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Phosphorus in agricultural soils of Finland
– characterization of reserves and
retention in mineral soil profiles

Tommi Peltovuori

Academic dissertation

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P reserves in cultivated mineral soils in Finland

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Abstract

An overwhelming majority of all the research on soil phosphorus (P) has been carried out with soil samples taken from the surface soils only, and our understanding of the forms and the reactions of P at a soil profile scale is based on few observations. In Finland, the interest in studying the P in complete soil profiles has been particularly small because of the lack of tradition in studying soil genesis, morphology, or classification.

In this thesis, the P reserves and the retention of orthophosphate phosphorus ($\text{PO}_4\text{-P}$) were examined in four cultivated mineral soil profiles in Finland (three Inceptisols and one Spodosol). The soils were classified according to the U.S. Soil Taxonomy and soil samples were taken from the genetic horizons in the profiles. The samples were analyzed for total P concentration, Chang and Jackson P fractions, P sorption properties, concentrations of water-extractable P, and for concentrations of oxalate-extractable Al and Fe. Theoretical P sorption capacities and degrees of P saturation were calculated with the data from the oxalate-extractions and the P fractionations.

The studied profiles can be divided into sections with clearly differing P characteristics by their master horizons Ap, B and C. The C (or transitional BC) horizons below an approximate depth of 70 cm were dominated by, assumingly apatitic, H_2SO_4 -soluble P. The concentration of total P in the C horizons ranged from 729 to 810 mg kg^{-1} . In the B horizons between the depths of 30 and 70 cm, a significant part of the primary acid-soluble P has been weathered and transformed to secondary P forms. A mean weathering rate of the primary P in the soils was estimated to vary between 230 and 290 $\text{g ha}^{-1} \text{ year}^{-1}$. The degrees of P saturation in the B and C horizons were smaller than 7%, and the solubility of $\text{PO}_4\text{-P}$ was negligible. The P conditions in the Ap horizons differed drastically from those in the subsurface horizons. The high concentrations of total P (689-1870 mg kg^{-1}) in the Ap horizons are most likely attributable to long-term cultivation with positive P balances. A significant proportion of the P in the Ap horizons occurred in the NH_4F - and NaOH -extractable forms and as organic P. These three P pools, together with the concentrations of oxalate-extractable Al and Fe, seem to control the dynamics of $\text{PO}_4\text{-P}$ in the soils. The degrees of P saturation in the Ap horizons were greater (8-36%) than in the subsurface horizons. This was also reflected in the sorption experiments: Only the Ap horizons were able to maintain elevated $\text{PO}_4\text{-P}$ concentrations in the solution phase – all the subsoil horizons acted as sinks for $\text{PO}_4\text{-P}$.

Most of the available sorption capacity in the soils is located in the B horizons. The results suggest that this capacity could be utilized in reducing the losses of soluble P from excessively fertilized soils by mixing highly sorptive material from the B horizons with the P-enriched surface soil. The drastic differences in the P characteristics observed between adjoining horizons have to be taken into consideration when conducting soil sampling. Sampling of subsoils has to be made according to the genetic horizons or at small depth increments. Otherwise, contrasting materials are likely to be mixed in the same sample; and the results of such samples are not representative of any material present in the studied profile. Air-drying of soil samples was found to alter the results of the sorption experiments and the water extractions. This indicates that the studies on the most labile P forms in soil should be carried out with moist samples.

Foreword

The work described in this thesis was initiated in 1997 when I joined a research project that studied the effects of controlled drainage on the particle and nutrient transport in subsurface drainage waters. This three-year-project was funded by The Finnish Drainage Research Foundation and the Ministry of Agriculture and Forestry, and it involved people from several research organizations (Agricultural Research Centre of Finland, Helsinki University of Technology, University of Helsinki). I was fortunate to start my scientific career in such an organized project that provided several valuable contacts and regular feed-back from the other participants. I am especially indebted to my fellow doctoral student, Risto Uusitalo, for his help in digging and sampling the soil pits, and for the hours spent on the pit-side – often puzzled by the soil classification manual.

A massive number of laboratory analyses, only some of which are dealt with in this thesis, were conducted during the project. Fortunately, I had good help in the laboratory, for which I warmly thank Elina Kerko, Mari Rätty, Mirva Levonmäki, and especially Helena Soinne. In addition to her significant contribution in the laboratory, I thank Helena for the invaluable help in data processing and for co-authoring various reports and articles. The data from the laboratory experiments were refined in this thesis with the help of several parties: I express my sincere appreciation to the Kone Foundation, to the Finnish Cultural Foundation, to the Land and Water Technology Foundation (Maa- ja vesitekniiikan tuki ry) and to the University of Helsinki for providing me grants for this purpose. I also want to acknowledge the official reviewers, Professor José Torrent and Doctor Peter Kleinman.

This thesis would look quite different without the influence of two teachers on my impression of soils. I am grateful to Professor Delbert Mokma and Doctor Markku Yli-Halla for revealing to me that there is much more to agricultural soils than just a plow layer. With all the shortcomings this theses may have, I hope it will inspire other soil scientists in Finland to extend their studies beyond the surface horizons.

It took almost ten years from writing the first research plan to finishing this dissertation. It is therefore most appropriate to express my sincere appreciation to the patience of my supervisor, Professor Helinä Hartikainen, who kindly gave me the opportunity to work at the Department of Applied Chemistry and Microbiology and who introduced me to the secrets of soil phosphorus.

Finally, I thank my family for the support that allowed me to spend all these years on soils and P.

Sajaniemi, June 2006

Tommi Peltovuori

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List of original articles and participation

The thesis is a summary and discussion of the following articles:

- I. Peltovuori, T., Uusitalo, R. and Kauppila, T. 2002. Phosphorus reserves and apparent phosphorus saturation in four weakly developed cultivated pedons. *Geoderma* **110**, 35-47.
- II. Peltovuori, T. and Soinne, H. 2005. Phosphorus solubility and sorption in frozen, air-dried, and field-moist soil. *European Journal of Soil Science* **56**, 821-826.
- III. Peltovuori, T. 2006. Sorption of phosphorus in field-moist and air-dried samples from four weakly developed cultivated soils. *European Journal of Soil Science* (in press; DOI 10.1111/j.1365-2389.2006.00789.x).
- IV. Peltovuori, T. 2002. Phosphorus extractability in surface soil samples as affected by mixing with subsoil. *Agricultural and Food Science in Finland* **11**, 371-379.

Article I was planned jointly with Tommi Peltovuori and Risto Uusitalo. They also dug, described and sampled three of the four pedons together; the fourth pedon was studied by T. Peltovuori alone. Most of the laboratory analyses were made by T. Peltovuori, but R. Uusitalo was responsible for the oxalate extractions and dissolutions for the total P analysis. Tommi Kauppila carried out the mineralogical analyses and their interpretation. T. Peltovuori had the main responsibility for preparing the manuscript.

The experiments described in Article II were originally planned by T. Peltovuori. The plan was refined by Helena Soinne who also carried out the practical laboratory work. Both authors took part in interpreting the results. T. Peltovuori prepared the manuscript and H. Soinne commented on it.

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1 Introduction

Soil phosphorus (P) has maintained its appeal to soil scientists for more than 150 years. During the first 100 of those years, research mainly focused on securing the P nutrition of cultivated plants. This was rational since few soils in the world can supply cultivated crops with sufficient amounts of P without fertilization or manuring. Due to the substantial response of yields to P fertilization and affordable products, the use of P fertilizers increased rapidly after the Second World War, and to date, nearly 600×10^6 Mg of fertilizer P has been applied on the Earth's agricultural soils (International Fertilizer Industry Association, 2005). Considerably less P has been removed from soils through harvest, and the consequent positive P balance has created soils having an excessive P content in many areas of the developed world (Sharpley and Withers, 1994; Barberis *et al.*, 1996; Dalgaard *et al.*, 2003). The statistics on intercontinental trade indicate that the P balance has been most positive in Europe, with more than double the net inputs of P per hectare than in any other region in the world (Beaton *et al.*, 1995).

Securing the P nutrition of crops with fertilizers has been one of the greatest successes in improving agricultural productivity, but long ago P fertilizers were discovered not to be a pure blessing. The first symptoms of the harmful effects of the increased P (and nitrogen) inputs in agriculture on the environment were noticed in the 1960's in North America and Great Britain, where the nutrient concentrations of the surface waters were elevated from their natural state with numerous harmful consequences. Obviously, there also were and are other sources of P affecting the quality of surface waters, but extensive evidence from Finland (e.g. Rekolainen, 1989; Vuorenmaa *et al.* 2002) and elsewhere (e.g. Carpenter *et al.*, 1998; Catt *et al.*, 1998; van der Molen *et al.*, 1998; Vagstad *et al.*, 2001) demonstrates that agriculture has an undisputable impact on the P loading of the surface waters wherever modern agriculture is being practiced.

The undesired effects of P fertilization shifted the focus of P research from agronomic issues to environmental ones. As a result, instead of studying ways to maximize the P supply for cultivated plants, an increasing number of soil scientists now work on the possibilities of reducing agricultural P inputs and balancing production with environmental values, ways of measuring and reducing the mobilisation of the various forms of P in enriched soils, and ways of reducing the P transport to the surface waters in drainage and runoff waters. Regardless of the related change in the norms and methodology applied in soil P research, the

primary processes governing the behavior of P in soil are essentially the same as 150 years ago when Justus Liebig and John Bennet Lawes made their first experiments on the P nutrition of plants (e.g. Speter, 1935). A strong basis in understanding these processes is required both in agronomically and in environmentally oriented P research.

Within the past one and a half centuries of soil P research, a massive amount of literature has been produced, and the escalating knowledge has been reviewed in a number of articles (e.g. Wild, 1950; Larsen, 1967; Mattingly, 1975; Dalal, 1977; Hartikainen, 1979; Sample *et al.*, 1980; Barrow, 1983a; Sharpley and Menzel, 1987; Sanyal and De Datta, 1991; Frossard, *et al.*, 1995). Today, the individual processes governing the behavior of P in various soils are well known. Then why is soil P still under active research? Most of the interest is, of course, explained by the widespread harmful effects of soil P on the surface waters and the increased public concern about this issue, but the research is also driven by purely scientific incentives. In short, many aspects of soil P are not well known even today.

The overwhelming majority of all research that forms the basis of our understanding of soil P – both from agronomic and environmental perspectives – has been carried out with soil samples taken from the surface soil only. This conventional approach on soils has its roots in the agronomic research tradition focusing on the cultivated plow layers. The overall shortage of P data of complete soil profiles (see McGechan, 2002) is somewhat surprising since the strong stratification of P reserves and the processes controlling the soil P cycle was demonstrated decades ago (Pearson *et al.*, 1940; Glenworth, 1947; Allaway and Rhoades, 1951; Wood *et al.*, 1984).

In Finland, only few observations have been reported on the P conditions of complete soil profiles (Kaila, 1956; Kaila, 1963a) or even on individual subsoil samples (e.g. Kaila, 1964a; Hartikainen, 1979). This negligible interest in studying complete soil profiles is, at least partly, explained by the lack of a tradition in studying soil genesis, morphology, or classification. For decades, these fields of soil science were not considered essential in this country as it has relatively young soils formed of very homogeneous parent materials. In recent times, however, the increased international co-operation and the related need to classify the soils of Finland according to the international classification systems, as well as the growing awareness of agricultural soils as three-dimensional systems have helped to extend the scope of soil research beyond the tilled Ap horizons.

The purpose of this thesis is to describe the general patterns of the soil P reserves and the basic reactions controlling the mobility of P in the cultivated mineral soils of Finland. The results increase our knowledge of the basics of soil P at a pedon scale, which is a fundamental soil unit, yet a neglected scale in the hierarchy of soil P research (see Bouma *et al.*, 1998; Haygarth *et al.*, 2005). Along the way, some new details of soil P methodology emerged and these are discussed, even though such issues were of secondary importance in this work. The thesis carries on the tradition of P research in Finland, and contributes another link to the chain of scholarly theses concerning the various aspects of soil P (Salonen, 1941; Kaila, 1948; Hartikainen, 1979; Turtola, 1999; Uusitalo, 2004).

1.1 Phosphorus and its reactions in soil

Phosphorus can be considered as one of the key elements in soil development because of its great ecological significance and because practically all the P in natural systems must be derived from the soil parent material. During soil genesis, this inherent P pool is transformed to various chemical forms and translocated within the soil or out of the soil by a multitude of processes. Moreover, plants take up their portion of this P to maintain vital biological functions – and ultimately, to support entire food chains outside the soil. In most agricultural soils, this natural sequence of P transformations has been altered by additions of fertilizers and manure.

1.1.1 Transformations of inherent soil phosphorus

At the onset of soil development, the P in most soils is in the form of apatitic minerals (e.g. $\text{Ca}_{10}(\text{PO}_4, \text{CO}_3)_6(\text{F}, \text{OH})_{2-3}$). This primary P is transformed to other forms by various soil forming processes. The rate of the weathering of the primary P depends on the exact chemical form of the apatite minerals and the degree of their inclusion into weathering-resistant minerals – as well as on the overall rate of soil genesis determined by the soil-forming factors: properties of the parent material, climate, organisms, topography and time (e.g. van Breemen and Buurman, 2002).

The apatitic primary P is incorporated into various secondary P forms during soil development. Ultimately, only the P occluded into persistent hydroxides and oxides of Fe and Al, and some organic P are considered to be stable, but the transformation takes place through several intermediate P forms (Walker and

Syers, 1976). The terminology for these intermediate products is diverse because a multitude of concepts, theories and methods has been applied in soil P research. Smeck (1985) described the weathering process of P as being simultaneous pedologic and biologic pathways: The apatitic primary P is slowly weathered and released into the soil solution as soluble P which attains equilibrium with the labile P pool in the soil. The soluble P in the soil solution may be taken up by plants or other organisms, be leached out of the soil, or be incorporated into secondary P minerals. The P in these secondary minerals is slowly but irresistibly transformed to occluded P forms (a “pedologic P sink”). In a competing biological P cycle, the soluble P taken up by the plants is eventually returned to the soil, where it may be released into the soil solution for another biological cycle, immobilized in secondary P forms, or incorporated into an increasing pool of organic soil P. The P within this system can be transferred from the one-way pedologic pathway to the biologic cycle, or vice versa, depending on the environmental conditions. Some P is lost from the soil system as these cycles proceed and the total amount of P per unit area decreases. A complete transformation of the primary P to occluded P takes thousands of years, and old soils reach a steady state in which practically all the P is in occluded or stable organic forms and infinitesimal changes take place in the P composition (Figure 1.1). The limited information on the transformations of organic P during pedogenesis suggests that these stable organic P forms are, at least partly, composed of the P in humic acids and inositol phosphates (Baker, 1976; Harrison, 1987).

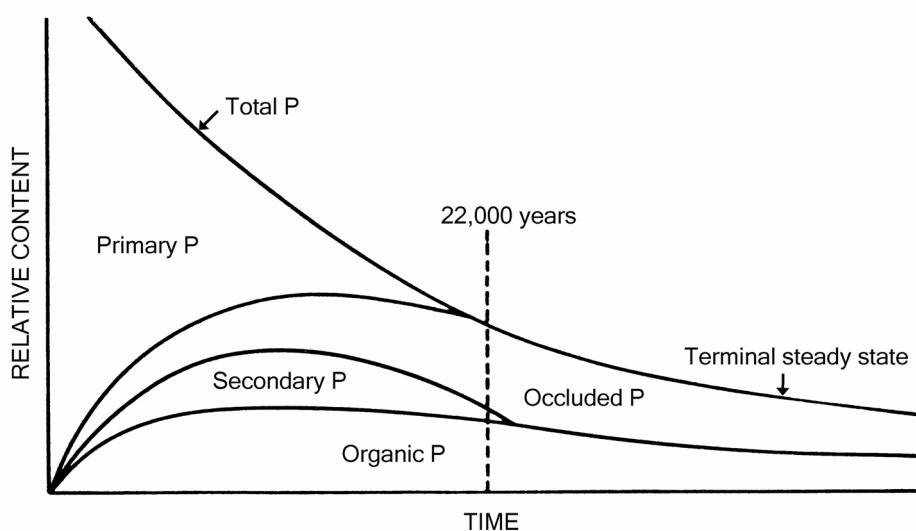


Figure 1.1 Changes in the amount and composition of soil P over time (Walker and Syers, 1976. © Elsevier, reproduced with permission).

