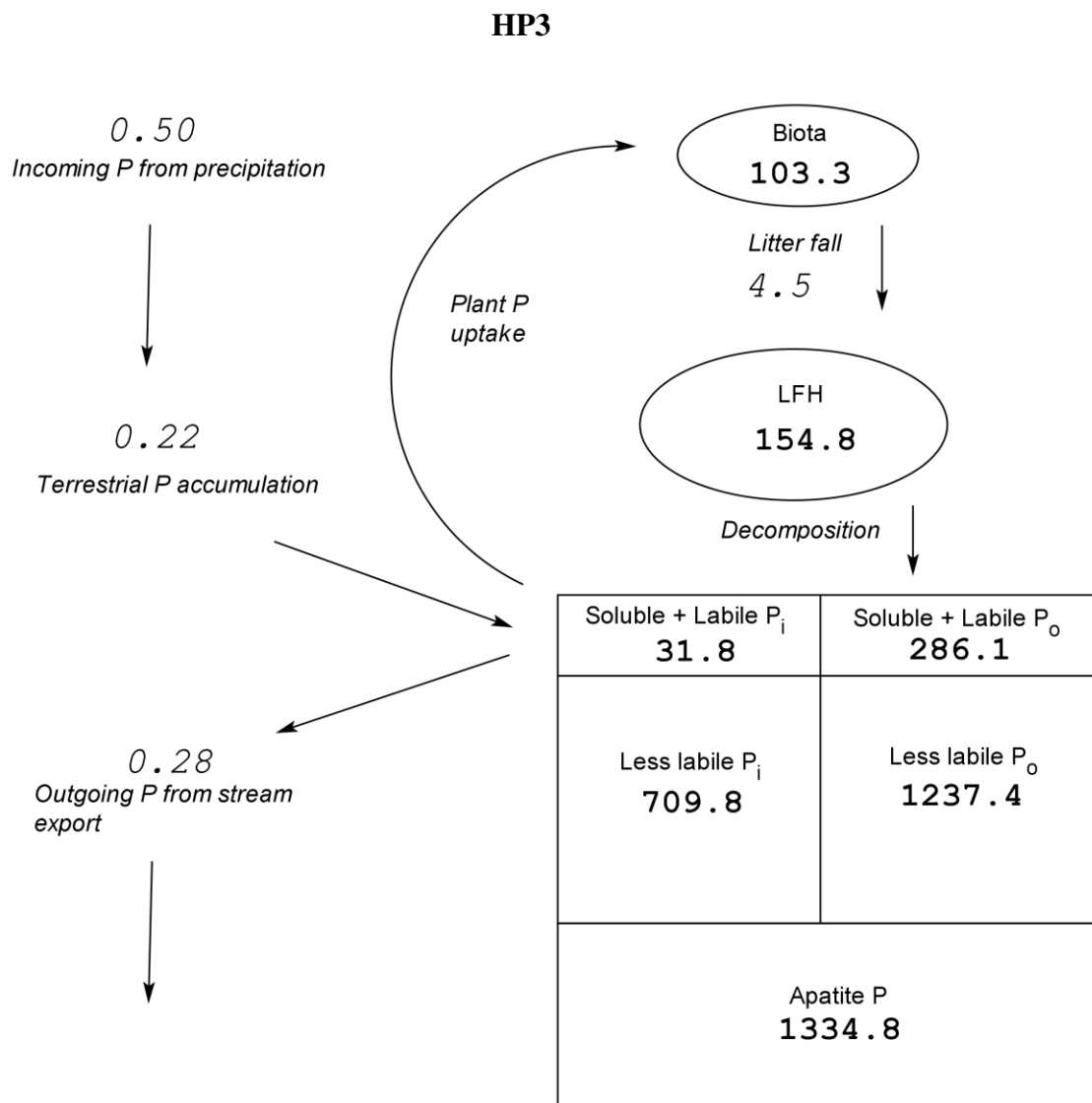
### 3.6 Phosphorus Budgets

Between 1980 and 2008 the three study catchments retained, on average, between 44 and 94% of the P in bulk deposition. The greatest accumulation of P was observed at PC1-08 ( $0.47 \text{ mmols} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ ) followed by HP3A ( $0.40 \text{ mmols} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ ) and HP3 ( $0.22 \text{ mmols} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$ ) (Figure 3.10). Biotic and soil P pools were very large relative to P fluxes in precipitation and streams. The soluble + labile P pools in mineral soil were comparable to the sum of P pools in the forest vegetation and forest floor (i.e. LFH) at HP3 (soluble + labile<sub>total</sub> =  $318 \text{ mmols} \cdot \text{m}^{-2}$ , Biota + LFH =  $258 \text{ mmols} \cdot \text{m}^{-2}$ ) and HP3A (soluble + labile<sub>total</sub> =  $342 \text{ mmols} \cdot \text{m}^{-2}$ , Biota + LFH =  $247 \text{ mmols} \cdot \text{m}^{-2}$ ) (Figure 3.10). In contrast, at PC1-08 the P pool in the thicker LFH layer ( $404 \text{ mmols} \cdot \text{m}^{-2}$ ) was approximately 2 times greater than the total soluble + labile soil P pool ( $222 \text{ mmols} \cdot \text{m}^{-2}$ ) (Figure 3.10); although the LFH depth at PC1-08 was highly variable at the observed soil pits (Table 3.1). The total NaOH extractable pool, which represents a less labile P fraction, was greater than the sum of the soluble + labile, biotic, and LFH P pools at all 3 catchments indicating substantial P storage in B-horizon soil (Figure 3.10). The mineral soil also contained more organic than inorganic P in all of the soluble + labile and less labile P pools in each catchment (e.g. at HP3 less labile  $P_i = 710 \text{ mmols} \cdot \text{m}^{-2}$ , less labile  $P_o = 1237 \text{ mmols} \cdot \text{m}^{-2}$ ); although the higher organic to inorganic P ratio was not as pronounced in the less labile inorganic and organic P pools in PC1-08 (Figure 3.10). There was an order of magnitude more P present as apatite at the two Harp catchments (HP3 =  $1335 \text{ mmols} \cdot \text{m}^{-2}$ , HP3A =  $1007 \text{ mmols} \cdot \text{m}^{-2}$ ) compared with the Plastic catchment ( $182 \text{ mmols} \cdot \text{m}^{-2}$ ) (Figure 3.10).

## PC1-08

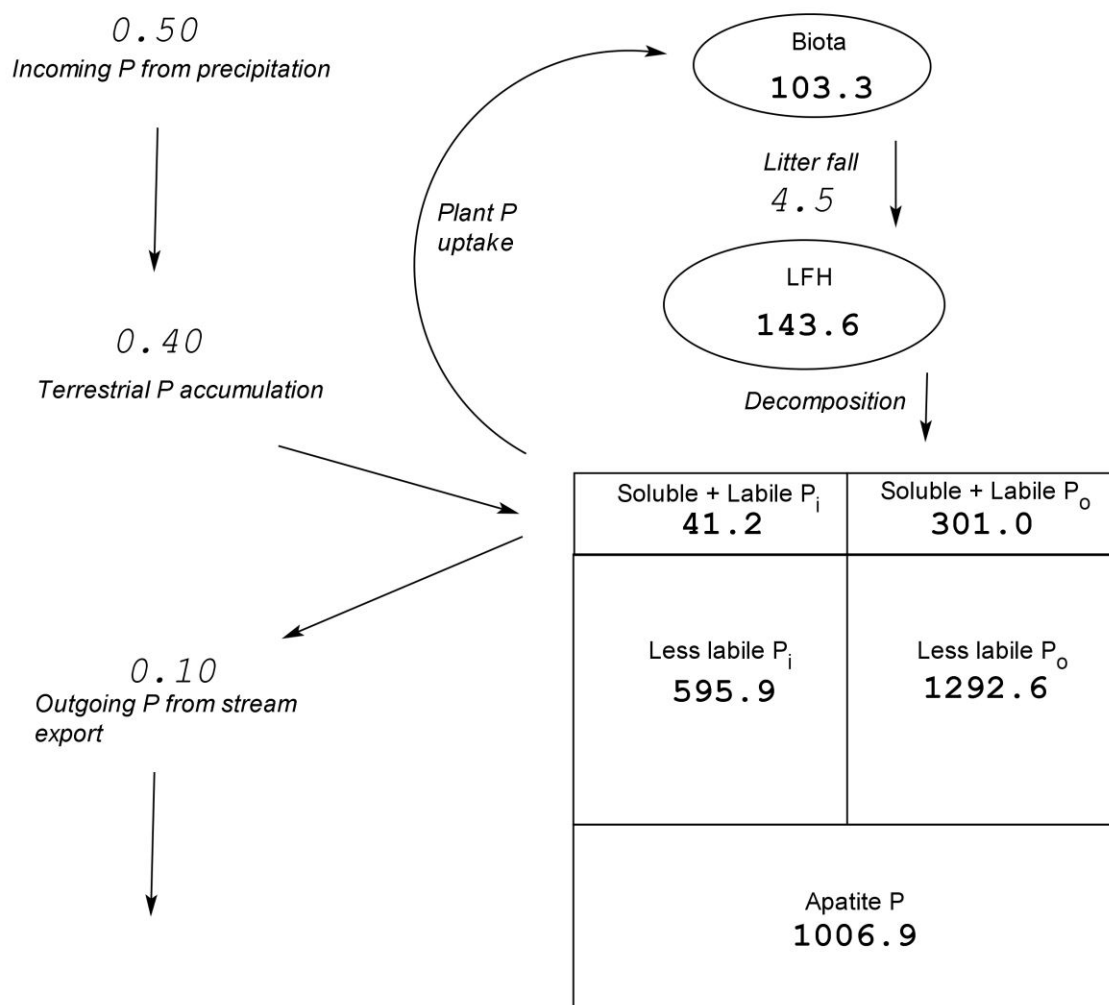


**Figure 3.10.** Phosphorus budgets for the three study catchments. All P pools are shown as  $\text{mmols} \cdot \text{m}^{-2}$ . Boxes represent P in the mineral horizon. Ovals represent P in vegetation and LFH layer pools. Annual fluxes are displayed in italics and shown as  $\text{mmols} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  from 1980 to 2008.



**Figure. 3.10. cont**

### HP3A



**Figure. 3.10. cont**

## 4.0 Discussion

### 4.1 Patterns in Stream Total Phosphorus Concentration at PC1-08, HP3 and HP3A

Annual volume-weighted stream  $TP_w$  concentrations at the three study catchments are low relative to other literature values (Van Nieuwenhuyse and Jones 1996, Smith et al. 2003) and have declined over the past 30 years. Van Nieuwenhuyse and Jones (1996) reported that  $TP_w$  concentrations in streams draining primarily forested catchments were between 0.16 and 1.55  $\mu\text{M}$  compared with 0.06 to 0.42  $\mu\text{M}$  in 2008 found in this study. The  $TP_w$  concentration in PC1-08 was lower than the lowest value found by Van Nieuwenhuyse and Jones (1996). Smith et al. (2003) established general background stream  $[TP_w]$  for various eco-regions in the United States, and found that natural stream  $[TP_w]$  ranged from 0.19 to 2.58  $\mu\text{M}$ , and that streams in eastern temperate forested catchments had a mean  $[TP_w]$  of 1.45  $\mu\text{M}$ . The 2008  $[TP_w]$  concentrations at the Harp streams (0.15 – 0.42  $\mu\text{M}$ ) are near the lowest values found by Smith et al. (2003) and the Plastic stream  $[TP_w]$  was below all of the streams considered by Smith et al. (2003). While stream concentrations at the study sites are at the lower end of reported ranges for forested catchments, low stream  $TP_w$  concentrations have been reported elsewhere. For example, Swank and Douglas (1977) reported that average  $[TP_w]$  in a stream draining a catchment in the Appalachian Mountains that was impacted by acid rain was only 0.06  $\mu\text{M}$ .