These general changes in the soil P composition were a major source of motivation for the developers of the Chang and Jackson soil P fractionation scheme, which is intended for the determination of primary, secondary, and occluded forms of soil P (Chang and Jackson, 1957; Chang and Jackson, 1958). Also a more detailed Hedley sequential extraction method has been used for characterizing the P composition at various stages of soil development, but the increased number of the separate P fractions measured have proven to form homogeneous groups very similar to the robust Chang and Jackson P pools used by Walker and Syers (1976) and Smeck (1985) (see Tiessen *et al.*, 1984).

Weathering of the primary P is not uniform within a soil profile. It is most intense in the surface horizons which are subject to the most extreme conditions and which have the highest biological activity, and it is negligible in the parent material. In a typical soil profile, the content of P is relatively high in the surface horizons, decreases to a profile minimum in the B horizons, and attains a maximum in the lower B or the C horizons (Smeck, 1973; Walker and Syers, 1976). The two main processes translocating P upwards and downwards from the B horizons is the P uptake of plants and leaching; in agricultural soils, fertilizing or manuring further increases the P content of the surface horizons. The combined effect of these intra-profile transport processes and weathering of the primary P typically results in a soil profile with a decreasing content of acid-soluble P and an increasing content of secondary P forms and organic P from the C horizons towards the soil surface (Allaway and Rhoades, 1951; Smeck and Runge, 1971; St. Arnaud *et al.*, 1988).

Parallel to the release of primary P, Al and Fe are also released into the soil solution during weathering. They readily form oxides and hydroxides – highly reactive variable-charge materials – that are considered to be the most important components affecting the solubility of P in non-calcareous soils (e.g. Barrow, 1983; Frossard *et al.*, 1995). The pedogenic environment has a strong influence on the type of oxide minerals formed (Schwertmann, 1985; Allen and Hajek, 1989) and various oxides may have strongly deviating reactions with soluble phosphate P (Parfitt, 1978; McLaughlin *et al.*, 1981). The role of these oxides is crucial in all soils because most transformations of P involve the reactions of soluble P. Therefore, all studies on the dynamics of P in soil profiles should involve an examination of the properties of soil oxides.

1.1.2 Fertilizer and manure phosphorus in soil

Soluble phosphate phosphorus (H_2PO_4^- , HPO_4^{2-} , PO_4^{3-} , all denoted as $\text{PO}_4\text{-P}$ in this text) added to the soil in fertilizers or manure can be considered as being a disturbance to the natural pedological and biological transformations of P. Some of the added P is taken up by the plants, as intended, but a significant fraction of the excess P in the soil solution is removed to the competing pedological sink. This “fixation” of P has been studied ever since P fertilizers were adopted in agriculture (Hibbard, 1934; Wild, 1950), but the actual mechanisms remained ambiguous for decades. The existence of adsorption and anion-exchange reactions in soil were recognized, but the P concentration in the soil solution was thought to be determined ultimately by the solubility products of various Ca-, Al- and Fe-compounds. During the 1960's and 1970's, the significance of the variable-charge surfaces in soil was discovered and the mechanism of specific adsorption of anions on them was recognized as a major factor controlling the solubility of $\text{PO}_4\text{-P}$ in soils (Hingston *et al.*, 1967; Bowden *et al.*, 1973; Parfitt, 1978; Goldberg and Sposito, 1985). The retention of $\text{PO}_4\text{-P}$ by variable-charge soil oxides and hydroxides is now considered the key reaction in the natural cycling of P and the reactions of P amendments, especially in non-calcareous soils.

When soluble $\text{PO}_4\text{-P}$ is retained by pure Al and Fe oxides, it is typically exchanged with the singly coordinated $[-\text{OH}]$ or $[-\text{OH}_2^+]$ groups on the oxide surface in a specific ligand-exchange reaction. This means that the maximum number of PO_4 -ions retained is limited by the number of exchangeable groups in the oxide mineral. The readiness of the individual $[-\text{OH}]$ or $[-\text{OH}_2^+]$ groups to exchange with the PO_4 -anion is not equal but depends on a myriad of interrelated physical, chemical and electrical parameters related to the adsorbent, adsorbate and the equilibrium solution (e.g. Ryden and Syers, 1975). The sorptive properties also change as adsorption proceeds: the negative charge of the adsorbent usually increases, making further adsorption less probable (Barrow, 1983a). The system can be described as a set of discrete adsorption sites with a continuum of sorptive properties (Parfitt, 1978). The complex factors affecting the adsorption of $\text{PO}_4\text{-P}$, including the effects of pH and electrostatic interactions of the components, have been successfully modelled on pure oxides (Bowden *et al.*, 1973; Posner and Barrow, 1982; Barrow, 1985) but the models are not applicable in regular soil research.

The properties of the synthetic oxides used in the adsorption experiments have been well determined. Even the individual atoms reacting with the $\text{PO}_4\text{-P}$ ions have

been portrayed with spectroscopic methods (e.g. Parfitt *et al.*, 1975). The adsorption system in soils is more complex. The oxides produced by weathering are rarely crystallized enough to allow such methods to be used, and several types of oxides occur together, often in transitional forms. The oxides typically found in weakly developed soils (short-range-ordered oxides; previously "sesquioxides" or "amorphous" oxides) have a defective crystalline structure, vacant metal positions, and usually very large specific surface areas, but they possess essentially similar ligand-exchange abilities as pure oxides (Parfitt, 1978). A high content of organic matter in the soil inhibits the crystallization of forming oxides, and this may further increase their capacity to adsorb P (Schwertmann, 1966; Borggaard *et al.*, 1990). A limited number of corresponding ligand-exchange sites also exists at the edges of clay minerals and in Fe and Al complexed with soil organic matter (Gerke and Hermann, 1992), but the high specific surface area and the porosity of the short-range-ordered oxides make them the most important component in P retention. In many soils, coarse particles are covered with coatings of such an oxide material (Jones and Uehara, 1973).

When soluble $\text{PO}_4\text{-P}$ is added to soil, it is adsorbed rapidly by the short-range-ordered oxides, and an apparent equilibrium is attained between the adsorbed $\text{PO}_4\text{-P}$ ions and those in the soil solution. After this fast initial adsorption, the $\text{PO}_4\text{-P}$ concentration in the soil solution keeps slowly decreasing, indicating that no true equilibrium was reached. According to current perception, this fast reaction is a ligand-exchange reaction on the oxide surfaces, and the slow decrease in the $\text{PO}_4\text{-P}$ concentration in the soil solution is induced by diffusion of the adsorbed P towards the interior of the porous oxide material (Barrow, 1983b). This diffusion is induced by a concentration gradient formed upon adsorption and it drives the apparent equilibrium of the fast adsorption reactions towards the oxide surface. As the reactions proceed, the negative charge of the oxide minerals increases and makes further adsorption less likely. Thus, the retention of P by soil oxides is actually a two-step and a three-dimensional process – and as such, it should be called "sorption" instead of "adsorption", a term reserved strictly for two-dimensional processes.

In laboratory sorption experiments where a small amount of soil is mixed with a solution containing $\text{PO}_4\text{-P}$, the fast reaction between the solution and the sorptive surfaces is completed within hours or days (e.g. Ryden *et al.*, 1977; Torrent, 1987). In incubation experiments imitating natural soil conditions, the "fast" reaction may take somewhat longer (Agbenin and Tiessen, 1995), but the slow diffusion into the

oxides lasts for weeks or months (Barrow and Shaw, 1975; Torrent, 1987; Willet *et al.*, 1988; van der Zee and van Riemsdijk, 1988; Agbenin and Tiessen, 1995). The longer the reactions proceed, the deeper the P diffuses, and the less of it is recovered using mild extractants. The P within the short-range-ordered oxides is not, however, “fixed”. This is because the slow reaction can be reversed and desorption from the oxide surfaces promoted by reducing the activity of $\text{PO}_4\text{-P}$ in the soil solution until it is small enough to allow outward diffusion in the oxides (Barrow, 1983a; Lookman *et al.*, 1995a). It is, therefore, more appropriate to treat sorbed soil P as a continuum retained at various strengths, rather than as distinct pools, such as “labile”, “non-labile” or “fixed” P.

The theory of reversible P sorption, which involves the specific adsorption on the oxide surfaces and a coupled slow diffusion phase, provides a conceptual framework for several widely applied methods in soil P research: 1) Studying the interactions between the P on the sorption surfaces and in the soil solution at varying P concentrations, i.e. the quantity-intensity relations or P buffering, is an extensively used method for studying the fast reaction of sorption (Barrow, 1978). It should be noted that this quantity-intensity concept was adopted to soil P research long before the details of sorption were discovered (Schofield, 1955; Beckett and White, 1964), so the use of the method is not constrained to the presented theory of sorption; 2) The total P sorption capacity of a soil has been estimated by measuring the contents of the short-range-ordered Fe and Al oxides with an acid ammonium oxalate extraction, and the degree of saturation of this capacity as a molar ratio of P to the sum of the Fe and Al in the oxalate extracts (e.g. Beauchemin and Simard, 1999); 3) The maximum amount of P that can be desorbed from a soil has been measured with an “infinite sink” approach, where the P activity of the extraction solution is lowered to negligible levels either with an anion exchange resin (Sibbesen, 1978) or an Fe oxide-coated filter paper (van der Zee *et al.*, 1995); 4) The presented theory of sorption is also relevant to the fractionation methods developed for separating soil P into pools which differ either in their strength of retention (Hedley *et al.*, 1982) or in their P retaining components (Chang and Jackson, 1957) when the methods are used for characterizing the composition of sorbed P.

Even though adsorption and slow diffusion in the short-range-ordered oxides are generally considered to be the most important mechanisms controlling the solubility of P in temperate non-calcareous soils at low P concentrations, the theory has not completely dispelled that of precipitation as a key reaction. According to Li

and Stanforth (2000), both sorption and precipitation control the solubility of P in goethite-suspensions at a wide pH-range, and the two mechanisms are indistinguishable in regular sorption experiments. In addition, the kinetics of the slow P retention have been successively modelled by using an approach based on diffusion of P through surface coatings that are precipitated on oxide surfaces upon sorption (van Riemsdijk *et al.*, 1984). This approach can, however, be considered to be closer to the adsorption-diffusion concept than to the precipitation of separate metal-phosphates in soil.

At high P concentrations, the role of precipitation reactions is widely accepted: In the vicinity of fertilizer granules, the concentration of P and other plant nutrients is typically high enough to facilitate precipitation of sparingly soluble P compounds, such as dicalcium phosphate ($\text{CaHPO}_4 \cdot \text{H}_2\text{O}$) or octocalcium phosphate ($\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$) (Sample *et al.*, 1984). In acid or neutral soils, these products are nevertheless unstable and the P retained in them temporarily enters the sorptive retention system when the P concentration in the soil solution is reduced. In calcareous soils, the precipitation reactions producing a variety of Ca-phosphates or even secondary apatites are common, but even in these soils, sorption on the oxide surfaces controls the behavior of soluble P at small concentrations (Borrero *et al.*, 1988; Frossard *et al.*, 1995; Castro and Torrent, 1998). The exact composition of the precipitated P compounds in natural soil environment is extremely difficult to determine (e.g. Pierzynski *et al.*, 1990), and the P precipitates allegedly identified in soils may actually be $\text{PO}_4\text{-P}$ sorbed on ambiguous oxides and hydroxides of Al and Fe.

Some of the P added to soil can also be retained by immobilization to organic forms. This immobilization can be rapid in soils having a low P status, and the amounts retained can be comparable to those taken up by plants (Harrison, 1987). In a study of Brookes *et al.* (1984), the amounts of P cycled through the active microbial population – the “immobilizing engine” – during a growing season were as large as 40 kg ha^{-1} . The contribution of immobilization to P retention is, however, not necessarily that great because changes in immobilization rates are generally balanced off with concurrent changes in mineralization rates. The sizes of the organic P pools do not typically change rapidly, but reflect the inherent properties and the environmental conditions of the soils (Tate, 1984; Harrison, 1987). On pedological time-scales, the transformation of primary P to stable, organic forms is an important factor, as was discussed above.

Even if immobilization is not considered to be a key mechanism of short-term retention for fertilizer P, the incorporation of P into organic forms may have a considerable impact on the fate of P in soil: Because organic P incorporated into small molecules is more mobile than $\text{PO}_4\text{-P}$, leaching of soluble organic matter may transport significant amounts of P downwards in the profile (Walker and Adams, 1959; Hannapel *et al.*, 1964; Rolston *et al.*, 1975; Schoenau *et al.*, 1989; Anderson and Magdoff, 2005). In extreme cases, the concentrations of organic P in the soil solution may equal or even exceed that of $\text{PO}_4\text{-P}$ (Dalal, 1977; Ron Vaz *et al.*, 1993), and high rates of leaching can be expected. The high solubility and mobility of the organic P applies to orthophosphate diesters. Orthophosphate monoesters, such as inositol phosphates and glucose phosphates, are sorbed effectively in the soil oxides with specific sorption through their active $\text{PO}_4\text{-}$ groups (Anderson *et al.*, 1974; Ognalaga *et al.*, 1994; Anderson and Magdoff, 2005). An unknown fraction of this sorbed, organic P is included in the soil P analyses intended for measuring $\text{PO}_4\text{-P}$ because the organic P is partly hydrolyzed in the acid environment of the regular colorimetric P analyses. The analyses based on the theory of reversible specific sorption of inorganic P on variable-charge surfaces are thus not strictly specific for $\text{PO}_4\text{-P}$. Organic P added to Finnish soils is, however, rapidly mineralized to $\text{PO}_4\text{-P}$ (Soinne and Peltovuori, 2005), and the approaches on the P dynamics based on the sorption and desorption reactions of $\text{PO}_4\text{-P}$ can be considered relevant.

1.2 Cultivated soils in Finland

1.2.1 General description

The mineral soils of Finland are formed of rather homogeneous parent materials detached from the Precambrian Fennoscandian shield, crushed and redeposited by glacial activity no more than 11,000 years ago (Donner, 1995). The mean thickness of the deposits covering the bedrock is 8.3 m and they consist for the most part of granitic materials. Due to the felsic parent material and the cold temperate climate with excess precipitation, most soils are naturally acidic. The pH of the cultivated surface soils ranges typically from 5 to 6.5 (Kähäri *et al.*, 1987), and there are practically no calcareous soils. The topography is comparatively flat, and approximately 80% of the agricultural land is artificially drained (Puustinen *et al.*, 1994). In addition to the regular mineral soils, fairly large areas of organic soils (Puustinen *et al.*, 1994) and acid sulfate soils (Yli-Halla *et al.*, 1999) are cultivated.

Their P characteristics deviate strongly from the typical mineral soils and are not discussed in this thesis.

Because the soils of Finland have formed on weathering-resistant parent materials and matured only for a short period of time in a climate not favorable for fast development, most of the soils are weakly developed from a global perspective. The combined immaturity and homogeneity of the soils in Finland probably explains the lack of scientific interest in the soil-forming processes, morphology and classification of soils, although some research along this line was done as early as in the 1950's (Aaltonen, 1951). For a practical categorization of soils, a system based on texture and organic matter content has been considered to be sufficient.

The increasing international cooperation in soil research has created a need for the classification of the soils in Finland according to the global taxonomic systems. During the last ten years, several studies have been conducted to describe the morphology and classification of the soils according to the U.S. Soil Taxonomy, the FAO/Unesco legend, or the World Reference Base for Soil Resources (WRB) (Mount *et al.*, 1995; Yli-Halla, 1997; Yli-Halla *et al.*, 2000; Mokma *et al.*, 2000; Yli-Halla and Mokma, 2001; Mokma *et al.*, 2004). These studies have made it clear that the essential characteristics needed for a meaningful classification of the soils in Finland are present and that the classification of these soils is reasonable even though the range of applicable taxa is narrow.

Characteristic soil-forming processes in the mineral soils of Finland can be summarized based on the few dozen soil profiles described in detail in the publications cited above: In fine-textured mineral soils, the most dominant processes appear to be weathering of the primary minerals and the associated oxidation of Fe compounds. Most clay soils are naturally poorly drained and can be characterized as hydromorphic soils, in which the oxidation state and the solubility of Fe and other redox-sensitive compounds fluctuate readily. In spite of the immaturity of the soils, emerging signs of clay eluviation have been recognized. In many clay soils, artificial drainage and consequent shrinkage have created a strong prismatic structure in the subsoil, but the platy substructure and visible lamellae deeper in the soil are reminders of the young age of the soils and the lacustrine origin of the clay parent material (see Donner, 1995). Most clay soils in Finland are classified as Cryaquepts in the Soil Taxonomy and as Cambisols according to the FAO/Unesco legend and to the World Reference Base for Soil Resources.

Silt and fine sand soils are, in general, the most weakly developed soils in Finland because they usually have a poor or nonexistent structure which hinders weathering and the translocation of the weathering products. These soils are typically classified as Cryorthents or Eutrocryepts in the Soil Taxonomy and Regosols or Cambisols in the FAO/Unesco system and the World Reference Base for Soil Resources.

Coarse mineral soils usually have red or brown colors because the particles are coated with the oxides and hydroxides of Fe. Podsolization has occurred in many fine sands and the eluvial and spodic horizons may be present in the cultivated soils below the plow layer. Nodules or concretions of Fe oxides can be found in the spodic horizons. Unlike most other soils, some Spodosols in Finland are well developed from a global perspective. These are classified as Haplocryods in the Soil Taxonomy and as Pod sols in the FAO/Unesco system and the World Reference Base for Soil Resources. Within the non-podsolized coarse soils, the most common are Cryorthents and Cryopsammets (Soil Taxonomy) and Regosols or Arenosols (FAO/Unesco, World Reference Base for Soil Resources).

The characteristic soil-forming processes and typical features in the mineral soils of Finland have most likely shaped the composition of soil P. The young age of the soils implies that a significant fraction of total P is still in primary apatitic forms, and that the transformations into secondary forms have occurred only at limited depths. Even the unaltered parent material of the soils may, however, contain some secondary or occluded P, since an unknown fraction of pre-weathered pre-Quaternary material has been mixed with the material detached from the bedrock during the last glaciation (Donner, 1995). Another factor that can be expected to have a strong impact on the chemistry of soluble $\text{PO}_4\text{-P}$ in these soils is the hydromorphic nature of most fine-textured soils and its effects on the soil Fe oxides through fluctuating redox-conditions. The emerging signs of eluvial and illuvial processes may not have a strong influence on soil P, except in the podzolized soils, where the accumulation of Fe and Al in the spodic horizons may have lead to extreme P affinities. Furthermore, several other processes are likely to have affected the soil P conditions, but the effects are, in general, not very well-known.

1.2.2 Phosphorus in soils of Finland

The mean concentration of total P in the fine fraction of till samples taken at the depths of 0.5–2 m in Finland is 690 mg kg^{-1} ($n=1057$; Koljonen, 1992). This concentration sets a point of reference for the cultivated mineral soils because

practically all of them are formed of redistributed till material. Some variation in the total P concentrations of till exists because of geological diversity, but the range of mean concentrations of all the common rock types of this area is rather narrow: from 570 to 760 mg kg⁻¹. The total P concentration in mineral agricultural subsoils ranges typically from 430 to 920 mg kg⁻¹ (Salonen, 1941; Kaila, 1963b; Kaila, 1963c). The highest concentrations of these have been measured in the clay soils of South-West Finland, and they may indicate an enrichment of P in the lacustrine parent material during the marine development stages of these soils (Koljonen, 1992). It is not, however, certain whether the results reported for the agricultural subsoils portray the concentration of the parent material, as details of the sampling depths or the profile descriptions of the soils are not reported.

Fairly high concentrations of total P in the plow layers of cultivated clay soils were measured even before the era of the most intensive fertilizer use (Kivinen, 1934: 880 mg kg⁻¹; Salonen, 1941: 1250 mg kg⁻¹). These soils may have had a long history of manuring, but natural enrichment of P in the surface soils due to the common soil-forming processes should also be expected. The natural enrichment of P in the surface soils is evident in the results of Kaila (1963c), who found higher total P concentrations in the uncultivated surface soils than in the adjacent subsoils. Application of P fertilizers increased strongly in the late 1940's, and the mean total P concentration of the cultivated surface soils increased by 30% in three decades (Saarela, 2002). The last extensive surveys of the total P concentration in the cultivated soils were carried out in the 1960's, and the concentrations in the mineral surface soils were found to range typically from 850 to 1200 mg kg⁻¹, although occasional values of up to 1830 mg kg⁻¹ were measured (Kaila, 1963b; Kaila, 1963c). In 18 cultivated mineral surface soils examined in the late 1970's, the mean total P concentration was 1210 mg kg⁻¹ and the range was from 780 to 1870 mg kg⁻¹ (Saarela *et al.*, 2003).

Few data are available of the vertical distribution of P in complete soil profiles in Finland. In five fine-textured and five coarse mineral soils studied by Kaila (1963c), the minimum concentration of total P was measured at the depths between 20 to 50 cm, and the concentration in that layer was roughly half of that in the plow layer. Below this depth, the concentrations increased again until they reached a stable level that most likely represented the concentration of the parent material. This point was usually reached at depths no deeper than 1 m, and the composition of P from this depth down was typically dominated by sulfuric acid-soluble, supposedly apatitic, P and contained very little ammonium fluoride-soluble

secondary P (Kaila, 1963c). These trends of total P and its composition of primary and secondary forms seem characteristic for most of the mineral soils in Finland.

According to the balance calculations of Saarela (2002), the cumulative surplus of P in the cultivated soils in Finland has been approximately 1000 kg ha⁻¹ during the last seven decades. Studies by Kaila (1963a) suggest that most of the surplus P has accumulated in the top 20 or 30 cm of soil (plow layer), but no detailed studies on the topic have been carried out. The fate of the fertilizer P within the plow layer soil, on the other hand, has been studied extensively: A massive amount of data indicates that the fertilizer P is retained in the plow layer soils predominantly as ammonium fluoride-soluble P, supposedly sorbed to the Al oxides, and as sodium hydroxide-soluble P, supposedly sorbed to the Fe oxides (e.g. Kaila, 1963a; Kaila, 1963d; Kaila, 1964a; Kaila, 1964b; Kaila, 1965; Hartikainen, 1989). As predicted by the theory of reversible sorption on the short-range-ordered oxides, these same P fractions are also active when the soil P reserves are depleted (Hartikainen, 1989). The size of the sulfuric acid-soluble P fraction, representing supposedly calcium phosphates, does not generally respond to fertilization, unless rock phosphates are used as fertilizers (Kaila, 1965; Hartikainen, 1989). These findings demonstrate that the retention of inorganic P in the surface soils of Finland is, by and large, controlled by reactions with the Fe and Al oxides. Some P may also accumulate in the surface soils in organic forms (Kaila, 1965). The content of organic P in the plow layers of the cultivated mineral soils in Finland varies typically from 100 to 940 mg kg⁻¹ representing, on average, 35% of the total P content (Kaila, 1963b). Both the absolute content of organic P, as well as its proportion of total P, diminishes rapidly below the surface horizon.

The increased saturation of the sorptive Fe and Al oxides due to the positive P balance has improved the solubility of P in the surface soils. The mean of thousands of commercial soil test results in Finland (acid ammonium acetate extraction) from 1955 until 1960 (5.4 mg dm⁻³) more than doubled for the period from 1981 to 1985 (11.8 mg dm⁻³, Kähäri *et al.*, 1987). The effects of the positive P balance on the P status of subsoils cannot be evaluated in the records of commercial soil test results because the method is commonly applied on surface soils only. Several less extensive studies involving other soil P tests (Kaila, 1963a; Jokinen, 1984), sorption-desorption experiments (Kaila, 1963a; Hartikainen, 1979) and calculated saturation degrees (Yli-Halla *et al.*, 1998) suggest, nevertheless, that the enhanced solubility of P is restricted to the surface soils only. This assumption

– like most assumptions of the P composition in the soil profiles in Finland – suffers from ambiguities in the descriptions of soil sampling in the research reports.

The P content of the agricultural soils in Finland is still increasing. Saarela (2002) estimated the mean P balance of the cultivated soils to be $+10 \text{ kg ha}^{-1} \text{ year}^{-1}$; Antikainen *et al.* (2005) made a somewhat higher estimate, $+13 \text{ kg ha}^{-1} \text{ year}^{-1}$. On most soils, a slightly positive P balance is a prerequisite of economically sustainable production: Saarela *et al.* (2003) estimated that a P balance from $+6$ to $+15 \text{ kg ha}^{-1} \text{ year}^{-1}$ is required to maintain the soil test results at levels considered to be “satisfactory” or “good”. This indicates that the “pedological sink” is active in these soils. From an environmental point of view, it is crucial that the capacity of this sink is not overloaded with excessively positive P balances. In this sense, the overall situation in Finland seems manageable compared to the areas of very intensive agricultural production with positive P balances of up to $57 \text{ kg ha}^{-1} \text{ year}^{-1}$ (Sibbesen and Runge-Metzger, 1995).

1.3 Objectives of the work

Soil P has been studied extensively in Finland, but most of the work has concentrated on analyzing soil samples from the surface soil only and few data exist on complete soil profiles. Consequently, many questions on the composition, reactions or mobility of P at a pedon scale, or on the behavior of soil P during soil development in our youthful soils can only be answered indirectly. The objectives of the experiments described in this thesis were to describe the P composition of complete soil profiles in cultivated mineral soils of Finland, to measure the vertical variability of the P retention capacity in the profiles, to test if the properties inferred from the general theory of P and soil formation apply in the studied soils, to improve research practices for studying soil P, and finally, to explore if the P retention properties of the soil profiles could be utilized for an improved soil P management.

2 Material and methods

2.1 Soil description

Most of the work described in this thesis was carried out on soil samples taken at four locations: Sjäkulla, Kotkanoja, Toholampi and Loppi (Figure 2.1). These sites were chosen primarily to represent fine-textured soils of poor (Kotkanoja) and good (Sjäkulla) P status and coarse-textured soils of poor (Toholampi) and good (Loppi) P status. The first three soils were located on established research sites which were equipped with facilities for monitoring the P losses through surface runoff and a subsurface drainage system. The Loppi site was chosen essentially for its exceptionally high P status: the agronomic P status of the soil, based on an acid ammonium acetate extraction, was “excessive”, while that of the other three soils was “fair” or “satisfactory”. All soils were located in principal agricultural areas of the country with typical crops of small grains and grass ley on the Kotkanoja and Toholampi sites, small grains on the Sjäkulla site, and small grains and sugarbeet on the Loppi site. All soils have a subsurface drainage system.

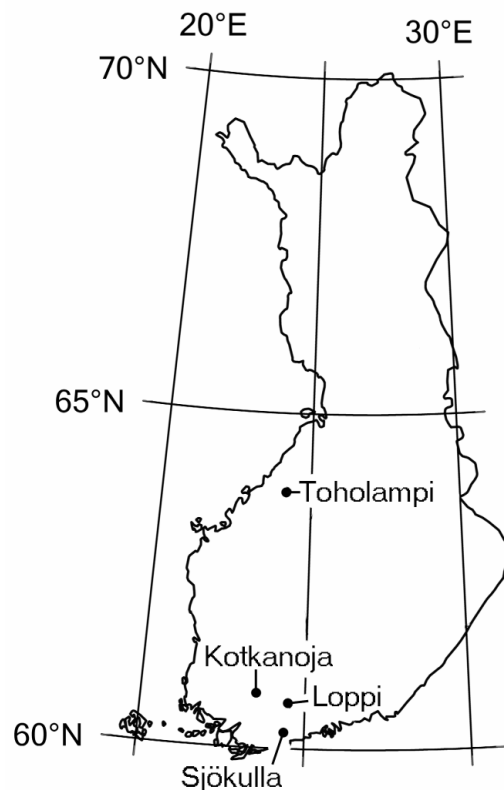


Figure 2.1 Locations of the soils used in the experiments.

The classification of the soils was made according to the eighth edition of the *Keys to Soil Taxonomy* (Soil Survey Staff, 1998). A common feature for all soils is a cryic soil temperature regime (see Yli-Halla and Mokma, 1998). In addition, the Sjököulla soil has a diagnostic cambic horizon (2Bw, Table 2.1) and aquic conditions (artificial drainage), as well as mottlings and chroma of 2 in the horizon 2Bw and chroma of 3 in the horizon Ap2. Based on these attributes, the soil is classified as an Aeric Cryaquept. The classification can be extended tentatively to a *very fine mixed Aeric Cryaquept*. The Kotkanoja soil also has a cambic horizon (Bw1-2Bw3), aquic conditions (artificial drainage), low chroma and mottlings in the Bw1 and 2Bw3 horizons, and is classified as a Typic Cryaquept. The tentative classification to the family-level is a *very fine mixed Typic Cryaquept*. The Toholampi soil has a spodic subsurface horizon containing redoximorphic features (Bs; and artificial drainage) and it is classified as a Typic Cryaquod. The albic horizon of the soil has been incorporated into the Ap horizon by tillage. A tentative family-level name for the soil is a *coarse-silty siliceous Typic Cryaquod*. The Loppi soil has a cambic horizon (Bs-Bw) and an anthropic epipedon (citric acid-soluble P₂O₅ 1752 mg kg⁻¹), and is classified as a Typic Haplanthrept – tentatively a *fine-silty siliceous frigid Typic Haplanthrept*.

The clay soils were classified into the same Great Group (Cryaquepts) as (supposedly) are most of the clay soils in Finland. The classification of the Toholampi Spodosol does not match exactly the most typical Great Group of the podsolized coarse mineral soils in Finland (Haplocryod). A near-by pedon at the same experimental field was, however, previously classified as an Aquic Haplocryod (Yli-Halla *et al.*, 2000) which can be expected to exhibit properties very similar to a Typic Cryaquod. The representativeness of the Loppi soil is uncertain since no Haplanthrepts have been previously reported in Finland. High soil P test results are not, however, uncommon in coarse mineral soils used for growing potatoes or sugarbeet. If the P content of the Ap horizon in this soil were lower, the soil would most likely be classified as an Oxyaquic Eutrocrept, which is considered a typical taxon for the fine sand soils in Finland.

In Article IV, two additional soils were used. One of them, the Lintupaju clay soil, is a Typic Cryaquept located close to the Kotkanoja site, and the other, the Loppi2 soil, is a Terric Cryosaprist located close to the Loppi soil. A short description of these soils is provided in Article IV.

Table 2.1 Properties of the soils.