All three streams may be classified as meso-oligotrophic to oligotrophic (Carlson 1977). There is little geological P to supply these streams, as the [P] of bedrock in the study region has generally been found to be low (Jeffries and Snyder 1983). For example Jeffries and Snyder (1983) reported that amphibolite from the Harp Lake catchment had a [P] of  $\leq 110$  ppm, and although apatite is present in these soils, it occurs in low concentrations. This study found that apatite comprises less than 0.02% of Plastic and less than 0.08% of Harp lake catchment B-horizon soils. Phosphorus deposition is also low in this area: the annual average  $TP_w$  deposition load for the Dorset region was 0.50  $\text{mmol} \cdot \text{m}^{-2} \cdot \text{yr}^{-1}$  between 1980 and 2000 (Eimers et al. 2009), as these locations are remote from large P point sources (Dillon et al. 1991).  $TP_w$  deposition is much higher in

areas where dust and particulate P transport are greater (Bergametti et al. 1992, Winter et al. 2002). For example Lake Simcoe, in southern Ontario (about 100 km south of the study sites) receives an annual  $TP_w$  deposition load of  $1.81 \text{ mmol} \cdot \text{m}^{-2}$  which likely results from wind deposition of exposed soil from agricultural use and urban development (Winter et al. 2002) and the Mediterranean region in Europe receives annual TP deposition loads of  $1.30 \text{ mmol} \cdot \text{m}^{-2}$  largely due to dust transport from arid landscapes during the dry season (Bergametti et al. 1992).

Although stream  $[TP_w]$  are generally low in the study region, stream  $[TP_w]$  varies 3-fold among the three catchments (Dillon et al. 1991, Eimers et al. 2009). Previous work in this region has attributed differences in  $[TP_w]$  among streams to catchment characteristics and in particular wetland coverage (Dillon et al. 1991). For example, HP3 has 9% wetland coverage compared with only 3% at HP3A, which is about the same difference as the ratio in stream  $[TP_w]$  between the HP3 and HP3A catchments (Eimers et al. 2009). In addition to wetlands, riparian zones have been noted as important sources of  $TP_w$  export in this landscape (Carlyle and Hill 2001; O'Brien et al. 2013) and seasonal changes in wetland/riparian water table height have been shown to be associated with changes in  $[TP_w]$  in pore and surface waters (Devito and Dillon 1993). In a recent study at Harp Lake, O'Brien et al. (2013) showed that  $TP_w$  concentrations in streams are strongly influenced by organic soils in near-stream riparian areas and argued that seasonal variation in  $[TP_w]$  can be explained by processes operating in these organic-rich riparian soils. While processes occurring in organic soils can explain seasonal patterns, the temporal pattern of declining TP remains unexplained (O'Brien et al. 2013). O'Brien et al. (2013) suggested that past disturbance events (such as logging) may have contributed to the observed pattern in stream  $[TP_w]$  although other possible mechanisms such as soil acidification cannot be discounted.

## 4.2 Soil Chemistry at HP3A, HP3 and PC1-08

Despite large differences in stream  $[TP_w]$ , soil P concentrations in upland soils were not significantly different among catchments with the exception of apatite ( $P_{HCl}$ ), which was

significantly higher at HP3 relative to PC-108. Apatite has not been previously detected in the study soils as the concentrations of  $P_{HCl}$  suggest that apatite is  $\leq 0.08\%$  of the B-horizon, which is below the detection limit of  $\sim 1\%$  for the X-ray diffraction method Kirkwood and Nesbitt (1991) used to determine the mineralogy of these soils. There was no apatite detected in the  $A_h$  or  $A_e$  horizons at PC1 or HP3 nor the  $A_e$  horizon at HP3A. The range in A-horizon  $P_{HCl}$  concentrations found in the present study ( $0.0 - 1.0 \mu\text{mol} \cdot \text{g}^{-1}$ ) are more comparable to the average  $P_{HCl}$  concentrations of highly weathered soils ( $1.6 \mu\text{mol} \cdot \text{g}^{-1}$ ) than slightly weathered soils ( $3.9 \mu\text{mol} \cdot \text{g}^{-1}$ ) reported by Sharpley et al. (1985). The average (including 0 values)  $A_h$ -horizon  $P_{HCl}$  ( $0.45 \mu\text{mol} \cdot \text{g}^{-1}$ ) is also much lower than the average B-horizon  $P_{HCl}$  ( $3.47 \mu\text{mol} \cdot \text{g}^{-1}$ ) measured in the present study. The discrepancy in the  $[P_{HCl}]$  between the A and B horizons is in contrast to other studies that have shown very similar concentrations of  $P_{HCl}$  between A and B horizons (Roberts et al. 1985, Levy and Schlesinger 1999). For example, Levy and Schlesinger (1999) reported  $P_{HCl}$  concentrations of  $0.02$  and  $0.05 \mu\text{mol} \cdot \text{g}^{-1}$  in the A and B horizon, respectively of a highly weathered Alfisol (Luvisol) and Roberts et al. (1985) reported average  $P_{HCl}$  concentrations of  $5.28$  and  $6.93 \mu\text{mol} \cdot \text{g}^{-1}$  in the A and B horizons respectively of Chernozemic and Luvisolic soils. Chen et al. (2000) reported that  $P_{HCl}$  declined with soil depth in both forest and grassland ecosystems in New Zealand. The low  $A_h$ -horizon  $P_{HCl}$  concentrations measured in the present study may be due to apatite dissolution in upper mineral soils that has been enhanced because of acidic precipitation (as discussed in SanClements 2009).

Phosphorus concentrations at the three catchments varied as expected with soil horizon (Figure 1.1). The highest soil  $[TP_s]$  was found in the LFH and the lowest soil  $[TP_s]$  was found in the  $A_e$ . The distribution of organic and inorganic P sub-fractions also differed with depth. The majority of P in LFH and  $A_h$  horizons was organic, whereas organic and inorganic fractions were similar in lower soil horizons. A higher  $TP_s$  content in the LFH horizon is consistent with observations that P cycling is tightly controlled by vegetation in forest ecosystems (Attiwill and Adams 1993), causing P to accumulate in upper organic horizons (Letkeman et al. 1996). Breemen (1995) showed that most of the P taken up by plants in a temperate forest ecosystem had been recycled from plant material.

Higher concentrations of  $P_{H_2O}$  in the LFH horizon are also consistent with higher stream  $[TP_s]$  concentrations measured during storm event runoff that travels along shallow/surface flows paths (O'Brien 2010). It is unlikely that  $P_{HCl}$  measured in the LFH layer is apatite, as the mineral content of the LFH is low (mean loss-on-ignition of LFH layer was 66%) and the  $[P_{HCl}]$  in the mineral soil horizon in contact with the LFH layer (i.e. the  $A_h$ -horizon) was also very low. Instead,  $P_{HCl}$  measured in the LFH may be biologically synthesized calcium phosphates (Dorozhkin and Epple 2002).

#### **4.3 Relationships Between Soluble Phosphorus, Labile Phosphorus, Extractable Metals and Soil $pH_{CaCl_2}$**

Concentrations of  $Al_{ox}$  and  $Fe_{ox}$ , which are operationally defined as amorphous Al and Fe, were comparable among the three catchments, although concentrations are high in these soils relative to other literature (Shanley 1992, Freese et al. 1992, Devau et al. 2009, Kaňa et al. 2011) and are higher than levels expected for geologically young/recently deglaciated soils (Peltovuori et al. 2002). Studies have shown that  $Al_{ox}$  and  $Fe_{ox}$  are important sorbents for phosphate and other anions (Freese et al. 1992, Lookman et al. 1995, Kaňa and Kopáček 2006); therefore high  $Al_{ox}$  and  $Fe_{ox}$  suggest that these soils may have a higher sorption capacity for P than what might be expected for their age (Yuan and Lavkulich 1994). The low concentration of soluble P in the B-horizon is likely due to relatively high concentrations of Al and Fe (hydr)oxides in the B horizon (Väänänen et al. 2008). However Al and Fe (hydr)oxides at the study sites were still much lower than those found in highly weathered soils such as Alabama Ultisols which range from 3000-7000  $\mu\text{mol Al} \cdot \text{g}^{-1}$  and 1500 – 10 000  $\mu\text{mol Fe} \cdot \text{g}^{-1}$  (Shaw 2001). Rochelle et al. (1987) discussed the generally low anion retention capacity of podzols in the Northern U.S. and Canada, stating that although these soils may have a considerable amount of Al and Fe (hydr)oxides able to bind P, organic matter accumulation in the B-horizon may be occupying these sorption sites (Johnson and Todd 1983).

$Al_{exg}$  concentrations in B-horizon soils in this study are similar to  $Al_{exg}$  levels reported for podzols in other studies (Pellerin et al. 2002, Ohno and Amirbahman 2010). In contrast to



Al and Fe (hydr)oxides,  $Al_{\text{exg}}$  (i.e.  $Al^{3+}$ ) concentrations in these soils are likely more comparable to other soils with similar pH, since the chemical reaction governing Al dissolution/precipitation is reversible but the weathering of primary minerals is not. Aluminium dissolution/precipitation is highly dependant on pH (Norton et al. 2006). Aluminium and iron (hydr)oxides form after Al and Fe have been weathered from primary minerals and then have precipitated out of solution (Schwertmann 1985, Yves and Daniel 1985). Primary mineral weathering is a slow, one-way process (in the absence of high temperature and pressure) and the rate at which it occurs is affected primarily by moisture, temperature, and the abundance of carbonic acid and biologically produced acids (Sverdrup and Warfvinge 1988, Lundström et al. 2000, Ruttenburg 2003). Therefore it is expected that soils with similar pH and parent material would have similar  $Al_{\text{exg}}$  as the concentration of  $Al_{\text{exg}}$  is dependant on current environmental conditions. However since  $Al_{\text{ox}}$  and  $Fe_{\text{ox}}$  concentrations are dependant on past environmental conditions it is difficult to relate present soil properties to their abundance. It is also possible that historically high levels of acid deposition in this region have led to increased weathering of Al and Fe primary minerals during the time period between 1850 and the present (Aherne et al. 2003) and therefore increased the development of secondary minerals.

Previous work has suggested that soils in this region have acidified due to high levels of acid deposition (Watmough and Dillon 2004, Miller and Watmough 2009). All of the soils sampled in this study are podzols (Soil Classification Working Group 1998), with acidic pH ( $pH_{\text{CaCl}} < 5$ ), and low exchangeable base cation concentrations (e.g. B-horizon  $Ca_{\text{exg}} < 1.5 \text{ meq} \cdot 100 \text{ g}^{-1}$ ) and % base saturation (e.g. B-horizon  $\leq 30 \%$ ). Nevertheless, the range in pH across the three study catchments spanned the range in historical pH decline ( $pH_{\text{CaCl}} 4.0 - 4.4$ ), which allowed substitution of ‘space for time’ and evaluation of relationships between soil pH, soil P fractions concentration and other chemical properties

Soils acidification has 3 primary effects on soluble [P] in soils. Firstly, decreased soil pH affects soluble [P] in soil solution by increasing the positive charge density around

variable-charged surfaces on soil particles, allowing for greater anion adsorption, and increasing the amount of free phosphate fixed by soil particles (Muljadi et al. 1966a, Bowden et al. 1980,). Secondly, decreasing soil pH increases the concentration of soluble Al (Norton et al. 2006), which is able to bind with dissolved P and precipitate (Traina et al. 1986). Thirdly, the decrease in soil pH increases the rate of primary mineral weathering, including primary minerals containing Al and Fe (White and Brantley 1995), which over long time scales could increase the amount of Al and Fe (hydr)oxides in the soil. Al and Fe (hydr)oxides are strong anion sorbents and an increase in the concentration of Al and Fe (hydr)oxides would also decrease soluble [P] in soil. However, increased primary mineral weathering could also increase the rate at which apatite dissolves releasing additional P into solution.

Contrary to expectation, there was higher labile [P] in the more acidic B-horizon soils and a negative relationship between labile P pool and B-horizon soil  $\text{pH}_{\text{CaCl}_2}$ . These labile and soluble P relationships with  $\text{pH}_{\text{CaCl}_2}$  are inconsistent with P sorption theory, which predicts increases in P sorption (i.e. reduced solubility) under increasingly acidic conditions (Muljadi et al. 1966a, Bowden et al. 1980). However, there are several examples in the literature that also describe negative relationships between soluble [P] and natural soil pH (Casson et al. 2011, Kerr et al. 2011, McCray et al. 2012), as well as negative relationships between labile [P] and natural soil pH (Beauchamp et al. 1976, Roberts et al. 1985, McCray et al. 2012).

**Table 4.1.** Literature on the relationship between P sorption and soil solution pH.

Source	Sorption/pH relationship direction	pH range <sup>†</sup>	Initial solution [P] (μM)	pH manipulated with <sup>*</sup>	Background electrolyte	Cited mechanism
Hsu and Rennie 1962	-‘ve	3.8 – 7	646 – 3229	Acetic acid, NaOH	1M NaCl	At lower pH values OH groups are bound to Al with less intensity allowing for easier displacement by PO <sub>4</sub> .
Muljadi et al. 1966a	-‘ve	3 – 10 (M)	10 – 6458	H <sub>3</sub> PO <sub>4</sub> , various alkali hydroxides (S)	H <sub>2</sub> O	Changes in the charge of PO <sub>4</sub> and the sorbent material at different solution pH values.
<sup>‡</sup> Murrmann and Peech 1968	-‘ve	6 – 9 (M)	0	HCl; Ca(OH) <sub>2</sub> (S)	0.01 M CaCl <sub>2</sub>	Al solubility is lowest at ~ pH 6, increases in solution P were due to Al dissolution and the liberation of Al bound to P.

**Table 4.1. *cont***

Source	Sorption/pH relationship direction	pH range <sup>†</sup>	Initial solution [P] (μM)	pH manipulated with*	Background electrolyte	Cited mechanism
Hingston et al. 1971	-‘ve	4 - 10 (M)	260 – 650	HCl ; NaOH (S)	0.1 M NaCl 270 μM NaH <sub>2</sub> AsO <sub>4</sub>	Empirical observation.
<sup>‡</sup> Hingston et al. 1974	-‘ve	4.5 – 9	0	Not cited	1 M NaCl	Increased surface charge on sorbent material at lower pH.
Lopez–Hernandez and Brunham 1974	-‘ve	4 - 8 (N)	10 000	N/A	0.2 M KCl	Higher pH soils had less Al <sub>exg</sub> and therefore had less active aluminum to sorb P.
Bowden et al. 1980	-‘ve	3 - 11 (M)	0 – 650	HCl ; NaOH (S)	0.01 M KCl	Lower pH increases the electrostatic potential in the plane of adsorption, and changes the speciation of present ions.

**Table 4.1. cont**

Source	Sorption/pH relationship direction	pH range <sup>†</sup>	Initial solution [P] (μM)	pH manipulated with*	Background electrolyte	Cited mechanism
Hiemstra and Van Riemsdijk 1996	-‘ve	4 – 11 (M)	0 – 650	HNO <sub>3</sub> ; NaOH (S)	0.01 M NaNO <sub>3</sub>	The surface charge of goethite increases with lower pH.
Geelhoed et al. 1997	-‘ve	2.5 – 8.5 (M)	0.1 - 5000	Not cited	0.01 M KNO <sub>3</sub>	Goethite becomes more positively charged at pH values below the point of zero charge, allowing for greater anion sorption.
Geelhoed et al. 1998	-‘ve	2.5 – 9 (M)	1000	Not cited	0.01 M KNO <sub>3</sub>	Goethite becomes more positively charged at pH values below the point of zero charge, allowing for greater anion sorption.
Juang and Chung 2004	-‘ve	2 – 6.5 (M)	200 – 1000	HNO <sub>3</sub> ; NaOH (S)	0.1 NaNO <sub>3</sub>	Relationship agreed with literature.

**Table 4.1.** *cont*

Source	Sorption/pH relationship direction	pH range <sup>†</sup>	Initial solution [P] (μM)	pH manipulated with*	Background electrolyte	Cited mechanism
Kaňa and Kopáček 2006	-‘ve	2.5 -6 (M)	6460	H <sub>2</sub> SO <sub>4</sub> + HNO <sub>3</sub> ; NaOH (S)	0.002M CaCl	Empirical observation.
<sup>a</sup> Kaňa and Kopáček 2011	-‘ve	3.3 - 6.1 (N)	0 – 6460	N/A	0.002M CaCl	Al becomes more positive at low pH and has a higher capacity to sorb P.
Costa et al. 2012	-‘ve	5.5 – 6.5 (M)	670	HCl ; NaOH (S)	0.03 M NaCl 670 μM NaH <sub>2</sub> AsO <sub>4</sub>	Density of positive charge on sorption materials increases as solution pH decreases.
Barrow 1984	N/A	3 - 7 (M)	0.969 – 969	HCl ; CaCO <sub>3</sub> (I)	0.01 M CaCl	Other factors complicate the relationship between pH and P sorption such as anions that are already sorbed onto sorption sites.

**Table 4.1. cont**

Source	Sorption/pH relationship direction	pH range <sup>†</sup>	Initial solution [P] (μM)	pH manipulated with*	Background electrolyte	Cited mechanism
Sibanda and Young 1986	N/A	3 – 6	0 – 145	HCl; NaOH (S)	0.1 M NaCl, added humic and fulvic acid	Humic acid and fulvic acid compete for P for sorption sites, especially at low solution pH values.
<sup>a</sup> Dodor and Ova 2000	N/A	3.6 – 7.9 (N)	Not cited	N/A	0.01 M CaCl	N/A
Hsu and Rennie 1962	+‘ve	3.8 – 7	65 – 387	Acetic acid, NaOH	1M NaCl	Increased solubility of Al phosphate at lower pH.
*Murrmann and Peech 1968	+‘ve	4 – 6 (M)	0	HCl; Ca(OH) <sub>2</sub> (S)	0.01 M CaCl <sub>2</sub>	Al solubility is lowest at ~ pH 6, increases in solution P were due to Al dissolution and the liberation of Al bound to P.

**Table 4.1.** *cont*

Source	Sorption/pH relationship direction	pH range <sup>†</sup>	Initial solution [P] (μM)	pH manipulated with <sup>*</sup>	Background electrolyte	Cited mechanism
Hingston et al. 1971	+’ve	3 - 5 (M)	130	HCl ; NaOH (S)	0.1 M NaCl 270 μM NaH <sub>2</sub> AsO <sub>4</sub>	Empirical observation.
<sup>‡</sup> Amarasiri and Olsen 1973	+’ve	3.7 – 7.0	0	CaCO <sub>3</sub> (I)	0.01 M CaCl <sub>2</sub>	Adsorption of P by freshly precipitated Fe and Al hydroxides.
<sup>‡</sup> Traina et al. 1986	+’ve	4 - 7 (M)	0	HCl ; NaOH (S)	0.02 M NaCl	Soluble Al compounds combine with phosphate to reduce phosphate solubility at higher pH values.
Bolan et al. 1988	+’ve	6.5 – 8.5 (M)	3230	Ca(OH) <sub>2</sub> (I)	H <sub>2</sub> O	Precipitation of Ca phosphates, and/or increase in ionic strength below the PZC, and/or the specific effect of Ca on electrostatic potential, and/or adsorption of P on to freshly precipitated Fe and Al hydroxides.



**Table 4.1. cont**

Source	Sorption/pH relationship direction	pH range <sup>†</sup>	Initial solution [P] (μM)	pH manipulated with <sup>*</sup>	Background electrolyte	Cited mechanism
Haynes and Swift 1989	+’ve	3.6 – 7 (M)	5 – 45	Ca(OH) <sub>2</sub> (I)	0.01 M CaCl	More Al becomes hydrolysed at higher pH allowing for additional P sorption sites.
Geelhoed et al. 1997	+’ve	2.5 - 5 (M)	22	Not cited	0.01 M KNO <sub>3</sub> 1000 μM K <sub>2</sub> SO <sub>4</sub>	Competitive adsorption with sulphate.
Geelhoed et al. 1998	+’ve	4.5 - 7 (M)	21	Not cited	0.01 M KNO <sub>3</sub> 1000 μM citrate	Competitive adsorption with citrate.

<sup>†</sup> M = manipulate, N = natural

<sup>‡</sup> desorption study

<sup>\*</sup>I = incubated with soil, S = added to solution during sorption experiment

<sup>a</sup> study relating soil properties to P sorption maxima

Note: Haynes (1982) suggested that liming studies involving incubating soil with lime would have +’ve relationships between pH and P sorption due to soil being allowed to dry before sorption testing, creating new highly active Al and Fe oxide surfaces.

Most studies show that the quantities of Al and Fe oxides in soils have a greater effect on P sorption than soil pH (Freese et al. 1992, Brennan et al. 1994, Nair et al. 1999). Kaňa et al. (2011) found that pH only improved the fit of a multiple regression model explaining  $P_{\max}$  if  $Al_{ox}$  was included in the model. Kaňa and Kopáček (2006) did not find any relationship between P sorption maximum and soil  $pH_{CaCl_2}$ , but they did find higher  $Al_{ox}$  and  $Fe_{ox}$  in A-horizon soils with higher  $pH_{CaCl_2}$  within a  $pH_{CaCl_2}$  range of 2.4 – 3.7. Kaňa and Kopáček (2006) suggested that differences in amorphous metal concentrations were a more important control on P sorption than pH and therefore higher concentrations of  $Al_{ox}$  and  $Fe_{ox}$  at higher pH soil would mask any direct affect that pH had on P sorption in the soil. There were no positive relationships between P-sorbing metals and pH in the present study and therefore the quantity of exchange sites is not causing the unexpected relationship observed between pH and labile P fractions.