Horizon	Depth cm	Texture	Clay %	Mineralogical features	OC ^a %	pH ^b	CEC ^c cmol(+) kg ⁻¹	Matrix color ^d Dry	Structure	Moist consistence
<i>Sjökulla, Aeric Cryaquept (Lat 60° 14.484', Lon 24° 23.123'^e; 43 m a.s.l.^f)</i>										
Ap1	0-20	sic ^g	49	quartz, K-feldspar, plagioclase, mica	2.1	4.4	23.7	2.5Y6/2	2 vf sbk ^h	fr ⁱ
Ap2	20-29	sic	50	quartz, K-feldspar, plagioclase, mica	2.5	5.2	26.0		2 m abk	fi
2Bw	29-46	c	83	illitic mica, chlorite	0.7	5.7	30.4	*	2 c abk	fi
2BC ^j	46-70	c	89	illitic mica, chlorite	0.4	6.2	30.7		2 m abk	fr
3C ^j	70-	c	80	mica, chlorite	0.2	7.0	27.7	*	3 c pl	fr
<i>Kotkanoja, Typic Cryaquept (Lat 60° 48.946', Lon 23° 30.638'; 99 m a.s.l.)</i>										
Ap	0-24	c	48	quartz, K-feldspar, hornblende, mica	2.5	6.5	25.2	7.5YR6/2	2 vf sbk	fr
Bw1	24-32	c	58	plagioclase, quartz, K-feldspar, mica	0.6	4.8	19.3	*	2 m abk	fr
2Bw2	32-56	c	80	illitic mica, chlorite	0.4	5.3	30.1		2 c abk	s (wet)
2Bw3	56-76	c	83	illitic mica, chlorite	0.3	5.6	30.2	*	2 m abk	fr
3C ^j	76-	c	76	mica, chlorite	0.3	5.8	22.8		3 c pl	fr
<i>Toholampi, Typic Cryaquept (Lat 63° 49.316', Lon 24° 9.660'; 84 m a.s.l.)</i>										
Ap	0-27	sil	4	K-feldspar, quartz, plagioclase	3.0	5.0	12.4	10YR5/3	1 f sbk	fr
Bs	27-39	sl	2	K-feldspar, quartz, plagioclase	1.2	4.5	7.9	*	1 f sbk	fr
2Bw	39-62	sil	8	plagioclase, quartz, hornblende	0.2	4.4	4.0	*	1 f sbk	fr
2BC	62-140	si	7	plagioclase, quartz, hornblende	0.1	4.4	4.4		2 m sbk	fr
2C	140-	si	8	n.d. ^k	0.1	4.6	2.6	n.d.	n.d.	n.d.
<i>Loppi, Typic Haplanthrept (Lat 60° 40.956', Lon 24° 29.213'; 115 m a.s.l.)</i>										
Ap	0-30	sl	9	quartz, plagioclase, K-feldspar	3.6	6.7	17.7	2.5Y5/2	2 m sbk	fr
Bs	30-49	sl	8	quartz, plagioclase, K-feldspar	0.5	6.2	5.1		2 c sbk	fr
Bw	49-65	sl	7	quartz, plagioclase, K-feldspar	0.3	6.0	3.5		2 c sbk	fr
2C	65-	sil	19	quartz, plagioclase, K-feldspar, mica	0.1	5.5	6.3	*	2 m abk	ef

^a OC = organic carbon; ^b pH measured in 0.01 M CaCl₂; ^c CEC = cation exchange capacity at pH 7.0; ^d Colors according to the Munsell notation, an asterisk refers to mottles or other redoximorphic features in the horizon; ^e Datum WGS84; ^f m a.s.l. = meters above sea level; ^g sic = silty clay, c = clay, sil = silty loam, sl = sandy loam, si = silt (Schoeneberger *et al.*, 1998); ^h 1 = weak, 2 = moderate, 3 = strong, vf = very fine, f = fine, m = medium, c = coarse, sbk = subangular blocky, abk = angular blocky, pl = platy (Schoeneberger *et al.*, 1998); ⁱ fr = friable, fi = firm, s = sticky, ef = extremely firm (Schoeneberger *et al.*, 1998); ^j Ditactic stratification; ^k n.d. = not determined.

The genesis and basic properties of the soils are discussed briefly in Article I. A characteristic feature for all the soils is that they have been formed from more than one parent material (different parent materials are denoted by the numerical prefixes of the horizons in Table 2.1.). This is common for many of the cultivated mineral soils of Finland because they are typically formed on alluvial and shallow eolian deposits with distinct textural variation within the profile. This feature prevents applying methods that are based on assumptions on the homogeneity of the parent material, such as the pedogenic index (e.g. St. Arnaud *et al.*, 1988).

2.2 Soil sampling and sample storage

The soils were described and sampled in August of 1997. On each site, a single pit was excavated, and the soil samples were taken from the pit wall after denoting the genetic horizons in the profiles. The bulk samples were transported to the laboratory in plastic bags, sieved through a 5 mm sieve, homogenized, and divided into subsamples that were stored at different conditions. The sets of subsamples were:

- stored at +5°C at the sampling moisture,
- stored frozen at -18°C at the sampling moisture,
- air-dried and stored at +25°C,
- air-dried and stored frozen at -18°C.

The effects of the storage conditions on the results of the P sorption experiments, the extractability of P with water, and on the solubility of Fe, Al, and Mn oxides in the samples are discussed in detail in Articles II and III. Air-drying altered the P sorption properties of the soils strongly in comparison to the field-moist samples – consequently, the use of air-dried soil samples in the sorption experiments was limited for comparative purposes. All laboratory analyses were completed within three years from the sampling.

2.3 Laboratory analyses

The descriptions of the major analyses used for describing soil P or the P sorption properties are given here. The details of the supporting analyses are provided in the original publications. Articles I and III are mainly characterizations of the soil profiles using various methods; Articles II and IV include also experimental arrangements.

Total concentration of P

The total P concentration of the soil was determined in air-dried soil samples: First, 0.1 g of soil was digested with aqua regia ($\text{HNO}_3 + \text{HCl}$) and concentrated hydrofluoric acid (HF) on a hot plate. The P was then dissolved in boric acid (H_3BO_3), and the P concentration was determined in diluted samples with a spectrophotometer using an ascorbic acid method of Kuo (1996).

Chang and Jackson P fractions

Soil P reserves in the air-dried soil samples were characterized using a sequential fractionation method developed originally by Chang and Jackson (1957) and modified by Hartikainen (1979):

- 1) Easily soluble P and exchangeable calcium were removed from the soil with 1 M ammonium chloride (NH_4Cl) using a soil-to-solution ratio of 1:50 and an extraction time of 30 minutes.
- 2) Secondary P that was supposedly bound to the Al oxides was extracted with 0.5 M ammonium fluoride (NH_4F) at pH 8.5 using a soil-to-solution ratio of 1:50 and an extraction time of one hour.
- 3) Secondary P bound to the Fe oxides was extracted with 0.1 M sodium hydroxide (NaOH) using a soil-to-solution ratio of 1:50 and an extraction time of 16 hours.
- 4) The P bound to calcium was extracted with 0.25 M sulfuric acid (H_2SO_4) using a soil-to-solution ratio of 1:50 and an extraction time of one hour.

In between the last three extractions, the soil was washed with a saturated solution of sodium chloride (NaCl). The concentration of P in the extracts was measured with a molybdenum blue method and a photometer. In the text, the fractions are referred to as $\text{NH}_4\text{Cl-P}$, $\text{NH}_4\text{F-P}$, NaOH-P , and $\text{H}_2\text{SO}_4\text{-P}$, respectively. The reductant-soluble and occluded P fractions of the original method were not determined, because prior studies (Kaila, 1963a; Kaila, 1964a) have shown that the proportion of these fractions of the total P is insignificant, and that the fractions do not respond to fertilizer treatments or display any variability according to soil type or sampling depth.

Oxalate-extractable Al, Fe, and Mn

Two methods were used to measure the concentrations of short-range-ordered oxides of Fe, Al, and Mn in the soils. In Article I, the metals were extracted in air-dried soil samples using a method described by Schwertmann (1964): 1.0 g soil samples were extracted with 50 ml of acid ammonium oxalate (57% 0.2 M ammonium oxalate ((NH₄)₂C₂O₄•H₂O) and 43% 0.2 M oxalic acid (H₂C₂O₄•2H₂O), pH 3.0) for four hours in the dark. The samples were then centrifuged and filtered through a Schleicher & Schüll 589³ filter paper. The concentrations of Al and Fe were determined in the filtrates with inductively coupled plasma atomic emission spectroscopy (ICP-AES), and the concentration of P was determined, after decomposition of the oxalate with hot concentrated nitric acid (HNO₃), with a molybdenum blue method. The results were also used in Article III.

In Articles II and IV, the oxalate-extractable metals were extracted with 0.05 M ammonium oxalate ((NH₄)₂C₂O₄•H₂O, pH 3.3). The amount of soil in the extractions was 2.5 g and it was extracted with 50 ml of ammonium oxalate for two hours in the dark (Niskanen, 1989). The suspensions were centrifuged and filtered through a Schleicher & Schüll 589³ filter paper prior to the measurement of Fe, Al and Mn with inductively coupled plasma mass spectroscopy (ICP-MS). This less concentrated extractant is commonly used in Finland to avoid analytical problems induced by the matrix of the strong oxalate-extractants. It is considered to extract Al and Fe from the same pools as the stronger extractants. In the soils of this study, this assumption held for Al but not for Fe – especially not in the clay soils (Table 2.2). In addition, the sample storage practice seemed to affect the results. Owing to the variation in the methodology and sample preparation, the interpretations and comparisons of the oxalate-extractable metals between the articles have to be made cautiously. The results obtained with the method of Schwertmann (1964) using the air-dried soil samples most likely corresponds best to previously published data. The denotions Al_{ox} and Fe_{ox} are used in the articles to refer to the oxalate-extractable metals irrespective of the extraction method.

P sorption capacity and P saturation of the oxides

The concentrations of oxalate-extractable metals (Fe_{ox} and Al_{ox}, mmol kg⁻¹) were used to calculate the theoretical P sorption capacities of the soils (PSC, mmol kg⁻¹) according to Lookman *et al.* (1995b):

$$\text{PSC} = 0.5 \times (\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}}) \quad (1)$$

Table 2.2 Results for the acid oxalate-extractable Al and Fe and the degrees of P saturation obtained with two different methods and air-dry or field-moist samples stored for various periods of time. The degree of P saturation is calculated as a molar ratio of the secondary Chang and Jackson P fractions (NH₄Cl-P + NH₄F-P + NaOH-P) in air-dry samples to 0.5 × the sum of oxalate-extractable Al and Fe.

Method ^a	Sample	Time from sampling (months)								
			<i>Sjökulla</i>		<i>Kotkanoja</i>		<i>Toholampi</i>		<i>Loppi</i>	
			Ap1	2Bw	Ap	2Bw2	Ap	Bs	Ap	Bs
			Oxalate-extractable Al (mmol kg ⁻¹)							
Schwertmann	Air-dry	14	86.9	103.6	103.3	109.0	91.1	103.1	131.4	221.4
Niskanen	Air-dry	22	80.5		89.4		93.8		129.1	
Niskanen	Moist	22	74.5		77.5		78.8		96.2	
Niskanen	Moist	36	61.1	61.0	76.3	58.9	91.5	101.8	115.7	190.3
			Oxalate-extractable Fe (mmol kg ⁻¹)							
Schwertmann	Air-dry	14	145.7	124.7	234.7	134.4	41.8	60.6	75.0	71.8
Niskanen	Air-dry	22	74.5		97.4		38.1		54.3	
Niskanen	Moist	22	64.4		64.4		32.8		40.3	
Niskanen	Moist	36	56.2	38.6	78.9	39.9	37.8	47.2	44.0	35.5
			Degree of P saturation (%)							
Schwertmann	Air-dry	14	7.7	2.6	8.4	3.8	9.7	2.6	36.0	7.2
Niskanen	Air-dry	22	11.5		15.1		9.8		40.5	
Niskanen	Moist	22	12.8		19.9		11.6		54.4	
Niskanen	Moist	36	15.4	4.9	18.3	8.9	10.2	3.1	46.0	9.3

^a The method of Schwertmann (1964) was used in Articles I and III (analyzed in duplicates), the method of Niskanen (1989) was used in Articles II and IV (analyzed in triplicates).

The saturation of the theoretical sorption capacity with P was estimated by calculating the molar ratio of the sum of the secondary Chang and Jackson P fractions (NH₄Cl-P, NH₄F-P and NaOH-P) to the sorption capacity:

$$\text{DPS} = (\text{NH}_4\text{Cl-P} + \text{NH}_4\text{F-P} + \text{NaOH-P}) / (0.5 \times (\text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}})) \times 100 \quad (2)$$

where DPS stands for the degree of P saturation (%), and the concentrations of P are expressed in mmol kg⁻¹. The original approach of using the oxalate-extractable P in the calculations for the P saturation (Lookman *et al.*, 1995b) was rejected because the acid oxalate solution extracts significant amounts of primary apatitic P in the poorly weathered soils of Finland and thus, overestimates the P saturation of the oxides. This issue is examined thoroughly in Article I.

The modifications of the oxalate extraction have self-evident effects on the results of the P sorption capacity and the degree of P saturation (Table 2.2). In addition, the results are strongly affected by the uncertainty related to the correction factor of PSC in Equation 1; hence, no hasty comparisons should be made across different oxalate extraction methods, sample preparations or drastically different soils.

Sorption properties of the soils

The sorption of P in the soils was studied with a quantity/intensity (Q/I) plot technique: 1 g (dry weight) of soil was equilibrated with 50 ml of P solution (KH_2PO_4) containing various concentrations of P for 21 hours at $+25^\circ\text{C}$ on an orbital shaker. No supporting electrolytes were added. After the equilibration, the suspensions were filtered through a 0.2- μm Nuclepore[®] polycarbonate filter and the P concentrations of the filtrates were measured with an ascorbic acid method in a flow-injection analyzer (the details of the method are provided in Section 2.4). The amount of sorbed or desorbed P was calculated from the difference in the P concentrations in the solution before (I_0) and after (I) the equilibration. For each soil, a total of ten Q/I points (five P concentrations with duplicates) were obtained using I_0 concentrations either from 0 to 10 mg l^{-1} or from 0 to 2 mg l^{-1} . The concentrations of water-extractable P ($\text{P}_{\text{H}_2\text{O}}$) were calculated from the filtrates of zero P addition.

In Articles II and IV, the following modification of the Freundlich adsorption equation (Russel and Prescott, 1916) was fitted to the Q/I points obtained:

$$Q = Q_0 + k \times I^N \quad (3)$$

where Q is the amount of P sorbed (or desorbed), Q_0 is a parameter for “readily desorbable” or “instantly labile” P (Beckett and White, 1964; Fitter and Sutton, 1975), I is the P concentration in the solution at the end of the equilibration, and k and N are fitting parameters. The fitting was made using a straightforward nonlinear least squares fitting by applying the Davidon-Fletcher-Powell iterative numerical method (Mustonen, 1992) that minimizes the residual sums of squares parallel to the Q -axis.

In the most recent Article III, a more sophisticated method of fitting the sorption equation was used. As above, the amount of sorbed or desorbed P was calculated from the difference between the initial P concentration (I_0) and the concentration after the equilibration (I) according to Equation 4. A modified Freundlich adsorption equation (Equation 5) was then fitted to the observations by applying Equations 4 and 5 simultaneously, and by minimizing the sum of squares for the difference between the predicted and measured values for I , as in Barrow (2000). The equations were:

$$Q = (I_0 - I) \times R \quad (4)$$

$$Q = a \times I^b - q \quad (5)$$

where Q and I are as in Equation 3, I_0 is the initial P concentration in the solution, R is the solution-to-soil ratio, a and b are fitting parameters, and q is the amount of P that would be desorbed if I were decreased to zero (corresponds to Q_0).

The first fitting procedure was rejected as being inappropriate. In sorption experiments, the amount of sorption is calculated using the observed concentration; Sorption (Q) and concentration (I) in Equation 3 are thus not independent variables, and this negates the regression theory. It is better to relate the observed concentration to the experimental variables: the solution-to-soil ratio and the initial P concentration. Nevertheless, even though the first method of fitting can be regarded as being fundamentally incorrect, it does produce sorption curves that are practically identical to the latter method (Figure 2.2).

Acid ammonium acetate extractable P

Acid ammonium acetate extraction is the commercial soil test for P in Finland. In Article I, this test was conducted according to the original procedure (Vuorinen and Mäkitie, 1955): 25 cm³ of soil was extracted with 250 ml of acid ammonium acetate solution (0.5 M CH₃COONH₄, 0.5 M CH₃COOH, pH 4.65) for one hour at room temperature, then the suspension was filtered through a Schleicher & Schüll 589³ filter paper, and the concentration of P was measured with an ascorbic acid

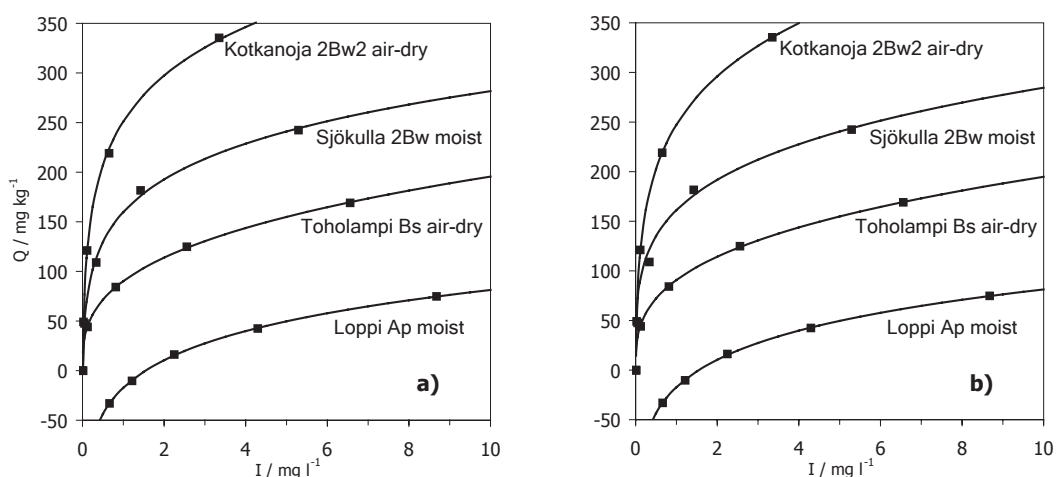


Figure 2.2 Modified Freundlich sorption curves fitted to the experimental data of four different soils with a) a regular least-squares-method (Articles II and IV) and b) with simultaneous equations according to Barrow (2000) (Article III).

method. The result was calculated for a volume of soil according to the standard procedures of commercial soil testing in Finland. In Article IV, where two soil samples were mixed for the extractions, the soils were weighed for the analysis to allow more accurate mixing of the samples. The results were also reported on a weight basis.