#### 4.4 Experimental Phosphorus Sorption Studies

P sorption was close to 100% for all P sorption experiments that were performed at solution  $[P] < 452.0 \mu M$  and no change in P sorption was observed when solution pH was manipulated within the range of observed soil pH change in the study region. Therefore these results do not support the hypothesis that soil acidification is responsible for observed declines in stream  $[TP_w]$ . The literature is somewhat contradictory on the relationship between pH and P sorption, and both positive and negative relationships have been reported (Table 4.1).

One possible reason for the discrepancy among studies is the concentration of the P solutions used in the various experiments. In the present study, a negative relationship between pH and P sorption was observed when a much higher than ambient soil solution  $[TP_w]$  was used. Different P sorption responses (Figure 3.7) at different  $[P]$  suggest that the dominant mechanism(s) controlling P sorption may be affected by solution  $[P]$ . Most natural forest ecosystems have mineral soil solution  $[P] < 100 \mu M$  (according to Geelhoed et al. 1997), which is much lower than is typically used in sorption studies (Table 4.1). Lysimeter data at the Plastic Lake catchment show that mineral B-horizon

soil pore water [ $TP_w$ ] is  $< 12 \mu\text{M}$  (Table 3.2) and highest labile P extracted from the studied B-horizon soils was  $< 46 \mu\text{M}$ . Therefore knowledge that has been acquired about how P behaves in high [P] agricultural soils may not apply to questions regarding P behaviour in low [P], natural forest soils.

Although more negative relationships between pH and P sorption (18) have been reported than positive relationships (9) (Table 4.1), almost all of the studies showing a positive relationship between pH and P sorption were conducted at low solution [P] (i.e.  $< 130 \mu\text{M}$ ). There are two exceptions to this generalization; Hsu and Rennie (1962), and Bolan et al. (1988). Hsu and Rennie (1962) conducted their sorption experiments in a sodium acetate buffer solution (i.e. mixture of sodium hydroxide and acetic acid). It is possible that acetate was competing with P for sorption sites, as the concentration of acetate would have increased at lower solution pH. Sorption experiments performed by Bolan et al. (1988) were conducted at high pH, and pH was manipulated through  $\text{Ca}(\text{OH})_2$  additions. At high pH, P sorption reactions are dominated by reactions with Ca (Cole et al. 1953), whereas at low pH P sorption reactions are dominated by Al and Fe (Devau et al. 2009). Therefore the experiments performed by Bolan et al. (1988) may not be representative of the P reactions that are occurring in the acidic soils of the present study. Some of the studies reporting positive relationships between pH and P sorption added competitive anions to the solution used in the sorption experiment (Table 4.1). Phosphorus is generally thought to out-compete other anions for sorption sites (Liu et al. 1999, Costa et al. 2012), but in acidic solutions (3.5 - 7) the sorption of other anions such as  $\text{SO}_4$  increases more per unit drop in pH than  $\text{PO}_4$  (Higston et al. 1972) (i.e. at a pH above 5,  $\text{PO}_4$  sorption is  $\gg \text{SO}_4$ , at a pH below 5,  $\text{PO}_4$  sorption is  $> \text{SO}_4$ ). Sorption is theoretically governed by equilibrium reactions (Hiemstra and VanRiemsdijk 1996) and high concentrations of a particular anion in solution should increase the total amount of that anion sorbed. Therefore when solution pH is low (i.e.  $< 5$ ) and concentrations of competitive anions are much higher than concentrations of  $\text{PO}_4$ , then  $\text{PO}_4$  could be out competed for soil sorption sites. It was concluded that increasingly acidic conditions often led to additional P sorption; however P was more vulnerable to anion competition

when solution [P] was low and concentrations of potentially competitive anions were high.

#### 4.5 Phosphorus Budgets

Soil P pools are expected to decline over time in geologically young soils such as those in the study area (Kirkwood and Nesbitt 1991, Walker and Syers 1976). However, catchment input (bulk deposition) - output (stream export) budgets indicate that P is accumulating in all three catchments, although average annual P fluxes from 1980 to 2008 were small relative to P pools in the soil. However, it is also possible that net accumulation in these catchments is overestimated if bulk deposition inputs are high relative to true net input to the catchments as a result of internal contamination by high P sources like pollen and dust (Doskey and Ugoagwu 1989).

At all three catchments, the total P pool in over-story vegetation and in the LFH layer was much larger than the P flux between the two pools (i.e. litterfall). At the current litterfall flux it would take ~ 30 – 60 years for litterfall to completely replace the existing LFH P pool. There is more organic P in the upper soil horizons but it is unclear whether organic P is *currently* accumulating in upper soil horizons or whether it had accumulated in upper soil horizons and organic P accumulation is now in balance with P mineralization. However, acidic litter is known to decompose more slowly than more neutral forest litter (Ivarson and Sowden 1959) and the forest floor has acidified in the study area (Watmough and Dillon 2004), and so it is possible that organic matter and the P associated with it could be accumulating in the LFH layer.

$P_{HCl}$  was the P fraction that varied most in the B-horizon amongst catchments and higher  $P_{HCl}$  in the HP3 subcatchment may help to partially explain the difference in stream  $[TP_w]$  between the two Harp catchments. If we estimate past apatite concentrations in the  $A_h$ -horizon (corrected for organic matter content) as equal to measured apatite concentrations in the B-horizon, then the apatite pool in the  $A_h$ -horizon would be 39.2, 180.8, and 155.5 mmols  $\cdot m^{-2}$ , at the PC1-08, HP3 and HP3A catchments respectively. This is a significant

source of P that has been exhausted; for example these hypothetical  $A_h$  apatite P pools could have supplied stream P export at the three catchments at their current rates for ~500 – 1000 years. There are no historic soil apatite concentration or weathering data available so it is unclear whether  $A_h$  apatite exhaustion was due to human activity and coincided with changes in stream  $[TP_w]$  export or whether it occurred naturally.

The amount of P that has accumulated in PC1-08, HP3 and HP3A is calculated to be 16, 57, and 79 mols per year for a total of 454, 1601, and 2201 mols of P accumulated between 1980 and 2008. Therefore if the sorption capacity in these three catchments was small relative to P that accumulated between 1980 and 2008, then P accumulation in the sorption pool could be discounted as being the dominant process responsible for the observed decline in catchment stream  $[TP]$  (Eimers et al. 2009). Phosphorus sorption experiments at natural soil pH showed that P sorption was almost 100% at  $[P]$  of 452.0  $\mu M$  (Table 3.3), which equates to 11.3  $\mu mols/g$ . Although maximum P sorption capacity is likely higher than 11.3  $\mu mols/g$ , if we use this value, as a conservative estimate then the total catchment sorption capacity is still much larger than the total amount of P that accumulated between 1980 and 2008. The catchment P sorption capacities for PC1-08, HP3 and HP3A are 59 465, 657 085, and 476 299 mols respectively, all of which are 2 orders of magnitude larger than the observed P accumulation in these three catchments between 1980 and 2008. Therefore small changes (i.e. <1 %) in the sorbed P pool could have observable effects on the stream chemistry of these catchments.

A P budget was performed at the Hubbard Brook experimental forest (Yanai 1992), which has also received considerable acid deposition (Hall et al. 1980) and where increased calcium export occurred as a result (Likens et al. 1998). The Hubbard Brook P budget, as well as two other P budgets performed in the Appalachian Mountains (Swank and Douglas 1975), and the Pacific coast of Mexico (Campo et al. 2001), all found that P was accumulating in their respective catchments. Yanai (1992) concluded that P was accumulating in both forest biomass and the forest floor at the Hubbard Brook catchment. Campo et al. (2001) similarly suggested that P may be accumulating in the LFH layer of the Mexican Pacific coast forest but suggested that occasional fires could release this

accumulated P. Greater understanding of P pools and fluxes in the study catchments may allow researchers to determine whether P is accumulating in the soil or forest biomass or both at PC1-08, HP3 and HP3A. Further research should be dedicated to determining unknown P pools and fluxes including occluded soil P, stream sediment P, apatite weathering rates, biological P uptake, and P mineralization.

## 5.0 Conclusion

This study tested the prediction that soil acidification increases P sorption and decreases the concentration of labile/soluble P in soil, thus contributing to the declines in stream TP that have been observed in central Ontario. Sequential P fractionations showed that concentrations of soil P fractions were comparable amongst the three catchments. Only apatite ( $P_{HCl}$ ) differed significantly across catchments, with the highest concentrations found at HP3, followed by HP3A and PC1-08. Upland soils from the 3 study catchments spanned the historical range in soil  $pH_{CaCl_2}$  (4.0 – 4.4). However, the hypothesis that labile/soluble P would decrease with pH was not supported, and both soluble and labile P showed negative relationships with  $pH_{CaCl_2}$  in some horizons. These negative relationships were not the result of greater amorphous Al and Fe concentrations at higher  $pH_{CaCl_2}$  as amorphous Fe also showed a negative relationship with soil  $pH_{CaCl_2}$  and amorphous Al showed no relationship with  $pH_{CaCl_2}$ . Soils were able to sorb almost all (> 90 %) of the P in solution at environmentally relevant [P] concentrations (4.5 – 45.2  $\mu M$ ) within a solution pH range of 3 – 6.5. The results from this study suggest that acidification-induced sorption in upland soils is not a contributing factor to decreases in stream  $[TP_w]$  at the study catchments. P budgets indicate that P is accumulating within all three catchments, although P pools were much larger than P fluxes. Future work should focus on where P is accumulating in these forested catchments as this may also address why  $[TP_w]$  has declined in surface waters.

### 5.1 Alternative Hypothesis: Mechanism of Competitive Sorption

Competitive sorption of  $PO_4$  with other anions may be able to explain some of the observed phenomena concerning P in the central Ontario region. It is hypothesized that during the period when this region received high levels of  $SO_4$  deposition, that increases in soil solution  $[SO_4]/[PO_4]$  ratio would have resulted in  $SO_4$  adsorption and  $PO_4$  desorption, which may have increased P export above background levels. During the time period when  $SO_4$  deposition declined, decreases in soil solution  $[SO_4]/[PO_4]$  ratio may have allowed  $PO_4$  to reclaim sorption sites previously occupied by  $SO_4$ , resulting in both P accumulation in soil and reduced stream P export.

The sorption of polyprotic anions tends to increase as pH decreases (Hingston et al. 1972); this is likely because additional protons reduce the charge demand of polyprotic anions. For example  $\text{SO}_4$  sorption has been shown to have a negative relationship with pH (Hingston et al. 1972, Shanley 1992, Liu et al. 1999, Wu et al. 2000, Kaiser and Kaupenjohann 1998) with  $\text{SO}_4$  sorption being highest between pH 3.8 and 4.2 (Courchesne and Hendershot 1989). Monoprotic anions, such as  $\text{Cl}^-$  and  $\text{NO}_3^-$  appear to be relatively poor competitors for sorption sites, and are easily out competed by  $\text{SO}_4$  and  $\text{PO}_4$  (Hingston et al. 1972, Kaiser and Zech 1996). Phosphate is one of the strongest binding anions in natural soil systems and can out compete other polyprotic anions for sorption sites such as arsenate, oxalate, and sulphate (Hingston 1971, Hingston 1972, Kaiser and Zech 1996, Liu et al. 1999) when present at similar concentrations. However,  $\text{PO}_4$  may be out-competed for sorption sites under the following conditions:

- 1) Low solution  $[\text{PO}_4]$ , which is usually the case in the soil solution of natural forest ecosystems (Geelhoed et al. 1998)
- 2) High solution  $[\text{SO}_4]$ , which can occur in regions that either have naturally high sulphur content in their parent material or have historically received elevated  $\text{SO}_4$  deposition, like the study region (Summer and Whelpdale 1976, Galloway et al. 1984, Aherne et al. 2003)
- 3) Aluminium is the dominant sorption surface; Gustafsson (2001) found that arsenate, phosphate and silicic acid formed stronger surface complexes on ferrihydrite than on Al molecules such as gibbsite or allophane, whereas the reverse was true for sulphate (Gustafsson 2001). Therefore where Al is the dominant sorption surface  $\text{PO}_4$  would be more vulnerable to  $\text{SO}_4$  competition.
- 4) Acidic soils; the increase in total  $\text{SO}_4$  sorption with declining pH is greater than the increase in  $\text{PO}_4$  sorption, which suggests that sulphate will be a more effective competing anion in acidic soils (i.e. pH ~ 4).

Sulphate is likely to be an important competitive anion in areas that have received elevated  $\text{SO}_4$  deposition, but organic acids have also been shown to compete for sorption sites and compete most effectively at pH ~ 4 (Sibanda and Young 1986, Fox et al. 1990).



Johnson and Todd (1983) found that spodosols with high extractable Al and Fe concentrations still had low anion sorption capacities, which they attributed to high organic matter content in their studied soils. Therefore soil acidification without the input of sulphate could also contribute to reduced  $\text{PO}_4$  sorption in the presence of high concentrations of organic acids.

Phosphorus is present in soil in a variety of organic chemical compounds (Turner et al. 2005). It is uncertain whether organic P compounds (or other P molecules measured during total P analyses) would be subject to the same mechanism as those that have been extensively studied for  $\text{PO}_4$ . However, P is constantly cycled and mineralized (Attiwill and Adams 1993) and some P is likely always present in  $\text{PO}_4$  form, therefore the competitive sorption mechanisms could still be relevant even if they only applied to  $\text{PO}_4$ .

## **5.2 Stages of Competitive Sorption at the Studied Sites**

### *Stage 1. Pre-disturbance*

Before  $\text{SO}_4$  deposition impacted the study region it is assumed that P geochemistry was in a dynamic equilibrium. Phosphorus inputs from deposition and primary mineral weathering would contribute to the biotic P pool and P export, but the geochemically sorbed P pool would essentially be constant. It is not expected that P weathering, deposition, biotic uptake or catchment export differed substantially between 1800 and 1850. The flat hypothesised TP export line represents the consistent TP export during stage 1 in Figure 5.1.

### *Stage 2. Sulphate loading*

Increasing sulphate input as deposition, likely increased sorbed  $\text{SO}_4$  in the soil. It is assumed that  $\text{PO}_4$  input from primary minerals remained constant during initial stages of acid deposition, as soil-buffering capacity would limit the initial soil pH response. The soil solution  $[\text{SO}_4]/[\text{PO}_4]$  would increase during this stage, as would the ability of  $\text{SO}_4$  to out compete  $\text{PO}_4$  for sorption sites, which would release soluble P in soil solution. This

soluble P could be consumed by biota and stored as organic matter, or exported in runoff from the catchment. If incoming  $\text{SO}_4$  remained constant then a new equilibrium would be reached and it would be expected that both  $\text{SO}_4$  sorption and  $\text{PO}_4$  desorption would cease (Rochelle et al. 1986). But,  $\text{SO}_4$  deposition in this region generally rose between 1850 and 1975 (Aherne 2003), allowing for continual increase in  $\text{SO}_4$  sorption and  $\text{PO}_4$  desorption. The hypothesised TP export line increases and decreases with  $\text{SO}_4$  deposition during stage 2 in Figure 5.1 as a result of the competitive interaction between the  $\text{SO}_4$  and  $\text{PO}_4$  anions.

### *Stage 3. Recovery from sulphate loading*

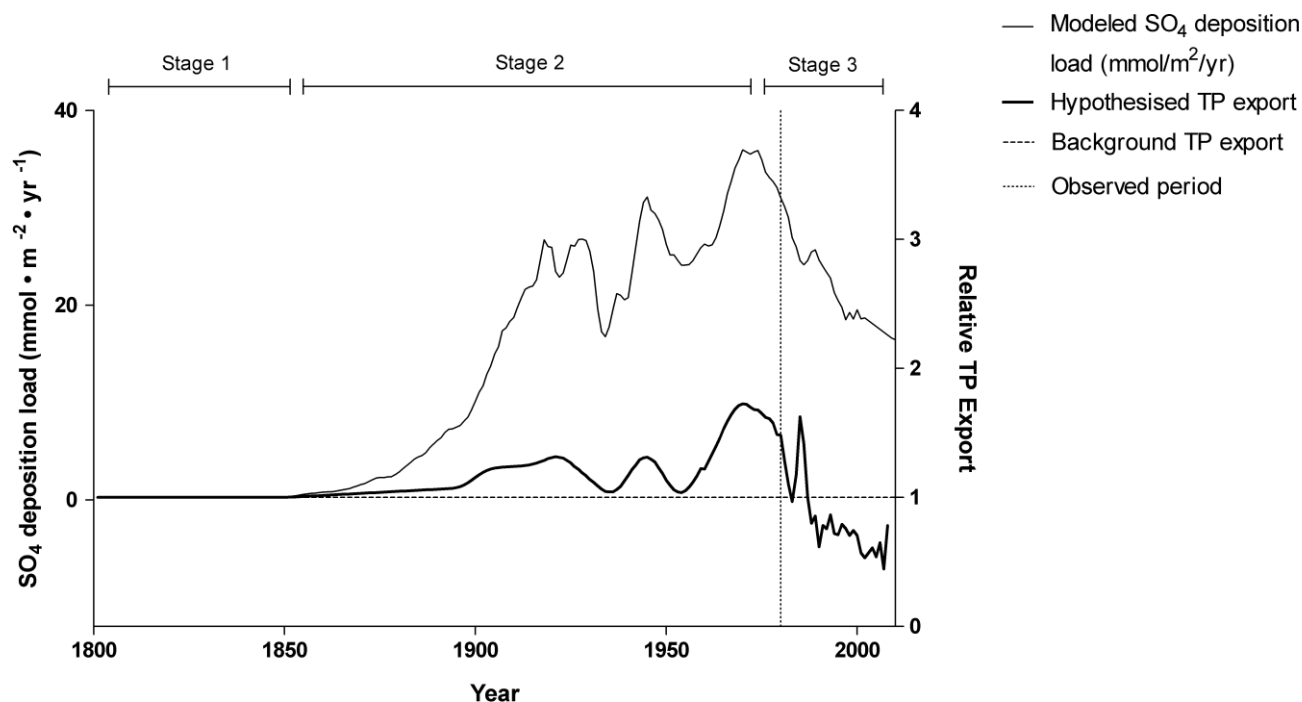
Upon the reduction of  $\text{SO}_4$  loading it would be expected that the reverse of the above process would begin to occur. The soil solution  $[\text{SO}_4]/[\text{PO}_4]$  ratio would decline and P weathered from primary minerals and released through mineralization would begin to replenish the adsorbed P pool. Although soils in the study region continue to acidify (Watmough and Dillon 2004, Miller and Watmough 2009), the relative change in the concentrations of  $\text{SO}_4$  and  $\text{PO}_4$  could be the dominant factor controlling  $\text{PO}_4$  sorption. Hypothesised TP export decreases in stage 3 of Figure 5.1 as  $\text{PO}_4$  is reclaiming sorption sites, which  $\text{SO}_4$  claimed during stage 2.

## **5.3 Explaining Observed Phosphorus Related Phenomena**

### *Paleolimnological records indicate current surface water TP concentrations are lower than background TP concentrations*

Hall and Smol (1996) and Quinlan et al. (2008) have conducted paleolimnological studies on lakes in the study region and have found that generally, current central Ontario lake  $\text{TP}_w$  concentrations are lower than inferred pre-industrial lake  $[\text{TP}_w]$ . Their results suggest that the surface water  $[\text{TP}_w]$  decline observed over 1980-2000 (Yan et al. 2008, Eimers et al. 2009) was not surface water recovery, but instead a decline below background  $[\text{TP}_w]$ . This pattern would be expected if the alternative hypothesis were correct. P export would have been elevated during the period of sulphate loading (i.e. stage 2).  $\text{TP}_w$  export would be expected to decline below background  $\text{TP}_w$  export during stage 3 due to P reclaiming

sorption sites that had been occupied by  $\text{SO}_4$  during the period of increased sulphate loading. Once P has re-occupied soil sorption sites it is expected that surface water  $[\text{TP}_w]$  will return to pre-industrial levels



**Figure 5.1.** TP export pattern that would be expected if the alternate hypothesis explained above were true. Observed TP export data from HP3. Background TP export is assumed to be approximately the median value between the highest and lowest hypothetical TP export. Modeled  $\text{SO}_4$  deposition data from Aherne et al. (2003).

Note: Hypothesised TP export values are in no way intended to be accurate, they are simply intended to illustrate the different stages expected to occur if the alternative hypothesis were correct i.e. TP export would be above background, but also related to  $\text{SO}_4$  deposition during stage 2 and below background during stage 3.