2.4 Quality control

Practically all laboratory analyses reported in this thesis were carried out in the laboratory of Agricultural Chemistry and Physics at the Department of Applied Chemistry and Microbiology. This laboratory does not have a comprehensive quality assurance system, but several measures were taken to guarantee the quality of the data. For example, all raw data was checked by two individuals prior to further processing. All analyses were also carried out in at least two replicates.

The water used in preparing the extractants and reagents fulfilled (at least) the criteria of Grade 3 for the water used in an analytical laboratory (SFS-ISO 3696). The quality of the water was routinely controlled by measuring its electrical conductivity and by plotting the results on a control chart. Batches of water having higher conductivity than the control limit ($3 \times$ standard deviation in the control chart) were rejected. The mean electrical conductivity of the water used was 0.08 mS m^{-1} . Analytical grade chemicals were used for preparing all reagents.

The stability of the balances used for weighing the soil samples for the analyses and the chemicals for the reagents were controlled daily by weighing a test weight (a nominal weight of 5.0 or 10.0 g) and recording the result on a control chart. In addition, the balances were calibrated twice during the experiments with a set of test weights traceable to the national measurement standards.

All the sorption experiments and water extractions were conducted in controlled-temperature rooms. The temperatures of these rooms were monitored with a data logger, and the output of the logger was verified by using a precision thermometer (Amarell Certificate #2623). The range of the temperature readings in the constant temperature room during the sorption experiments was from 22.4 to 24.9 °C (nominal 25 °C). The same constant temperature rooms were also used to study the effects of sample storage practices (Article II).

All the PO₄-P concentrations of the samples from the sorption experiments (Articles II, III and IV) and the water extractions (Articles I, III and IV) were measured with a Lachat flow injection analyzer (FIA) applying a modified Lachat QuikChem Method 10-115-01-1-B (Lachat Instruments, 1994). The essential characteristics of the modified method were: limit of detection 0.001 mg l⁻¹, relative standard deviation less than 5% at concentrations higher than 0.01 mg l⁻¹, and linearity up to 2.0 mg l⁻¹. The sample throughput was approximately 1 sample in 50 seconds, at which a small memory effect was detected at the highest concentrations. Therefore, the samples were diluted to obtain concentrations typically between 0.1 and 1.0 mg l⁻¹. The absorbance was measured for all samples both with all reagents (of the ascorbic acid method) and without the ascorbic acid reductant (blank). The difference in the readings was converted to a PO₄-P concentration in a spreadsheet with a linear regression against the readings of standard solutions made of dried potassium dihydrogen phosphate (KH₂PO₄) and treated identically with the samples. Two readings were obtained for each sample, and the mean of the results was used in the calculations. When the difference between the two absorbance readings was suspiciously large, the result was rejected and the sample was reanalyzed. Control charts were used to monitor the stability of the flow injection analyzer. In each run of samples, a minimum of four reference solution samples were included, and the primary signal (in μVs) for these samples was measured and recorded on a control chart. An example of such a chart

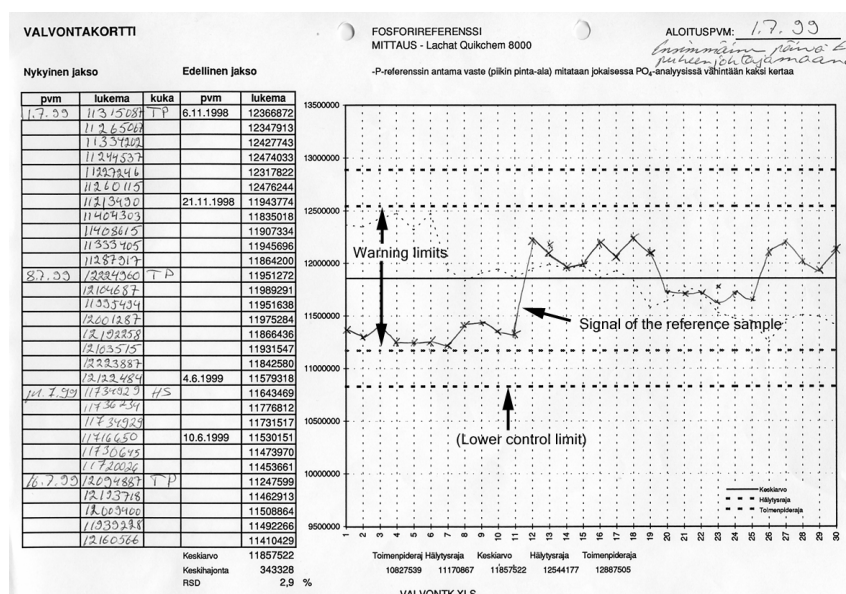


Figure 2.3 An example of a control chart used in quality assurance: The chart used for monitoring the stability of PO₄-P analysis with a flow injection analyzer in July, 1999 shows that the reference P sample has produced a stable signal not crossing the warning limits determined during the preceding monitoring period (11.2×10^6 and 12.5×10^6 μVs; $2 \times$ standard deviation of the readings during the period).

is given in Figure 2.3. The stock reference solution was prepared by dissolving KH_2PO_4 into a sodium hydroxide (NaOH) solution (American Public Health Organization, 1985). For the analyses, the stock solution was diluted to obtain a reference sample concentration of 0.62 mg l^{-1} .

The use of control samples in the laborious sorption experiments is not feasible, and it is difficult to obtain quantitative estimates of the precision of the Q/I method. A crude perception of the repeatability can be based on sorption curves determined at discrete occasions – keeping in mind that besides deficient repeatability, the differences in sorption curves can be induced by possible changes in the sorption properties of the soils during the sample storage. Figure 2.4 presents an example of repeatedly determined sorption curves for two soils. It shows that the general form of the curve is reasonably well reproduced on separate occasions with the method used, but the repeatability of the estimates obtained for the parameters of the modified Freundlich equation is poor. The statistical problems in estimating the values of the individual parameters of the equations are discussed in detail in Article III.

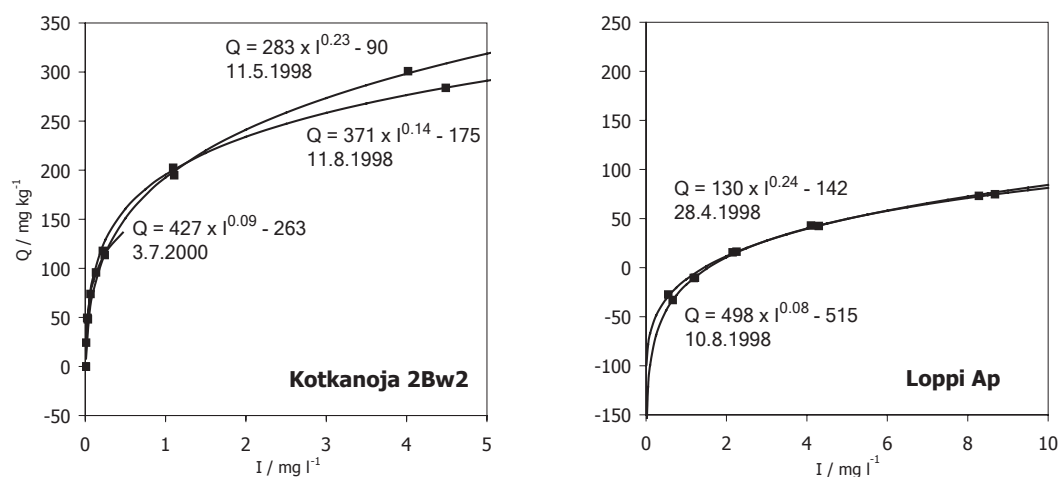


Figure 2.4 Sorption curves and the modified Freundlich equations determined for two soil samples on different occasions. The range of the initial P concentrations of the solutions was from 0 to 10 mg l^{-1} except in the experiment on the Kotkanoja 2Bw2 soil on July 3, 2000, where it was from 0 to 2 mg l^{-1} . Note the different scales on the Q and I axes.

3 Results and discussion

3.1 Phosphorus in the soil profiles

The distribution and forms of P in the four pedons corresponded well to the expectations based on the general theory of the effects of soil formation on P, and on previous inexplicit observations of P in soil profiles in Finland. Overall, the P composition of the soils reflected weakly developed soils having an apparent human impact only in the Ap horizons.

3.1.1 Total phosphorus

The concentrations of the total P in the C horizons (729–810 mg kg⁻¹; Table 3.1) were higher than the mean concentration of the most typical parent material of the mineral soils in Finland (690 mg kg⁻¹; Koljonen, 1992) probably because only the most fertile soils have been cleared for cultivation. Previously, Salonen (1941) has measured comparable total P concentrations (810–880 mg kg⁻¹) for samples taken at depths from 60 to 80 cm.

In all four soils, the minimum concentration of total P was encountered in the B horizons at a mean depth of 40 cm. This agrees with the results of Kaila (1963c), who measured the minimum total P concentrations at depths from 20 to 50 cm in ten cultivated mineral soils. The good agreement in the total P concentrations between the studied C horizons and the samples taken previously at corresponding depths, as well as the common increase in the concentrations below a minimum no deeper than at 50 cm, suggests that the approximate depth of 70 cm of the upper boundaries of the C (or BC) horizons observed in this study is typical for the cultivated mineral soils in Finland.

The total P concentrations in the Ap horizons were distinctly higher than those in the below-laying B horizons in all soils (Table 3.1; Figure 1 in Article I). Phosphorus is enriched in the surface horizons through natural processes, but the total P concentration of the uncultivated surface soils in Finland varies typically from 600 to 880 mg kg⁻¹ (Kaila, 1963c). Of the four soils examined, only the P-poor Toholampi soil fits into this range. In the Ap horizons of the three other soils, especially in the Loppi and Kotkanoja soils which have concentrations in the Ap horizons that noticeably exceed those in the C horizons, a significant proportion of the P must originate in fertilizers and manure. Also Williams and Saunders (1956)

assigned higher total P concentrations in the surface horizons than in the parent material to fertilization. In sloping areas, the total P concentration of the surface horizons may be increased by lateral transport of P (Smeck, 1985; Letkeman *et al.*, 1996). This is not likely in the studied soils since all profiles were located in shoulder or backslope positions.

In the Loppi Ap horizon, the intensive fertilization of sugarbeets and past manuring has increased the total P concentration to a level (1870 mg kg^{-1}) that affects even the classification of the soil. Such concentrations are excessive but not unforeseen in Finland; total P concentrations as high as 1830 mg kg^{-1} in the surface soils were reported more than forty years ago (Kaila, 1963c). This, together with the continuous surplus in the P balance of our soils during the last decades, suggests that Anthropogenic epipedons may not be extremely rare in Finland. One estimate of their occurrence can be based on the records of the results of commercial soil tests: approximately 2–3% of the agricultural soils in Finland have a soil P status as high or higher than the Loppi soil (see Yli-Halla, *et al.*, 2001).

The general distribution of the total P in the studied profiles is typical for weakly weathered soils: high concentrations in the fertilized Ap horizons, a minimum in the B horizons, and a concentration in the C horizons that corresponds approximately to the concentration of the parent material. In mature soils, the distribution of the total P may have more complicated patterns and may contain more than one peak of total P within the profile (Smeck and Runge, 1971).

3.1.2 Phosphorus fractions

C horizons

The most characteristic features in the P composition of the C and transitional BC horizons below an approximate depth of 70 cm were the dominance of the acid-soluble P ($\text{H}_2\text{SO}_4\text{-P}$) that supposedly represents the primary apatitic P, as well as the resemblance of composition in all four soils. In these horizons, $\text{H}_2\text{SO}_4\text{-P}$ accounted for 81–88% of all the P extractable in the fractionation procedure – or from 50% to 65% of the total P (Table 3.1; Figure 1 in Article I). Secondary P fractions ($\text{NH}_4\text{Cl-P}$, $\text{NH}_4\text{F-P}$, NaOH-P) only represented from 8 to 12% of all the P in the C horizons. According to Kaila (1964a), from 65 to 150 mg kg^{-1} (12–32%) of the P not extracted in Finnish soils during the Chang and Jackson procedure occurs in apatite inclusions inside silicate and quartz crystals. Assuming a similar composition in the studied C horizons, it can be estimated that from 70 to 80% of

the total P in them is apatitic primary P. The rest of the P not accounted for in the fractionation procedure probably occurred in reductant-soluble and occluded forms (not determined in this study). Their combined concentration ranges typically from 45 to 125 mg kg⁻¹ in the subsoils in Finland (Kaila, 1964a). A minute fraction of the subsoil P may be organic (Kaila, 1963b), and a small amount of the P may also replace silica in the silicate minerals (Koritnig, 1965). However, this P, as well as that found in the apatite inclusions in quartz crystals is very persistent against weathering. The most interesting changes in the P composition during soil formation can be expected in the easily soluble P fractions – those extracted with the fractionation procedure used.

Table 3.1 Total phosphorus concentration and the Chang and Jackson phosphorus fractions^a in the soils.

Horizon	Depth cm	NH ₄ Cl-P	NH ₄ F-P	NaOH-P	H ₂ SO ₄ -P	Total P	Unaccounted P ^b
mg kg ⁻¹							
<i>Sjökulla, Aeric Cryaquept</i>							
Ap1	0-20	1.3	66	209	124	969	569
Ap2	20-29	0.6	61	241	130	976	543
2Bw	29-46	0	15	75	175	584	318
2BC	46-70	0	5	41	324	626	256
3C	70-	0	14	49	496	810	250
<i>Kotkanoja, Typic Cryaquept</i>							
Ap	0-24	1.3	99	337	197	1355	720
Bw1	24-32	0	13	117	41	638	468
2Bw2	32-56	0	10	132	41	587	403
2Bw3	56-76	0	10	114	210	668	334
3C	76-	0	10	82	383	770	295
<i>Toholampi, Typic Cryaquod</i>							
Ap	0-27	1.3	136	63	138	689	351
Bs	27-39	0	35	30	296	523	162
2Bw	39-62	0	7	41	430	608	129
2BC	62-140	0	15	90	402	641	134
2C	140-	0	12	61	469	729	186
<i>Loppi, Typic Haplanthrept</i>							
Ap	0-30	25.8	842	284	296	1870	422
Bs	30-49	0	220	108	121	606	157
Bw	49-65	0	170	60	232	695	233
2C	65-	0	15	50	449	741	227

^a Phosphorus soluble in sequential extractions with NH₄Cl, NH₄F, NaOH and H₂SO₄ solutions.

^b Phosphorus not extracted with the fractionation solutions.

The dominance of the acid-soluble P in the subsoil horizons not deeper than 70 cm demonstrates the weak development stage of the soils. High concentrations of acid-soluble P have been measured previously in samples taken at corresponding depths in mineral soils in Finland (Kaila, 1963a; Kaila, 1964a; Hartikainen, 1979) and in Canada (St. Arnaud *et al.*, 1988; Frossard *et al.*, 1989; Zheng *et al.*, 2004). The fractionation results reported by Kaila (1963a) imply that in the coarsest mineral soils in Finland, the weathering of primary P may have extended somewhat deeper than 70 cm, but the sampling scheme of that study does not allow any definite conclusions to be drawn. The P in the C horizons of the more weathered soils is also typically dominated by an acid-soluble component but the upper boundaries are not as close to the soil surface. Allaway and Rhoades (1951) reported that in Nebraska, the C horizons containing mostly acid-soluble P occurred at depths between 70 and 220 cm. In well developed soils, the upper part of the C horizon may also be rich in secondary P due to the leaching from the A and B horizons.

B horizons

The P composition of the B horizons has been altered by soil forming processes. The differences in the P fractions between adjoining horizons can not be explained by the lithological discontinuities within the profiles because the P composition of the horizons formed of *the same parent materials* has clearly been altered (Table 3.1). This is perhaps most evident in the B horizons of the clay soils. The geological history of the parent materials (Donner, 1995) and the similar P compositions of the unaltered C horizons do not imply any significant differences in the original P composition of the parent materials either.

In the B-horizons of the Inceptisols (Sjökulla, Kotkanoja, Loppi), the supposedly primary $\text{H}_2\text{SO}_4\text{-P}$ represented less than 66% of the P extracted in the fractionation procedure (Table 3.1; Figure 1 in Article I), and the proportion of NH_4F - and NaOH -extractable secondary P had increased to up to 78% (Kotkanoja 2Bw2). This transformation from primary to secondary P had occurred concurrently with a decrease in the total P concentration in the B horizons, and it clearly indicates the effects of the soil-forming processes on P. Some of the P released from the parent material in the B horizons through weathering has probably been leached downwards in the profiles, and as a consequence, was measured as secondary P in the C horizons. According to the general concepts of P cycling in developing soils, some of the P has also been translocated to the (current) Ap horizons, stored there, or removed from the soils by lateral transport processes on the soil surface or through harvest. Some of the P in the B horizons may also have been transformed

to occluded P within the B horizons. Examining only the current material does not, however, facilitate any detailed estimates of the amounts of P in each destination.

The unusually high accumulation of P in the Loppi Ap horizon, the small deviations (10-13%) in the sum of the P fractions between the B and C horizons, and the very large proportion of $\text{NH}_4\text{F-P}$ in the B horizons suggest that fertilizer P has moved downwards in the Loppi soil (Table 3.1). Without further evidence, however, this conclusion also remains tentative. Previously, Jokinen (1984) has reported signs of P translocation in another soil used for sugarbeet production in Finland. In areas of intensive agricultural production, fertilizer P, and especially manure P, has increased the secondary P reserves as deep as in the C horizons (e.g. Kao and Blanchard, 1973; Simard, *et al.*, 1995; Eghball *et al.*, 1996; Hountin *et al.*, 2000; Whalen and Chang, 2001).

In the Toholampi Spodosol, a surprisingly large proportion of P was acid-soluble even in the B horizons (Table 3.1; Figure 1 in Article I). Generally Spodosols are not considered to contain much primary P, but secondary and occluded P in addition to organic P (Smeck, 1985). The result may at least partly be due to the young age and to the cold temperature of the Toholampi soil. It is located farthest north, and it emerged from water at least 2000 years later than the Loppi soil (see Donner, 1995). The hydrology of the Toholampi soil also differs from the other soils: Despite the installed subsurface drainage system, infiltration of the runoff water into the Toholampi soil is minimal and in some years, practically all the runoff will occur on the soil surface (Turtola and Kemppainen, 1998). This is likely to decrease the depth of weathering in this soil. Furthermore, the podsolized soil has most likely developed under different vegetation than the three Inceptisols of this study.

Even though the relative distribution of the primary and secondary P fractions in the Toholampi Spodosol differed somewhat from the distribution found in the Inceptisols, all four soils share the typical pattern of subsoil P composition: a decrease of primary P components and an increase of secondary P components towards the soil surface. The most dramatic changes have occurred in the Kotkanoja soil with only one-fifth of the fractionable P in the H_2SO_4 -soluble fraction in the Bw1 and 2Bw2 horizons.

Ap horizons

As noted earlier, the most striking feature in the P composition of the Ap horizons was the high total P concentration as compared to the B horizons. The P added in fertilizers and manure has accumulated primarily in the NH_4F - and NaOH -extractable fractions, but also the amount of P not accounted for in the fractionation procedure is significantly larger in the surface horizons than in the subsoil horizons (Table 3.1). The large NH_4F -soluble and NaOH -soluble fractions in the Ap horizons were expected, because the accumulation of fertilizer P into these fractions in the surface soils has been demonstrated in numerous previous studies (e.g. Kaila, 1963d; Kaila, 1964b; Kaila, 1965; Hartikainen, 1989; Yli-Halla, 1989; Turtola and Yli-Halla, 1998). Moreover, the relative amounts of NH_4F -P and NaOH -P in the soils conform to previous results: It is normal that the clay soils contain more NaOH -P and the coarse mineral soils more NH_4F -P because the allocation into these fractions reflects the concentration of the oxalate-extractable Fe being typically higher than that of Al in the fine-textured soils (Kaila, 1964a; Kaila, 1964b; Kaila, 1965). The relationship between the secondary P fractions and the oxalate-extractable metals is discussed in more detail in Article I.

The attempt to separate secondary P to pools attached supposedly to the Al or Fe compounds in the Chang and Jackson fractionation procedure has been criticized on several occasions (e.g. Olsen and Khasawneh, 1980). According to the critics, NH_4F is not strictly specific for the P in the Al compounds, and the P extracted with NH_4F is resorbed to the Fe compounds during the extraction. Barrow (1989) did not consider the division to separate Al and Fe compounds to be meaningful at all because the soil oxides rarely occur as pure Al or Fe oxides, but usually as mixtures of the two. Were this criticism justified, the two P fractions could be added, and the combined fraction could be considered to represent all the secondary P in the soils. This approach would not, however, affect the essential outcome of this work, which is the interpretation of the effects of soil formation and fertilization on the distribution of the primary and secondary P in the soils. The separation of P into NH_4F -P and NaOH -P fractions can be justified based on their deviating retention and release dynamics in soils (Article I; Hartikainen, 1979; Hartikainen, 1982a; Hartikainen, 1991). In the experiments described in Article IV, the two solutions – as well as H_2SO_4 – also proved to extract highly consistent pools of P even in intentionally mixed soil samples containing 25% or 50% of the material from the B horizons and 75% or 50% material from the Ap horizons (Figure 3.1). The first extractant of the fractionation method, NH_4Cl , did not produce consistent results for the mixed samples because it can not prevent

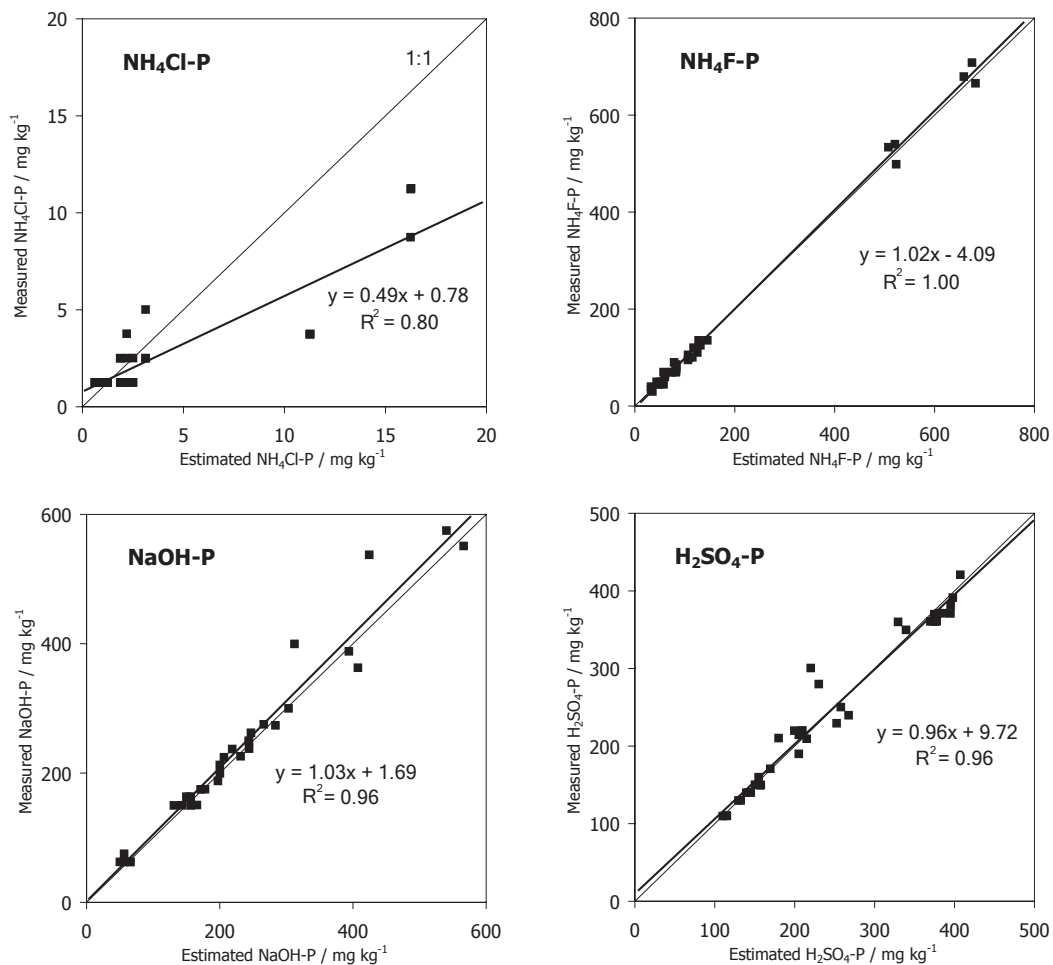


Figure 3.1 Selectivity of the Chang and Jackson P fractionation solutions in intentionally contaminated soil samples. The measured values on the y axes are experimentally determined for soil samples prepared by mixing either 75% or 50% material from the Ap horizon and 25% or 50% material from the associated B horizon. The estimated values on the x axes are calculated for each mixed sample as a mass-weighted average of the pure Ap and B horizon samples. Details of the experiment are given in Article IV.

resorption during the extraction (see Article IV). The experiment on mixed soil samples did not, of course, reveal the true composition of the P pools, and the solutions of the modified Chang and Jackson fractionation scheme can, at best, be described as being selective with unknown specificity.

The concentrations of H₂SO₄-soluble P in the Ap horizons of the Kotkanoja and Loppi soils were clearly higher than in the below-laying B horizons (Table 3.1; Figure 1 in Article I). If all the acid-soluble P in the Ap horizons is primary apatitic P, this would contradict the hypothesis of the most intense weathering occurring at the soil surface. The acid-soluble fraction is usually considered to be inert in the P retention in the mineral soils in Finland, but fertilization with rock-phosphate

(Kaila, 1963d) or generous fertilization with simultaneous liming can increase the acid-soluble P pool in soils (Chang and Jackson, 1958; Kaila 1965; Sample *et al.*, 1980). Both the P content and pH in the Ap horizons of the Kotkanoja and Loppi soils were clearly higher than in the other two soils (Tables 2.1 and 3.1) and the formation of secondary acid-soluble P seems probable. In calcareous soils, analytical problems encountered in the Chang and Jackson fractionation procedure may produce erroneously large results for the acid-soluble fraction if the P extracted with NH_4F is retained as calcium fluoride formed during the NH_4F extraction, and released during the H_2SO_4 extraction (Olsen and Khasawneh, 1980). It is not, however, plausible that the pH values of 6.5 and 6.7 and the modest Ca concentrations of the non-calcareous Kotkanoja and Loppi soils could produce these types of errors.

Organic P

Also in the Ap horizons, the difference between the concentrations of total P and the sum of the P fractions contains some P in apatite inclusions, silicate minerals and in the reductant-soluble and occluded fractions – but also P in organic forms. The amount of P not accounted for in the Chang and Jackson fractionation was considerably larger in the Ap horizons than in the uppermost B horizons: the difference was 189 mg kg^{-1} in the Toholampi soil and from 238 to 265 mg kg^{-1} in the other soils (Table 3.1). In addition, the content of organic matter was significantly higher in the Ap horizons than in the B horizons (Table 2.1). This suggests that a large part of the difference in the P not accounted for between the Ap horizons and the B horizons is organic P. In a study of Kaila (1963b), the mean content of organic P in the surface horizons of cultivated clay soils in Finland was 390 mg kg^{-1} , in loam soils it was 340 mg kg^{-1} , and in fine sand soils, 260 mg kg^{-1} . In the subsoils, the concentration varied less – typically from 60 to 80 mg kg^{-1} . Assuming that the B horizons of this study contain approximately 70 mg kg^{-1} of organic P and that the concentration of the inorganic P not accounted for in the fractionation procedure is similar in the Ap and B horizons, gives an estimate of organic P concentration of 260 mg kg^{-1} for the coarse and P-poor Toholampi Ap horizon and of approximately 325 mg kg^{-1} for the other soils. These figures agree well with the measured results reported by Kaila (1963b). Even these rough estimates indicate that the concentration of organic P is from four to five times higher in the Ap horizons than in the subsoil horizons. This demonstrates the general prevalence of biological processes on soil P in the uppermost horizons and the dominance of geochemical processes in the subsoil horizons (see Wood *et al.*, 1984).

Weathering of primary phosphorus

The basic assumption of the originally homogeneous parent materials together with the present P composition of the soils allow estimates to be made of the total amount of P weathered in the soils. Some of the information needed for these estimates were not measured in the present soils, and they have to be taken from previously published results. Additional uncertainty is introduced by the multiple parent materials of the soils and the uncertainties related to the phenomena extending to geological timescales, and the results should therefore be treated with some caution. According to the calculated estimates, the amount of primary P that has been transformed to secondary P forms in the studied soils varies from 2100 to 2800 kg ha⁻¹ (Table 3.2). These estimates correspond to mean weathering rates from

Table 3.2 Estimated weathering of the primary P (H₂SO₄-P) in the soils.

Horizon	Depth	H ₂ SO ₄ -P		Bulk density ^a	Weathered P	Age of soil ^b	Weathered P
		Measured	Difference to the C horizon				
	cm	mg kg ⁻¹	mg kg ⁻¹	kg dm ⁻³	kg ha ⁻¹	years	kg ha ⁻¹ year ⁻¹
<i>Sjökulla, Aeric Cryaquept</i>							
Ap1	0-20	124	372	1.1	818	9500	0.260
Ap2	20-29	130	367	1.1	363		
2Bw	29-46	175	321	1.3	709		
2BC	46-70	324	172	1.3	538		
3C	70-	496			total 2428		
<i>Kotkanoja, Typic Cryaquept</i>							
Ap	0-24	197	342 ^c	1.1	903	9500	0.290
Bw1	24-32	41	342	1.3	356		
2Bw2	32-56	41	341	1.3	1065		
2Bw3	56-76	210	173	1.3	450		
3C	76-	383			total 2773		
<i>Toholampi, Typic Cryaquod</i>							
Ap	0-27	138	331	1.1	983	8500	0.250
Bs	27-39	296	173	1.4	291		
2Bw	39-62	430	39	1.4	125		
2BC	62-140	402	67	1.4	730		
2C	140-	469			total 2129		
<i>Loppi, Typic Haplanthrept</i>							
Ap	0-30	296	327 ^c	1.1	1079	10500	0.230
Bs	30-49	121	327	1.4	871		
Bw	49-65	232	217	1.4	485		
2C	65-	449			total 2435		

^a Estimates of bulk density based on Erviö (1970).

^b Estimates based on Donner (1995) and Article I.

^c The result of the uppermost B horizon used because of secondary H₂SO₄-P in the Ap horizon.

230 to 290 g ha⁻¹ year⁻¹. This is roughly two or three times more than the estimated leaching losses of total P in the undisturbed forested areas in Finland, which are estimated to average 90 g ha⁻¹ year⁻¹ (Vuorenmaa *et al.*, 2002). Smaller figures for the P losses than for the weathering rate are, of course, expected because not all the P released from the parent material is lost from the soil but transformed to other forms – ultimately to occluded and organic compounds. It is not possible to make more detailed estimates of the long-term P losses from the soils because the records of the P inputs to the soils are not complete.

3.2 Sorption of phosphorus in the soil profiles

The most characteristic features in the sorption properties of all four soils were an enhanced solubility of P in the Ap horizons enriched with secondary and organic P, and a very low solubility in all the subsurface horizons. Besides the amount of secondary P, the sorption properties of the horizons were strongly affected by the concentrations of oxalate-extractable Al and Fe.