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## Appendix

### Appendix I. Geographical location of soil pits. Study site located within UTM zone 17T.

Soil pit ID	Easting	Northing
PC1-08-1	670614	5005048
PC1-08-2	670444	5005185
PC1-08-3	670444	5005304
PC1-08-4	670477	5005386
PC1-08-5	670610	5005438
PC1-08-6	670566	5005115
HP3-1	645546	5026005
HP3-2	645537	5025935
HP3-3	645514	5025893
HP3-4	645497	5025862
HP3-5	645429	5025865
HP3-6	645469	5025838
HP3A-1	645321	5026207
HP3A-2	645217	5026145
HP3A-3	645207	5026110
HP3A-4	645208	5026086
HP3A-5	645299	5026155
HP3A-6	645165	5026118

**Appendix II.** Physical and chemical variables of the LFH layer from each soil pit. Standard error in italics.

Soil pit ID	pH <sub>CaCl2</sub>	<i>SE</i>	P <sub>H2O<i>i</i></sub> (μmol/g)	<i>SE</i>	P <sub>H2O<i>o</i></sub> (μmol/g)	<i>SE</i>	P <sub>NaHCO3<i>i</i></sub> (μmol/g)	<i>SE</i>	P <sub>NaHCO3<i>o</i></sub> (μmol/g)	<i>SE</i>	P <sub>NaOH<i>i</i></sub> (μmol/g)	<i>SE</i>	P <sub>NaOH<i>o</i></sub> (μmol/g)	<i>SE</i>
PC1-08-1	3.3	<i>0.0</i>	2.3	<i>0.1</i>	1.0	<i>0.1</i>	1.7	<i>0.1</i>	3.7	<i>0.1</i>	1.7	<i>0.1</i>	9.8	<i>0.1</i>
PC1-08-2	3.3	<i>0.0</i>	0.6	<i>0.0</i>	0.5	<i>0.0</i>	1.9	<i>0.0</i>	3.6	<i>0.1</i>	1.0	<i>0.0</i>	8.5	<i>0.2</i>
PC1-08-3	3.0	<i>0.0</i>	5.5	<i>0.2</i>	0.7	<i>0.3</i>	1.5	<i>0.2</i>	2.8	<i>0.3</i>	0.6	<i>0.0</i>	6.9	<i>0.3</i>
PC1-08-4	3.2	<i>0.0</i>	2.5	<i>0.0</i>	0.3	<i>0.0</i>	0.7	<i>0.0</i>	2.1	<i>0.1</i>	0.6	<i>0.0</i>	6.2	<i>0.1</i>
PC1-08-5	3.7	<i>0.1</i>	0.0	<i>0.0</i>	0.5	<i>0.0</i>	0.7	<i>0.0</i>	2.2	<i>0.1</i>	2.5	<i>0.1</i>	4.9	<i>0.1</i>
PC1-08-6	3.0	<i>0.0</i>	6.1	<i>0.1</i>	1.2	<i>0.2</i>	2.2	<i>0.1</i>	3.7	<i>0.1</i>	0.5	<i>0.0</i>	7.3	<i>0.3</i>
HP3-1	4.3	<i>0.0</i>	0.0	<i>0.0</i>	0.1	<i>0.0</i>	2.4	<i>0.1</i>	2.6	<i>0.1</i>	3.1	<i>0.2</i>	14.2	<i>0.3</i>
HP3-2	3.5	<i>0.0</i>	8.1	<i>0.4</i>	1.2	<i>0.3</i>	2.1	<i>0.0</i>	2.8	<i>0.1</i>	0.7	<i>0.1</i>	7.8	<i>0.1</i>
HP3-3	4.5	<i>0.0</i>	1.1	<i>0.1</i>	0.5	<i>0.0</i>	2.6	<i>0.1</i>	2.4	<i>0.1</i>	2.4	<i>0.1</i>	7.6	<i>0.2</i>
HP3-4	3.8	<i>0.0</i>	3.5	<i>0.3</i>	0.7	<i>0.0</i>	2.2	<i>0.1</i>	2.8	<i>0.1</i>	1.4	<i>0.0</i>	7.5	<i>0.3</i>
HP3-5	3.1	<i>0.0</i>	4.7	<i>0.1</i>	0.8	<i>0.0</i>	1.5	<i>0.0</i>	3.1	<i>0.1</i>	0.7	<i>0.0</i>	6.9	<i>0.1</i>
HP3-6	3.5	<i>0.0</i>	3.7	<i>0.4</i>	0.9	<i>0.1</i>	2.5	<i>0.0</i>	4.1	<i>0.2</i>	1.0	<i>0.0</i>	7.8	<i>0.0</i>
HP3A-1	4.6	<i>0.0</i>	0.2	<i>0.0</i>	0.7	<i>0.1</i>	1.9	<i>0.1</i>	1.0	<i>0.1</i>	1.1	<i>0.0</i>	5.3	<i>0.2</i>
HP3A-2	3.6	<i>0.0</i>	5.9	<i>0.2</i>	0.6	<i>0.1</i>	2.1	<i>0.1</i>	2.4	<i>0.1</i>	0.7	<i>0.0</i>	7.6	<i>0.1</i>
HP3A-3	3.8	<i>0.0</i>	5.7	<i>0.1</i>	0.8	<i>0.1</i>	2.3	<i>0.0</i>	2.6	<i>0.2</i>	0.9	<i>0.0</i>	7.6	<i>0.0</i>
HP3A-4	4.3	<i>0.0</i>	0.3	<i>0.0</i>	0.5	<i>0.0</i>	1.0	<i>0.1</i>	1.8	<i>0.0</i>	2.0	<i>0.1</i>	4.5	<i>0.4</i>
HP3A-5	3.5	<i>0.0</i>	5.3	<i>0.1</i>	1.0	<i>0.1</i>	1.8	<i>0.0</i>	3.9	<i>0.2</i>	1.3	<i>0.1</i>	8.9	<i>0.1</i>
HP3A-6	3.4	<i>0.0</i>	7.8	<i>0.1</i>	0.8	<i>0.1</i>	1.9	<i>0.4</i>	4.5	<i>0.0</i>	0.7	<i>0.0</i>	9.2	<i>0.0</i>

**Appendix II. cont**

Soil pit ID	P <sub>HCl</sub> (μmol/g)	SE	P <sub>H2SO4</sub> (μmol/g)	SE	% LOI	SE	% C	SE	% N	SE	Al <sub>ox</sub> (μmol/g)	SE	Fe <sub>ox</sub> (μmol/g)	SE
PC1-08-1	0.7	0.2	32.3	0.6	52.1	1.8	31.6	0.1	1.4	0.0	69	1	71	1
PC1-08-2	0.0	0.0	54.8	0.5	88.0	0.1	48.9	0.2	1.2	0.0	155	1	10	0
PC1-08-3	0.0	0.0	67.4	0.5	84.7	0.6	48.5	0.0	1.4	0.0	26	1	11	0
PC1-08-4	0.0	0.0	32.5	0.6	59.8	0.9	11.9	1.0	0.6	0.0	62	1	33	1
PC1-08-5	0.6	0.1	18.8	0.6	37.0	2.4	23.2	1.3	0.8	0.0	268	5	201	4
PC1-08-6	0.0	0.0	75.8	1.3	86.6	0.1	12.0	0.8	0.6	0.0	22	1	11	1
HP3-1	0.6	0.2	46.1	0.8	74.1	0.4	42.0	0.0	2.0	0.0	323	23	68	1
HP3-2	0.0	0.0	53.8	0.7	83.0	0.4	46.4	0.0	2.1	0.0	13	1	50	0
HP3-3	0.9	0.0	27.0	0.5	49.8	2.5	26.1	0.1	1.5	0.0	68	2	108	2
HP3-4	0.6	0.0	30.6	0.7	63.0	1.7	36.0	4.0	1.8	0.2	48	3	88	3
HP3-5	0.0	0.0	36.7	1.3	80.9	0.1	28.9	0.9	1.2	0.0	22	1	52	0
HP3-6	0.0	0.0	32.5	1.3	67.1	0.3	36.3	4.3	1.9	0.2	28	2	75	2
HP3A-1	1.5	0.3	17.0	0.2	46.1	0.9	26.3	0.1	0.7	0.0	125	2	127	4
HP3A-2	0.0	0.0	44.7	0.3	76.2	0.4	42.6	0.2	2.1	0.0	17	1	21	0
HP3A-3	0.8	0.1	44.7	0.7	68.1	0.1	38.4	0.2	1.9	0.0	15	0	27	0
HP3A-4	8.9	0.4	28.4	0.2	33.0	1.5	20.0	0.1	0.9	0.0	180	3	238	2
HP3A-5	0.7	0.1	43.3	0.4	67.5	0.5	36.8	0.1	2.1	0.0	26	0	51	1
HP3A-6	0.8	0.1	71.1	0.5	83.2	0.2	49.2	1.7	2.1	0.1	18	0	14	0

**Appendix II. cont**

Soil pit ID	Mn <sub>ox</sub> (μmol/g)	SE	P <sub>ox</sub> (μmol/g)	SE	K <sub>exg</sub> (μmol/g)	SE	Ca <sub>exg</sub> (μmol/g)	SE	Mg <sub>exg</sub> (μmol/g)	SE	Al <sub>exg</sub> (μmol/g)	SE	CEC (meq/100g)	SE
PC1-08-1	9	0	3.5	0.2	13.6	0.7	68	2	10.2	0.3	7	1	25	4
PC1-08-2	12	0	2.6	0.2	18.5	0.7	70	1	13.5	0.3	22	0	57	2
PC1-08-3	17	0	3.2	0.1	23.1	0.5	126	5	24.9	0.6	1	0	70	7
PC1-08-4	3	0	1.9	0.1	13.1	0.0	58	3	9.9	0.3	11	0	30	1
PC1-08-5	7	0	6.4	0.2	12.2	1.0	64	4	9.1	0.7	8	0	20	2
PC1-08-6	35	0	3.2	0.3	26.9	0.3	165	19	18.1	0.5	0	0	55	4
HP3-1	16	1	2.6	0.2	26.3	0.1	174	3	33.5	0.6	4	2	64	5
HP3-2	10	0	1.8	0.1	27.9	0.7	171	6	34.6	0.9	0	0	65	9
HP3-3	13	0	2.3	0.3	23.8	0.6	155	5	32.3	0.8	0	0	39	1
HP3-4	13	1	1.9	0.3	22.1	0.4	154	3	26.0	0.2	0	0	26	4
HP3-5	5	0	1.6	0.1	19.8	0.4	126	2	23.0	0.3	1	1	49	2
HP3-6	7	0	1.2	0.0	18.7	0.6	145	9	18.3	0.5	1	1	80	2
HP3A-1	8	0	4.0	0.1	16.2	1.1	97	4	42.9	4.2	2	0	42	4
HP3A-2	10	0	2.4	0.1	29.8	0.8	195	8	30.2	0.4	3	2	84	2
HP3A-3	20	0	2.9	0.0	17.1	0.6	189	6	17.0	0.3	1	0	61	2
HP3A-4	8	2	8.1	0.1	12.0	0.5	95	4	15.9	0.4	3	0	28	4
HP3A-5	11	1	3.0	0.0	15.4	0.5	145	3	17.4	0.5	2	0	52	1
HP3A-6	6	1	3.6	0.1	28.0	0.3	175	3	34.0	0.3	2	0	57	2



**Appendix III.** Physical and chemical variables of the A<sub>h</sub> layer from each soil pit. Standard error in italics.