Air-drying of the soil samples prior to the sorption experiments affected the results markedly. The drying increased the dissolution of P at small P concentrations, increased sorption at large P concentrations, increased the estimates of the equilibrium P concentration, and thus altered the general shape of the quantity/intensity (*Q/I*) graphs determined for the soils. These effects of drying on the results of the soil P analyses were in agreement with previously published information (e.g. Schofield, 1955; Wiklander and Koutler-Andersson, 1966; Barrow and Shaw, 1980; Olsen and Court, 1982; Haynes and Swift, 1985), and they are discussed in detail in Articles II and III. Because the data obtained with air-dried soil samples may give a biased impression of the dynamics of soluble P in natural conditions, this summary focuses primarily on the results obtained using field-moist samples.

3.2.1 Sorption experiments

A tendency of a soil to sorb P from the soil solution or to release it into the soil solution depends on the relative magnitudes of the concentration of PO₄-P in the soil solution and the equilibrium P concentration (EPC₀; “Null point concentration” in Article III) of the soil. An estimate for the equilibrium P concentration is determined as the crossing point of the sorption curve and the *I*-axis in the *Q/I*

graphs (Figures 2.2 and 2.4). Mathematically, this is the value of I when Q is zero in Equations 3 or 5 (Chapter 2.3).

In this study, the estimates for the equilibrium P concentration were very small for all the subsurface horizons indicating that the subsoils are not likely to release any $\text{PO}_4\text{-P}$ into the soil solution. In most of the B horizons, the estimates were indistinguishable from zero (Table 3.3). The estimates for the Ap horizons were clearly higher than in the subsurface horizons – especially in the Loppi Ap horizon that was enriched with anthropogenic P. Desorption of $\text{PO}_4\text{-P}$ to water is thus possible and probable from all the studied Ap horizons. An overall representation of the estimates for the equilibrium P concentrations (the null point concentrations) in the soil profiles is provided in Figure 3a in Article III.

Table 3.3 Water-extractable P ($\text{P}_{\text{H}_2\text{O}}$) and parameters describing the sorption properties of field-moist soil samples: equilibrium P concentration (EPC_0), P buffering capacity at equilibrium P concentration (PBC_0), sorption at equilibrium concentration of 2 mg l^{-1} (S_2), and P buffering capacity at an equilibrium concentration of 2 mg l^{-1} (PBC_2).

Horizon	Depth cm	$\text{P}_{\text{H}_2\text{O}}$ mg kg^{-1}	EPC_0 mg l^{-1}	PBC_0 liter kg^{-1}	S_2 mg kg^{-1}	PBC_2 liter kg^{-1}
<i>Sjökulla, Aeric Cryaquept</i>						
Ap1	0-20	2.7	0.06	155	71	19
Ap2	20-29	2.7	0.08	172	79	20
2Bw	29-46	0.1	0.00	100139	192	24
2BC	46-70	0.2	0.01	2559	191	21
3C	70-	1.1 ^a	0.02 ^a	878 ^a	130 ^a	20 ^a
<i>Kotkanoja, Typic Cryaquept</i>						
Ap	0-24	4.3	0.09	234	123	33
Bw1	24-32	0.1	0.01	2090	149	21
2Bw2	32-56	0.1	0.01	3566	235	29
2Bw3	56-76	0.1	0.02	1907	211	27
3C	76-	0.2	0.01	1899	147	18
<i>Toholampi, Typic Cryaquod</i>						
Ap	0-27	1.1	0.04	336	114	28
Bs	27-39	0.0	0.00	∞^b	147	29
2Bw	39-62	0.0	0.00	∞^b	62	13
2BC	62-140	0.1	0.01	841	63	11
2C	140-	1.0 ^a	0.04 ^a	192 ^a	42 ^a	8 ^a
<i>Loppi, Typic Haplanthrept</i>						
Ap	0-30	33.0	1.55	26	10	21
Bs	30-49	0.2	0.00	5267	229	27
B	49-65	0.0	0.00	16732	181	24
2C	65-	0.5	0.04	164	47	10

^a Result of an air-dried sample.

^b PBC_0 not applicable because of an extreme buffering capacity; $\lim_{(t \rightarrow 0)} \text{PBC}_0 = \infty$.

The differences in the equilibrium P concentrations between the Ap horizons and the subsurface horizons appeared to be even more extreme when measured in the air-dried soil samples because drying increased the solubility of PO₄-P most radically in the surface horizons (Table 2 in Article III). Especially the estimate for the air-dry Loppi Ap soil (1.82 mg l⁻¹) was very high in comparison to the results reported previously for the surface soils in Finland (mean 0.67 mg l⁻¹; Hartikainen, 1982b). A high equilibrium P concentration in this Anthropogenic epipedon was expected, since the equilibrium P concentrations have been shown to respond readily to fertilization: In the study by Hartikainen (1991), the P amendments of 60 kg ha⁻¹ year⁻¹ for seven years increased the estimates of the equilibrium P concentration in the Ap horizons by as much as 104%. The subsurface soils have been studied less extensively in Finland. The data available suggests that the equilibrium P concentrations in the uppermost B horizons in cultivated soils are typically small (0.01–0.18 mg l⁻¹), even though the results for the respective Ap horizons would be large (0.28–1.72 mg l⁻¹; Sippola and Saarela, 1992; air-dried soils). No reference data for field moist soil samples is available in Finland.

The differences in the (de)sorption properties between the Ap and B horizons are also evident in the results for water-extractable P (Table 3.3). Up to 33 mg kg⁻¹ of P was released into water from the field-moist Ap horizons, but very little from all the subsurface horizons. This result supports the conclusion that desorption of P to water is not likely from any of the studied subsurface horizons. The amount of P extractable with water in the air-dried samples from the Ap horizons ranged from 2.4 to 50.6 mg kg⁻¹ (Table 3 in Article I). This falls within the typical range in Finland: Hartikainen (1982a) measured a mean value of 11.5 mg kg⁻¹ for air-dried samples from the plow layers of cultivated mineral soils. The results for the air-dried samples from the subsurface horizons of this study were all smaller than 1.1 mg kg⁻¹. This is very little when compared to measurements from other studies on air-dried soil samples, and especially when compared to the cases where the impact of fertilization extends to the subsoil horizons. For instance, Simard *et al.* (1995) determined the concentrations of water-extractable P with comparable methods in the B and C horizons to be from 2.1 to 4.1 mg kg⁻¹, and Beauchemin and Simard (2000) from 2.1 to 4.8 mg kg⁻¹.

The P buffering capacity expresses the ability of a soil to resist the changes of the P concentration in the soil solution. In this study, buffering capacities were determined for the soils as the slope of the *Q/I* graphs at the equilibrium P concentration (PBC₀) and at the P concentration of 2.0 mg l⁻¹ (PBC₂). The P

buffering capacity typically decreases when the P status of a soil increases. This is also evident when comparing the buffering capacities of the Ap horizons and the respective B horizons at the equilibrium P concentration (Table 3.3). The highest buffering capacities were measured in all soils for the B horizons, where also the estimates of the equilibrium P concentrations were practically zero. This result is partially attributable to the inherent properties of the Freundlich equation: the slope of the sorption curve increases radically at small concentrations because $\lim_{I \rightarrow 0} dQ/dI = \infty$. This explains why the extreme buffering capacities of the Toholampi B horizons could not even be mathematically resolved. Nevertheless, the great buffering capacities and infinitesimal equilibrium P concentrations in the B horizons illustrate a very high affinity for PO₄-P in the mid-sections of all the profiles. The affinity of the C horizons for PO₄-P seems to be somewhat lower than in the B horizons; the results of the water-extractable P, the equilibrium P concentration and the buffering capacity at the equilibrium P concentration all suggest this (Table 3.3). A graphic representation of the buffering capacities in the soil profiles is given in Figure 3b of Article III.

The amount of sorption in the *Q/I* experiments at the P concentration of 2 mg l⁻¹ (S₂ in Table 3.3) was generally greatest in the B horizons. The difference in sorption at 2 mg l⁻¹ between the Ap and B horizons was not as distinct as in the estimates for either the equilibrium P concentration (EPC₀) or for the P buffering capacity at the equilibrium P concentration (PBC₀), but the effects of the P enrichment on the P retention in the surface soils are still visible. The profile distribution of the sorption results (S₂) is very similar to the distributions of the adsorption maxima found in some previous studies (Eghball *et al.*, 1996). An illustration of this is provided in Figure 3c of Article III. Whereas comparable distributions of sorption results in complete soil profiles have not been published previously in Finland, the superior capacity of the subsoils to retain P as compared to the surface soils has been demonstrated in many studies (e.g. Kaila, 1963a; Hartikainen, 1979).

The modest sorption of P in the subsurface horizons of the Toholampi soil in comparison to the three Inceptisols was unexpected (S₂ in Table 3.3). This result may be explained, at least partially, by the low degree of weathering noted in the fractionation results. Against a common perception, the sorption affinities in Spodosol profiles are also not usually very high (Burnham and Lopez-Hernandez, 1982), although the affinity of the spodic material, as such, might be.

The results of the P sorption experiments carried out with a *Q/I* technique are typically reported using the estimates obtained for the parameters of the sorption equations. In this work, the precision of the estimates for the individual parameters in the modified Freundlich equation (*a*, *b* and *q* in Equation 5) proved to be inferior to the figures calculated from the fitted sorption equations (the equilibrium P concentration, EPC_0 ; sorption at a defined P concentration, S_2 ; the buffering capacity at certain P concentrations, PBC_0 and PBC_2). This issue is discussed more thoroughly in Article III. The poor precision of the Freundlich parameters is also evident in the parameters given in Figure 2.4 of this summary. A primary reason for the poor precision is the correlation among the parameters of the modified sorption equation. This poor precision should discourage us from placing too much emphasis on the individual estimates – unless the precision is evaluated and reported together with the results. Unfortunately, this is hardly ever done. Comparing the sorption properties of soils by consulting the estimates of the individual parameters has become almost a standard procedure, even though Russel and Prescott (1916) warned against overinterpreting these almost a hundred years ago. The results of Article III suggest that comparison of the sorptive properties of soils is safer with the numbers derived from the fitted sorption equations than with the estimates for the individual parameters.

3.2.2 Sorptive components

The amount of P sorbed by the soils in the *Q/I* experiments correlated well with the concentrations of the oxalate-extractable Al and Fe in the soils (Al_{ox} and Fe_{ox}). Excluding the Ap horizons, the concentrations of oxalate-extractable Al and Fe explained 80% of the variation in sorption at the P concentration of 2 mg l^{-1} (Table 3 in Article III). In the Ap horizons, old P occupying the sorption sites had reduced the available sorption capacity, just as expected on the basis of the theory of sorption on variable-charged surfaces. The concentrations of oxalate-extractable Al and Fe also explained 75% of the variation in the estimates for the P buffering capacity at the P concentration of 2 mg l^{-1} . The close correlation between the concentrations of oxalate-extractable metals and the most precise figures describing the sorption properties of the soils (S_2 and PBC_2 ; Article III) illustrates the close connection between the short-range-ordered oxides and the P retention properties of the soils, and justifies the use of instruments based on oxalate-extractable Al and Fe, such as the theoretical P sorption capacity (PSC).

The P sorption properties of the soils are shaped by soil development. The effects of this are most evident in the decline of the theoretical P sorption capacities (PSC) that occur in the subsoil horizons with increasing depth (Table 3.4). The weathering of the primary minerals and subsequent formation of the oxides of Al and Fe is a prerequisite for an efficient sorption of P. This is why the smallest theoretical P sorption capacities were measured in the unweathered C horizons in all soils. In the coarse Toholampi and Loppi soils, the largest P sorption capacities found in the Bs horizons were partly attributable to illuvial Al and Fe in the horizons. A similar reduction of the theoretical P sorption capacities in soil profiles with increasing depth has been reported in Belgian soils by Lookman *et al.* (1995b).

Table 3.4 Acid oxalate-extractable aluminium (Al_{ox}) and iron (Fe_{ox}) in the soils and estimates of the phosphorus sorption capacity (PSC) and the degree of phosphorus saturation (DPS) based on the oxalate-extractions and the Chang and Jackson phosphorus fractions calculated according to equations 1 and 2^a.

Horizon	Depth cm	Al _{ox}	Fe _{ox} mmol kg ⁻¹	PSC	DPS %
<i>Sjökulla, Aeris Cryaquept</i>					
Ap1	0-20	87	146	116	7.7
Ap2	20-29	85	142	114	8.6
2Bw	29-46	104	125	114	2.6
2BC	46-70	100	104	102	1.5
3C	70-	87	84	86	2.4
<i>Kotkanoja, Typic Cryaquept</i>					
Ap	0-24	103	235	169	8.4
Bw1	24-32	82	207	144	2.9
2Bw2	32-56	109	134	122	3.8
2Bw3	56-76	98	99	99	4.1
3C	76-	76	72	74	4.0
<i>Toholampi, Typic Cryaquod</i>					
Ap	0-27	91	42	66	9.7
Bs	27-39	103	61	82	2.6
2Bw	39-62	25	55	40	3.9
2BC	62-140	19	77	48	7.1
2C	140-	13	56	35	6.9
<i>Loppi, Typic Haplanthrept</i>					
Ap	0-30	131	75	103	36.0
Bs	30-49	221	72	147	7.2
Bw	49-65	160	42	101	7.3
2C	65-	28	61	45	4.7

^a Results obtained from air-dried soil samples.

Also the amounts of P sorbed in the *Q/I* experiments at the P concentration of 2 mg l⁻¹ were smaller in the C horizons than in the B horizons in all the soils (Table 3.3). In the Inceptisols, sorption at the P concentration of 2 mg l⁻¹ was smaller in the Ap horizons than in the C horizons because the sorption capacities in the Ap horizons were partially saturated. In the P-poor Toholampi Spodosol, the sorption measured in the *Q/I* experiments (S₂) was smallest in the C horizon.

Due to the negligible weathering in the C horizons and the impact of the P enrichment in the Ap horizons, the bulk of the available sorption capacity in the studied soils is located in a rather thin stratum within the B horizons at an approximate depth from 30 cm to 70 cm. In general, the theoretical P sorption capacities calculated for the soils (range 35-169 mmol kg⁻¹) were large when compared to the figures reported for other soils in Northern Europe (Freese *et al.*, 1992, range 10-117 mmol kg⁻¹; Lookman *et al.*, 1995b, typical range 8-80 mmol kg⁻¹; Börling *et al.*, 2001, range 31-102 mmol kg⁻¹). According to Burnham and Lopez-Hernandez (1982), P sorption capacities that are greater than average are common for poorly drained Inceptisols and shallow Spodosols.

The accumulation of secondary P in the Ap horizons is perhaps most evident in the results of the P saturation of the soils (Table 3.4). The theoretical P saturation (Equation 2 in Chapter 2.3) of the Ap horizons of the Sjäkkulla, Kotkanoja and Toholampi soils range from 8% to 10%. In the Anthropogenic Loppi Ap horizon, the degree of P saturation reached a value of 36%. Results from 20% to 30% upwards are generally considered to indicate soils saturated to a degree that may cause an environmental threat because such soils are able to maintain high soluble P concentrations in the soil solution (e.g. Lookman *et al.*, 1995b; De Smet *et al.*, 1996; Beauchemin and Simard, 1999; Hooda *et al.*, 2000; Nair *et al.*, 2004). Of the studied soils, only the Loppi Ap horizon can be considered to be a potentially significant source of soluble P loading. By contrast, the results for all other horizons indicate low degrees of P saturation and low PO₄-P release potentials. It is noteworthy, that the P saturation is rather low in all the subsurface horizons, including the Loppi soil. This outcome is in accordance with the results for the equilibrium P concentrations and the concentrations of water-extractable P.