Soil pit ID	pH <sub>CaCl2</sub>	<i>SE</i>	P <sub>H2O<i>i</i></sub> (μmol/g)	<i>SE</i>	P <sub>H2O<i>o</i></sub> (μmol/g)	<i>SE</i>	P <sub>NaHCO3<i>i</i></sub> (μmol/g)	<i>SE</i>	P <sub>NaHCO3<i>o</i></sub> (μmol/g)	<i>SE</i>	P <sub>NaOH<i>i</i></sub> (μmol/g)	<i>SE</i>	P <sub>NaOH<i>o</i></sub> (μmol/g)	<i>SE</i>
PC1-08-1	3.1	<i>0.1</i>	0.0	<i>0.0</i>	0.4	<i>0.0</i>	0.5	<i>0.0</i>	1.9	<i>0.0</i>	1.6	<i>0.1</i>	6.3	<i>0.3</i>
PC1-08-6	2.7	<i>0.0</i>	0.7	<i>0.0</i>	0.5	<i>0.1</i>	0.7	<i>0.0</i>	2.4	<i>0.1</i>	1.3	<i>0.0</i>	4.7	<i>0.1</i>
HP3-2	3.6	<i>0.0</i>	0.9	<i>0.0</i>	0.8	<i>0.0</i>	0.3	<i>0.0</i>	2.2	<i>0.1</i>	0.6	<i>0.0</i>	6.1	<i>0.2</i>
HP3-4	3.2	<i>0.0</i>	0.5	<i>0.0</i>	0.4	<i>0.0</i>	0.5	<i>0.0</i>	1.6	<i>0.1</i>	1.1	<i>0.0</i>	4.7	<i>0.2</i>
HP3A-2	3.4	<i>0.0</i>	0.4	<i>0.0</i>	0.4	<i>0.0</i>	0.3	<i>0.0</i>	1.1	<i>0.1</i>	1.2	<i>0.0</i>	4.0	<i>0.1</i>
HP3A-3	3.2	<i>0.0</i>	1.0	<i>0.1</i>	0.6	<i>0.0</i>	0.2	<i>0.0</i>	1.1	<i>0.1</i>	0.3	<i>0.0</i>	1.5	<i>0.4</i>
HP3A-4	3.6	<i>0.0</i>	0.0	<i>0.0</i>	0.4	<i>0.0</i>	0.3	<i>0.1</i>	1.8	<i>0.1</i>	1.8	<i>0.0</i>	5.6	<i>0.1</i>

**Appendix III. cont**

Soil pit ID	P <sub>HCl</sub> (μmol/g)	SE	P <sub>H2SO4</sub> (μmol/g)	SE	% LOI	SE	% C	SE	% N	SE	Al <sub>ox</sub> (μmol/g)	SE	Fe <sub>ox</sub> (μmol/g)	SE
PC1-08-1	0.0	0.0	15.0	0.5	14.4	0.9	7.2	0.0	0.5	0.0	120	2	173	3
PC1-08-6	0.0	0.0	13.9	0.2	22.0	0.8	17.3	1.5	0.6	0.1	84	2	153	6
HP3-2	0.0	0.0	9.1	0.5	18.4	1.7	8.3	0.1	0.5	0.0	29	2	105	2
HP3-4	0.0	0.0	8.0	0.3	13.8	0.7	7.0	0.3	0.3	0.0	35	6	120	17
HP3A-2	0.8	0.1	10.9	0.0	13.2	0.2	6.9	0.1	0.4	0.0	65	4	136	5
HP3A-3	0.0	0.0	5.6	0.0	11.4	0.6	6.2	0.1	0.4	0.0	35	0	157	4
HP3A-4	2.3	0.3	14.6	0.3	15.3	0.2	7.1	0.0	0.5	0.0	130	1	305	4

**Appendix III. cont**

Soil pit ID	Mn <sub>ox</sub> (μmol/g)	SE	P <sub>ox</sub> (μmol/g)	SE	% Clay	SE	% Silt	SE	% Sand	SE	K <sub>exg</sub> (μmol/g)	SE	Ca <sub>exg</sub> (μmol/g)	SE
PC1-08-1	8	0	2.6	0.2	2	0	71	2	29	2	3.1	0.2	10	0
PC1-08-6	0	0	3.9	0.1	2	0	52	3	48	3	3.5	0.2	7	1
HP3-2	1	0	0.9	0.2	1	0	30	1	70	1	3.2	0.1	37	1
HP3-4	1	0	0.9	0.3	1	0	39	2	61	2	2.5	0.1	17	0
HP3A-2	0	0	3.0	0.2	2	0	42	1	58	1	3.1	0.1	24	0
HP3A-3	1	0	1.4	0.1	1	0	31	1	69	1	2.1	0.2	19	1
HP3A-4	0	0	5.2	0.1	2	0	43	1	57	1	2.8	0.2	14	0

**Appendix III. cont**

Soil pit ID	Mg <sub>exg</sub> ( $\mu$ mol/g)	SE	Al <sub>exg</sub> ( $\mu$ mol/g)	SE	CEC (meq/100g)	SE
PC1-08-1	2.3	0.1	10	1	12	1
PC1-08-6	2.5	0.0	17	0	12	1
HP3-2	6.9	0.4	0	0	15	1
HP3-4	2.8	0.1	5	0	9	0
HP3A-2	5.1	0.1	5	0	12	1
HP3A-3	3.2	0.1	2	0	7	1
HP3A-4	3.0	0.1	8	0	11	0

**Appendix IV.** Physical and chemical variables of the A<sub>e</sub> layer from each soil pit. Standard error in italics.

Soil pit ID	pH <sub>CaCl2</sub>	<i>SE</i>	P <sub>H2O<i>i</i></sub> (μmol/g)	<i>SE</i>	P <sub>H2O<i>o</i></sub> (μmol/g)	<i>SE</i>	P <sub>NaHCO3<i>i</i></sub> (μmol/g)	<i>SE</i>	P <sub>NaHCO3<i>o</i></sub> (μmol/g)	<i>SE</i>	P <sub>NaOH<i>i</i></sub> (μmol/g)	<i>SE</i>	P <sub>NaOH<i>o</i></sub> (μmol/g)	<i>SE</i>
PC1-08-3	3.1	<i>0.0</i>	0.2	<i>0.0</i>	0.1	<i>0.0</i>	0.1	<i>0.0</i>	0.5	<i>0.1</i>	0.2	<i>0.0</i>	1.3	<i>0.1</i>
PC1-08-4	3.2	<i>0.0</i>	0.1	<i>0.0</i>	0.0	<i>0.0</i>	0.1	<i>0.0</i>	0.2	<i>0.0</i>	0.1	<i>0.0</i>	0.6	<i>0.0</i>
HP3-5	3.0	<i>0.0</i>	0.2	<i>0.0</i>	0.1	<i>0.0</i>	0.0	<i>0.0</i>	0.3	<i>0.1</i>	0.1	<i>0.0</i>	0.5	<i>0.1</i>
HP3-6	2.9	<i>0.0</i>	0.1	<i>0.0</i>	0.1	<i>0.0</i>	0.1	<i>0.0</i>	0.5	<i>0.0</i>	0.6	<i>0.0</i>	2.2	<i>0.1</i>
HP3A-3	3.4	<i>0.0</i>	0.2	<i>0.0</i>	0.2	<i>0.0</i>	0.1	<i>0.0</i>	0.4	<i>0.1</i>	0.4	<i>0.0</i>	3.7	<i>0.5</i>
HP3A-5	3.4	<i>0.0</i>	0.3	<i>0.0</i>	0.3	<i>0.0</i>	0.1	<i>0.0</i>	0.8	<i>0.0</i>	0.4	<i>0.0</i>	2.8	<i>0.1</i>
HP3A-6	3.0	<i>0.1</i>	0.2	<i>0.0</i>	0.2	<i>0.0</i>	0.2	<i>0.1</i>	0.8	<i>0.2</i>	0.4	<i>0.0</i>	2.2	<i>0.1</i>

**Appendix IV. cont**

Soil pit ID	P <sub>HCl</sub> (μmol/g)	SE	P <sub>H2SO4</sub> (μmol/g)	SE	% LOI	SE	% C	SE	% N	SE	Al <sub>ox</sub> (μmol/g)	SE	Fe <sub>ox</sub> (μmol/g)	SE
PC1-08-3	0.0	0.0	3.3	0.3	5.5	0.1	2.9	0.0	0.1	0.0	47	0	121	12
PC1-08-4	0.0	0.0	1.5	0.2	2.9	0.2	10.7	0.2	0.5	0.0	55	2	120	6
HP3-5	0.0	0.0	0.7	0.2	3.3	0.1	2.0	0.1	0.1	0.0	30	1	105	2
HP3-6	0.0	0.0	4.7	0.3	5.6	0.1	3.0	0.0	0.2	0.0	75	0	112	3
HP3A-3	0.0	0.0	2.4	0.3	3.8	0.1	1.8	0.0	0.1	0.0	43	1	195	2
HP3A-5	0.0	0.0	3.7	0.5	4.9	0.1	2.4	0.0	0.2	0.0	38	0	128	5
HP3A-6	0.0	0.0	2.1	0.5	6.2	0.2	3.3	0.0	0.2	0.0	50	1	155	2

**Appendix IV. cont**

Soil pit ID	Mn <sub>ox</sub> (μmol/g)	SE	P <sub>ox</sub> (μmol/g)	SE	% Clay	SE	% Silt	SE	% Sand	SE	K <sub>exg</sub> (μmol/g)	SE	Ca <sub>exg</sub> (μmol/g)	SE
PC1-08-3	0	0	1.0	0.0	3	0	79	3	21	3	1.6	0.1	3	0
PC1-08-4	0	0	1.4	0.1	2	0	41	2	59	2	0.9	0.0	0	0
HP3-5	1	0	0.2	0.0	2	0	29	1	71	1	0.6	0.0	2	0
HP3-6	0	0	1.3	0.0	2	0	42	0	58	0	0.8	0.0	5	0
HP3A-3	0	0	1.7	0.0	1	0	23	2	77	2	0.8	0.0	5	0
HP3A-5	2	0	1.6	0.0	2	0	36	1	64	1	1.0	0.0	8	1
HP3A-6	0	0	1.4	0.0	3	0	55	2	45	2	1.1	0.0	5	0

**Appendix IV. cont**

Soil pit ID	Mg <sub>exg</sub> (μmol/g)	SE	Al <sub>exg</sub> (μmol/g)	SE	CEC (meq/100g)	SE
PC1-08-3	1.3	0.1	6	0	5	0
PC1-08-4	0.4	0.0	7	0	3	0
HP3-5	0.5	0.0	3	0	1	0
HP3-6	0.6	0.0	8	0	5	0
HP3A-3	1.1	0.0	3	0	3	0
HP3A-5	1.3	0.1	3	0	3	0
HP3A-6	1.7	0.0	8	0	4	0



**Appendix V.** Physical and chemical variables of the B<sub>hf</sub> layer from each soil pit. Standard error in italics.

Soil pit ID	pH <sub>CaCl2</sub>	<i>SE</i>	P <sub>H2Oi</sub> (μmol/g)	<i>SE</i>	P <sub>H2Oo</sub> (μmol/g)	<i>SE</i>	P <sub>NaHCO3i</sub> (μmol/g)	<i>SE</i>	P <sub>NaHCO3o</sub> (μmol/g)	<i>SE</i>	P <sub>NaOHi</sub> (μmol/g)	<i>SE</i>	P <sub>NaOHo</sub> (μmol/g)	<i>SE</i>
PC1-08-4	4.5	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.8	<i>0.1</i>	2.4	<i>0.1</i>	4.4	<i>0.2</i>
PC1-08-5	4.5	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.5	<i>0.1</i>	5.2	<i>0.2</i>	3.5	<i>0.2</i>
HP3-3	4.2	<i>0.0</i>	0.0	<i>0.0</i>	0.1	<i>0.0</i>	0.0	<i>0.0</i>	1.2	<i>0.0</i>	1.5	<i>0.0</i>	2.9	<i>0.4</i>
HP3-5	4.4	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.9	<i>0.0</i>	2.7	<i>0.1</i>	3.8	<i>0.1</i>
HP3-6	4.4	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.9	<i>0.0</i>	2.9	<i>0.0</i>	4.5	<i>0.1</i>

**Appendix V. cont**

Soil pit ID	P <sub>HCl</sub> (μmol/g)	<i>SE</i>	P <sub>H<sub>2</sub>SO<sub>4</sub></sub> (μmol/g)	<i>SE</i>	% LOI	<i>SE</i>	% C	<i>SE</i>	% N	<i>SE</i>	Al <sub>ox</sub> (μmol/g)	<i>SE</i>	Fe <sub>ox</sub> (μmol/g)	<i>SE</i>
PC1-08-4	0.7	0.1	12.3	1.3	12.5	0.0	7.8	0.2	0.4	0.0	893	24	261	5
PC1-08-5	2.0	0.3	14.4	0.2	8.3	0.1	8.9	0.2	0.3	0.0	721	22	230	9
HP3-3	1.5	0.1	7.7	0.4	12.0	0.1	5.1	0.0	0.2	0.0	265	6	203	4
HP3-5	1.2	0.2	8.7	0.4	15.3	0.5	5.0	0.2	0.3	0.0	1396	35	186	2
HP3-6	1.9	0.2	13.3	0.3	11.4	0.1	5.0	0.0	0.2	0.0	786	20	293	16

**Appendix V. cont**

Soil pit ID	Mn <sub>ox</sub> (μmol/g)	SE	P <sub>ox</sub> (μmol/g)	SE	% Clay	SE	% Silt	SE	% Sand	SE	K <sub>exg</sub> (μmol/g)	SE	Ca <sub>exg</sub> (μmol/g)	SE
PC1-08-4	0	0	15.2	0.1	2	0	33	0	67	1	0.9	0.0	6	1
PC1-08-5	0	0	14.4	0.8	3	0	42	1	58	1	0.6	0.0	1	0
HP3-3	1	0	3.3	0.1	2	0	32	1	67	1	0.7	0.0	10	0
HP3-5	1	0	13.0	2.0	2	0	23	2	77	2	0.6	0.0	1	0
HP3-6	0	0	11.9	0.4	2	0	28	1	72	1	0.4	0.0	3	0

**Appendix V. cont**

Soil pit ID	Mg <sub>exg</sub> (μmol/g)	SE	Al <sub>exg</sub> (μmol/g)	SE	CEC (meq/100g)	SE
PC1-08-4	0.5	0.0	4	0	13	1
PC1-08-5	0.2	0.0	3	0	9	0
HP3-3	0.9	0.0	11	0	8	0
HP3-5	0.3	0.0	6	0	13	0
HP3-6	0.3	0.0	6	0	9	0

**Appendix VI.** Physical and chemical variables of the B<sub>f</sub> layer from each soil pit. Standard error in *italics*.

Soil pit ID	pH <sub>CaCl2</sub>	<i>SE</i>	P <sub>H2O<i>i</i></sub> (μmol/g)	<i>SE</i>	P <sub>H2O<i>o</i></sub> (μmol/g)	<i>SE</i>	P <sub>NaHCO3<i>i</i></sub> (μmol/g)	<i>SE</i>	P <sub>NaHCO3<i>o</i></sub> (μmol/g)	<i>SE</i>	P <sub>NaOH<i>i</i></sub> (μmol/g)	<i>SE</i>	P <sub>NaOH<i>o</i></sub> (μmol/g)	<i>SE</i>
PC1-08-1	4.2	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.1	<i>0.0</i>	1.0	<i>0.1</i>	2.3	<i>0.0</i>	6.0	<i>0.0</i>
PC1-08-2	4.3	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.4	<i>0.1</i>	2.0	<i>0.1</i>	3.2	<i>0.1</i>
PC1-08-3	4.5	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.6	<i>0.1</i>	3.0	<i>0.1</i>	3.3	<i>0.2</i>
PC1-08-6	4.0	<i>0.0</i>	0.0	<i>0.0</i>	0.1	<i>0.0</i>	1.1	<i>0.0</i>	2.3	<i>0.1</i>	10.6	<i>0.3</i>	5.6	<i>0.1</i>
HP3-1	4.4	<i>0.0</i>	0.0	<i>0.0</i>	0.5	<i>0.0</i>	0.1	<i>0.0</i>	0.9	<i>0.1</i>	1.7	<i>0.0</i>	8.9	<i>1.4</i>
HP3-2	4.4	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.9	<i>0.1</i>	1.4	<i>0.0</i>	4.4	<i>0.4</i>
HP3-3	4.6	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.1	<i>0.0</i>	0.3	<i>0.1</i>	3.5	<i>0.1</i>	1.7	<i>0.2</i>
HP3-4	4.3	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.8	<i>0.1</i>	4.4	<i>0.0</i>	4.2	<i>0.1</i>
HP3A-1	4.6	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.2	<i>0.0</i>	0.8	<i>0.0</i>	1.6	<i>0.0</i>	6.6	<i>0.1</i>
HP3A-2	3.9	<i>0.0</i>	0.0	<i>0.0</i>	0.2	<i>0.1</i>	0.1	<i>0.0</i>	1.2	<i>0.0</i>	4.0	<i>0.1</i>	5.6	<i>0.2</i>
HP3A-3	4.1	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	1.0	<i>0.1</i>	2.0	<i>0.0</i>	4.6	<i>0.1</i>
HP3A-4	4.4	<i>0.0</i>	0.0	<i>0.0</i>	0.0	<i>0.0</i>	0.1	<i>0.0</i>	1.0	<i>0.1</i>	2.3	<i>0.0</i>	5.6	<i>0.0</i>
HP3A-5	4.5	<i>0.0</i>	0.0	<i>0.0</i>	0.1	<i>0.0</i>	0.1	<i>0.0</i>	1.5	<i>0.3</i>	4.3	<i>0.1</i>	6.6	<i>0.1</i>
HP3A-6	4.0	<i>0.0</i>	0.0	<i>0.0</i>	0.1	<i>0.0</i>	0.1	<i>0.0</i>	1.1	<i>0.0</i>	1.5	<i>0.0</i>	2.6	<i>0.1</i>

**Appendix VI. cont**

Soil pit ID	P <sub>HCl</sub> (μmol/g)	SE	P <sub>H<sub>2</sub>SO<sub>4</sub></sub> (μmol/g)	SE	% LOI	SE	% C	SE	% N	SE	Al <sub>ox</sub> (μmol/g)	SE	Fe <sub>ox</sub> (μmol/g)	SE
PC1-08-1	1.2	0.2	13.0	0.5	9.1	0.1	4.3	0.0	0.2	0.0	356	9	301	9
PC1-08-2	0.0	0.0	8.7	0.3	8.0	0.1	3.8	0.0	0.2	0.0	372	3	249	3
PC1-08-3	1.1	0.2	11.2	0.5	7.7	0.4	3.6	0.0	0.2	0.0	552	4	300	2
PC1-08-6	2.4	0.1	25.2	0.0	11.1	0.1	1.5	0.0	0.1	0.0	380	16	462	22
HP3-1	7.5	0.3	17.2	0.4	6.5	0.0	2.7	0.0	0.1	0.0	350	9	269	3
HP3-2	8.1	0.2	14.1	0.0	6.4	0.1	2.5	0.0	0.1	0.0	331	29	203	4
HP3-3	7.5	0.2	14.1	0.5	4.5	0.0	1.8	0.0	0.1	0.0	288	8	105	1
HP3-4	4.0	0.3	12.6	0.3	8.9	0.1	1.9	0.1	0.1	0.0	601	98	255	20
HP3A-1	5.3	0.2	15.3	0.5	5.7	0.0	2.5	0.0	0.2	0.0	257	6	160	8
HP3A-2	2.3	0.4	16.0	0.0	10.1	0.0	4.4	0.0	0.3	0.0	283	3	580	6
HP3A-3	2.9	0.2	11.2	0.1	9.4	0.1	4.5	0.0	0.2	0.0	356	6	440	5
HP3A-4	8.6	0.3	20.5	0.4	8.4	0.2	4.0	0.0	0.2	0.0	426	3	304	8
HP3A-5	7.7	0.2	20.1	0.3	9.3	0.0	4.4	0.0	0.2	0.0	426	5	267	3
HP3A-6	0.0	0.0	5.7	0.3	9.4	0.2	4.4	0.0	0.2	0.0	300	3	287	18

**Appendix VI. cont**

Soil pit ID	Mn <sub>ox</sub> (μmol/g)	SE	P <sub>ox</sub> (μmol/g)	SE	% Clay	SE	% Silt	SE	% Sand	SE	K <sub>exg</sub> (μmol/g)	SE	Ca <sub>exg</sub> (μmol/g)	SE
PC1-08-1	3	0	5.7	0.1	4	0	71	0	29	0	0.8	0.0	2	0
PC1-08-2	1	0	5.9	0.3	3	0	65	4	35	4	1.0	0.1	0	0
PC1-08-3	1	0	9.3	0.3	2	2	44	21	56	21	0.7	0.0	0	0
PC1-08-6	2	0	15.0	0.7	2	0	36	2	64	2	1.4	0.0	2	0
HP3-1	1	0	9.0	0.3	2	0	32	2	68	2	0.8	0.0	5	0
HP3-2	1	0	7.0	0.6	3	0	38	2	62	2	0.4	0.0	8	0
HP3-3	0	0	8.6	0.2	3	0	37	1	63	1	0.2	0.0	2	0
HP3-4	1	0	6.5	0.6	3	0	31	2	69	2	0.6	0.0	3	0
HP3A-1	1	0	6.6	0.2	2	0	28	0	72	0	0.4	0.0	7	0
HP3A-2	1	0	10.0	0.4	2	0	38	1	62	1	1.5	0.0	8	0
HP3A-3	1	0	7.4	0.1	2	0	27	1	73	1	0.6	0.0	8	0
HP3A-4	0	0	11.5	0.5	3	0	33	1	67	1	0.5	0.0	2	0
HP3A-5	0	0	10.4	0.0	2	0	33	1	67	1	0.6	0.0	16	1
HP3A-6	0	0	3.6	0.0	2	0	40	3	60	3	0.8	0.0	1	0

**Appendix VI. cont**

Soil pit ID	Mg <sub>exg</sub> (μmol/g)	SE	Al <sub>exg</sub> (μmol/g)	SE	CEC (meq/100g)	SE
PC1-08-1	0.5	0.0	8	0	6	1
PC1-08-2	0.3	0.0	7	0	5	1
PC1-08-3	0.3	0.0	4	0	6	0
PC1-08-6	0.7	0.0	14	0	7	0
HP3-1	1.0	0.0	5	0	5	0
HP3-2	1.3	0.0	5	0	4	0
HP3-3	0.2	0.0	3	0	3	0
HP3-4	0.4	0.0	6	0	4	1
HP3A-1	0.8	0.0	3	0	3	0
HP3A-2	1.7	0.0	12	0	8	1
HP3A-3	0.9	0.0	10	0	7	0
HP3A-4	0.4	0.0	6	0	4	0
HP3A-5	0.6	0.0	5	0	5	0
HP3A-6	0.6	0.0	17	0	8	1