Variants of the P saturation index became popular in the 1990's for describing the environmental PO₄-P loading potential of soils. The approach using a single oxalate-extraction for simultaneous analysis of Al, Fe and P is a good example of applying the theory of reversible P sorption in practice. It was originally developed

for non-calcareous soils in temperate regions (Freese *et al.*, 1992) and has since been applied widely on different kinds of soils (e.g. Beauchemin and Simard, 1999). The results described in Article I demonstrate that this practice is not suitable for the weakly developed soils of Finland because a significant amount of primary apatitic P is extracted by the acid oxalate solution, and erroneously high estimates for the degree of P saturation are obtained. Better estimates for the degree of P saturation of the sorptive components in these soils can be obtained by combining the information for the oxalate extraction and the P fractionation. This approach is not completely new: Hartikainen (1982a) found that the concentration of water-extractable P of soils follows closely the P saturation of the Al oxides and Fe oxides quantified as ratios of NH_4F -extractable P to oxalate-extractable Al and NaOH-extractable P to oxalate-extractable Fe, but she did not combine the results to get a single parameter for the P saturation.

4 General discussion

4.1 Phosphorus in the soil profiles

All four profiles can be divided into sections with clearly differing P characteristics according to their master horizons Ap, B and C. The C horizons consist – by definition – of minimally altered parent material. All C horizons in this study were characterized by the following: a dominance of acid-soluble primary P; a smaller capacity to sorb soluble P than the more weathered horizons above; very small concentrations of water-soluble P; practically zero equilibrium P concentrations in the soil solution. The upper boundaries of the C, or the transitional BC horizons with similar properties, occurred at an approximate depth of 70 cm. The data published previously in Finland suggest that the dominance of the acid-soluble P at corresponding depths is typical for most mineral soils, although some soils may be weathered slightly deeper (Kaila, 1963a). In a large group of mineral soils described by Yli-Halla *et al.* (2000), the upper boundaries of the C or BC horizons occurred commonly at depths from 60 to 90 cm, even though few shallow (30 cm) and deep (190 cm) soils were also reported. It appears that most cultivated mineral soils in Finland are weathered to similar depths as the four soils of this study. This may reflect natural soil-forming factors, such as the maximum rooting depth of past natural or present cultivated vegetation, or the relatively flat topography of the agricultural areas combined with a relatively constant depth of ground water in the soils. Human activities may also be involved: Mokma *et al.* (2000) suspected that

the widespread tiling of cultivated soils at an approximate depth of one meter may have affected the depth of the cultivated soils in Finland.

The impacts of soil-forming processes on the soil P were most evident in the B horizons. The smaller concentrations of total P than in the C horizons, the peak sorption capacities within the profiles, the lowest degrees of P saturation, low concentrations of water-soluble P, small concentrations of equilibrium P concentrations, as well as the extreme buffering capacities all mirrored results reported previously elsewhere (e.g. Smeck and Runge, 1971; Kao and Blanchard, 1973; St. Arnaud *et al.*, 1988; Frossard *et al.*, 1989). The mid-sections of the soils have a massive capacity for storing P because weathering and illuvial processes have created large amounts of short-range ordered oxides in this layer.

The impact of human activity is evident in the surface soils only. A slight enrichment of P due to natural processes is expected in the surface soils, but the considerable accumulation of secondary P in the Ap horizons points to an anthropogenic source. With the exception of the Loppi soil, no significant accumulation of secondary P was observed in the subsurface horizons, thus only the Ap horizons seem to have provided a sink for the P added to the soils. According to Saarela (2002), the cumulative P balance of the cultivated soils in Finland since the 1930's is approximately $+1000 \text{ kg ha}^{-1}$, and roughly one-third of the P in the plow layers comes from manure and fertilizers.

Several previous studies carried out in Northern Europe report also that most of the surplus P from reasonable P inputs has accumulated in the surface horizons only, and the solubility of the P in the Ap horizons has been markedly higher than in the B horizons (Kaila, 1963a; Jokinen, 1984; Anderson and Xia, 2001; Börling *et al.*, 2004). In cases where the P inputs greatly exceed the sorption capacity of the Ap horizon, the P reserves and the solubility of P may be increased as deep as in the C horizons (Simard *et al.*, 1995; Eghball *et al.*, 1996; Whalen and Chang, 2001). Such P enrichment has typically been reported in areas where intensive animal husbandry is practiced on coarse-textured soils. At worst, the P-enriched soils may cover thousands of hectares (e.g. Mozaffari and Sims, 1994; Lookman *et al.*, 1995b; De Smet *et al.*, 1996). The results of this work, together with previously published results, imply that a deep and widespread P saturation of soils is not probable in Finland.

The solubility of $\text{PO}_4\text{-P}$ was superior in the Ap horizons in comparison to the subsurface horizons. The secondary P in the Ap horizons has accumulated primarily in the NH_4F -soluble and NaOH -soluble fractions. Also the content of organic P was clearly larger in the Ap than in the B horizons. It is evident that these three P pools control the dynamics of the soluble $\text{PO}_4\text{-P}$ in the studied soils. They have partially saturated the P sorption capacity in the Ap horizons, reduced the buffering capacities in the surface soils, increased the solubility of the P in water, and increased the equilibrium P concentrations in the soil. The accumulation of organic matter in the Ap horizons may also increase the solubility of $\text{PO}_4\text{-P}$ by a competitive adsorption of organic anions to the same sorption sites as P (Sibanda and Young, 1986; Bolan *et al.*, 1994) or by inactivating the sorption sites by blocking them within soil aggregates (see Linquist *et al.*, 1997). Irrespective of the specific mechanisms involved, only the Ap horizon soils seem to be capable of providing plants with P, or of releasing significant amounts of soluble P into the runoff water. All the subsurface horizons are likely to act as sinks for soluble P.

4.2 Management of P-enriched soils

A high P status of the surface soil increases the risk of P losses in the surface runoff. It is self-evident that the higher the total P content of the soil, the more P is removed from the soil with eroding material. The losses in erosion respond readily to an increasing P status of a soil because particles enriched with P are transported preferentially in relation to the bulk soil (Sharpley, 1985a). A close connection also exists between the soluble P concentration in the runoff water and the P status of the surface soil: the $\text{PO}_4\text{-P}$ concentrations in the runoff water have been shown to follow closely the degree of P saturation in the top few centimeters of soil (e.g. Sharpley, 1995; Pote *et al.*, 1996; Vadas *et al.*, 2005). This observation demonstrates the operation of the theory of reversible sorption of $\text{PO}_4\text{-P}$ in practice. During the last decade, the theory has also been utilized in attempts to reduce the losses of soluble P from excessively fertilized soils. A variety of soil or manure amendments – such as alum, ferrous sulphate or water treatment residuals – have been tested as potential substances for increasing the P sorption capacity of the surface soils, and consequently for decreasing the degree of P saturation and the concentration of soluble P in the runoff water (e.g. Shreve *et al.*, 1995; Gallimore *et al.*, 1999; Novak and Watts, 2004; Torbert *et al.*, 2005).

The experiment described in Article IV demonstrates that corresponding effects on the solubility of P are achievable in the studied soils by mixing sorptive material

from the subsoil into the Ap horizons by conducting deep tillage. Because the response of the equilibrium P concentration to the fraction of the sorptive material added to the mixture is unlinear (Figure 2 in Article IV), small additions of highly sorptive soil mixed with a P-enriched surface soil may reduce the equilibrium P concentration radically. In the Loppi soil, as little as 25% of the material from the Bs horizon that was mixed into the Ap horizon decreased the equilibrium P concentration by 70% with a simultaneous increase in the P buffering capacity. Deep tillage could offer a quick solution for reducing the losses of soluble P from those soils having an excessive P status but a highly sorptive subsoil horizon within a practical depth for mixing. The results of Yli-Halla *et al.* (1998) suggest that for most P-enriched mineral soils in Finland, this criterion is met. A similar solution for reducing the excessive solubility of P in the surface soil has later been proposed also by Sharpley (2003). Apart from the P sorptive soil amendments, there are no other quick solutions for reducing the solubility of P in soils because the excessive soil P concentrations decrease very slowly in normal cultivation even with zero P fertilization (Jaakkola *et al.*, 1997; Yli-Halla *et al.*, 2001).

4.3 Implications of the results on soil sampling

The substantial deviations in the P reserves and sorption properties between adjoining horizons in the studied profiles have implications for soil sampling. Unbiased results for the P characteristics of soil profiles can only be obtained by taking samples from the genetic horizons or at depth increments small enough to avoid the mixing of materials having different properties. If sampling is carried out at pre-determined depths – for instance from 20 to 40 cm – the samples are likely to contain materials differing widely in their P properties and the results of the analyses do not represent correctly any material present in the studied profile. Unfortunately, there is no shortage of results obtained by using such sampling.

The Ap horizons in most of the cultivated soils in Finland are fairly homogeneous and the boundaries against the uppermost B horizons are typically abrupt or clear because of an extensive use of moldboard plowing as the primary tillage method. The Ap and B horizons are also visually distinct, and unintentional mixing of them is easy to avoid in soil sampling. In some cases, however, an apparently homogeneous surface horizon may contain layers that should be sampled separately. A continued surface application of fertilizers or manure on grasslands may create notable P gradients close to the soil surface because most of the P tends to accumulate in the top few centimeters of soil (Humphreys *et al.*, 1998; Turtola

and Yli-Halla, 1999). A substantial enrichment of P in the topmost layer is also typical in minimum-till or no-till cultivation (Oloya and Logan, 1980; Guertal *et al.*, 1991; Rehm *et al.*, 1995; Howard *et al.*, 1999).

Minimum-till and no-till farming is increasing rapidly in Finland, and almost half of the winter crops are currently planted without prior tillage. Appropriate sampling guidelines should be developed for the increasing area of minimum-tilled soils. The results obtained for these potentially strongly stratified soils with a traditional sampling (to the bottom of the old Ap horizon) overestimates the agronomic P status of the soils because the accessibility of the P in the thin surface layer is limited (Guertal *et al.*, 1991) and underestimates the potential for the P losses because the P concentration in the surface run-off water is determined by the P status of the top few centimeters of soil (Sharpley, 1985b; Torbert *et al.*, 2002). From an environmental point of view, the analyses of samples from the topmost horizon provide the best estimates for the potential P losses in the surface runoff. The agronomic interpretation of the results obtained for the split Ap horizon samples remains unresolved, and requires further research.

When improving soil sampling instructions, the sample storage practices should also be taken into consideration. The overwhelming majority of soil P analyses, including all commercial soil tests in Finland, is made on air-dried soil samples. In routine analyses, there is no point in changing to more expensive sample storage practices. In soil P research, however, the goals are typically complex. If we want a better grasp on the true P dynamics in the field conditions, we should take into account all factors affecting the results of our analyses. The results of Articles II and III suggest that valid data for the most dynamic P compounds in the soils are only achieved using field-moist soil samples. This conclusion is supported by the recent results of Turner and Haygarth (2003), Nguyen and Marchner (2005), and Turner (2005).

4.4 Relevance of the profile P data

The methods used in this study for describing the reserves and retention of P in the soil can be considered universal in the sense that the interpretation of the results is not tied to a soil type, pH, or to any other external information. For example, water-extractions, sorption experiments, and P fractionation can be carried out on almost any kind of soil. Many profile studies have been carried out using methods developed originally for agronomic purposes (such as Olsen, Bray-1, or Mehlich-

III extractions). The results obtained for the subsoil samples using these methods are somewhat ambiguous because the methods were developed primarily for quantifying plant-available P, and the results are assessed against a scale based on the plant response in field experiments on certain (surface) soil types.

The specificity of the Chang and Jackson P fractionation solutions has been questioned on many occasions. Their specificity may be imperfect, but hardly to a degree to give a severely incorrect impression of the contrasting P conditions in the B and C horizons, of the low degree of weathering, or of the low degree of P saturation in the soils. A clear advantage of the Chang and Jackson fractionation method in the profile P inventories is the coherence of the fractions with the concepts commonly used in the P weathering studies (Walker and Syers, 1976; Smeck, 1985).

In this work, the studies of P retention were restricted to $\text{PO}_4\text{-P}$. This is not the only mobile form of P in soils, however, as many organic P compounds are generally considered to be even more mobile (e.g. Schoenau *et al.*, 1989; Anderson and Magdoff, 2005). Eventually all the P in the soil is, nevertheless, cycled through a $\text{PO}_4\text{-P}$ form, and it is generally considered to be the key compound in P cycling. A main part of the organic P added to the Finnish surface soils in manure is also mineralized quite rapidly to $\text{PO}_4\text{-P}$ (Soenne and Peltovuori, 2005). Furthermore, the organic P in monoesters is sorbed to the soil oxides by essentially the same mechanism as the $\text{PO}_4\text{-P}$ (Anderson *et al.*, 1974; Ognalaga *et al.*, 1994; Anderson and Magdoff, 2005). Understanding the reactions of $\text{PO}_4\text{-P}$ in soils thus helps to depict the dynamics of both the inorganic and organic P in the soils.

The relevance of the sorption data obtained with the *Q/I* experiments depends on several factors. The potential uncertainty of the estimates obtained for the parameters of the sorption equations has been addressed in Chapter 3.2.1. There are also caveats in upscaling the results. A common problem in the results of the *Q/I* experiments is their sensitivity to the soil-to-solution ratio. Experiments typically use too tight ratios to properly imitate natural systems. This is why the estimates obtained for the term Q_0 in Equation 3 (or q in Equation 5) commonly underestimate the amounts of desorbable P in the surface soils (Yli-Halla *et al.*, 1995). The estimates for the equilibrium P concentrations in the surface soils have the potential for predicting the $\text{PO}_4\text{-P}$ concentrations in run-off waters but they also face similar constraints (Yli-Halla *et al.*, 1995; Koopmans *et al.*, 2002; McGechan, 2002).

The very low equilibrium P concentrations and high sorption affinities in the B horizons of this study suggest a negligible mobility of PO₄-P in the subsurface horizons. Yet significant concentrations of PO₄-P have been measured in the subsurface drainage waters from the experimental fields on the Sjökölla and Kotkanoja soils (see Article III). In general, attempts to predict the concentrations of P in the subsurface drainage water with soil data have been less successful than the attempts to predict the concentrations in the surface runoff (e.g. Sharpley *et al.*, 1977). The main reason for this is the insufficient contact between the P in the drainage water and the sorptive components in the soil. The contact is especially poor in tiled clay soils because the drainage water typically runs rapidly through the profile via preferential flow paths (e.g. Djodjic *et al.*, 2000). A continuous macropore network from the soil surface to a tile drain through cracks and earthworm burrows has been, in fact, documented in a clay soil close to the Lintupaju profile described in Article IV (Shipitalo *et al.*, 2004). The enhanced transport of P with preferential flow is not confined to clay soils; significant transport of P in the preferential flow channels has also been observed in coarse-textured soils (Cox *et al.*, 2000; Simard *et al.*, 2000).

Chemical analyses of bulk soil samples alone are not sufficient to predict the P concentrations in the subsurface drainage water because the geometric and kinetic factors that determine the contact between the sorptive components and the P in water are ignored (Cox *et al.*, 2000; Kleinman *et al.*, 2003). To improve our understanding of the dynamics of the P in soils, chemical analyses have to be complemented with corresponding data of the physical soil properties. Furthermore, improving our understanding of the agronomic aspects of soil P at a profile scale probably requires consideration of biological factors, such as the root growth dynamics of the cultivated crops. These remarks indicate that this thesis is merely a first step towards soil P research beyond the Ap horizons in Finland.

The material of this study was narrow but practically all results were in line with the previously published irregular observations of the soils in Finland. The detailed description of the present four pedons, together with the summary of the previously published data, provides a comprehensive image of the P reserves as well as the factors affecting the solubility of PO₄-P in the weakly developed non-calcareous soils of Finland. This image forms a basis for a better understanding of the dynamics of P in the weakly developed young soils, and helps us improve the sampling practices and the methodology currently applied in soil P research.

5 Conclusions

All of the four soil profiles studied can be divided into sections having clearly differing P characteristics by their master horizons Ap, B and C. The upper boundaries of the C – or BC horizons with similar properties – occurred at an approximate depth of 70 cm. Below this depth, the P composition of all soils was dominated by an acid-soluble primary P. The high proportion of this assumingly apatitic P in the C horizons illustrates the immaturity of the soils. In the B horizons, a significant amount of primary P has been weathered and transformed to secondary forms. It was estimated that the average rate of weathering in the soils since their emergence from the evolving Baltic Sea ranges from 230 to 290 g ha⁻¹ year⁻¹. The results of the P composition of the soils illustrate that the common theory of changes in soil P composition at various stages of soil development also applies to the weakly developed soils of Finland.

Human impact on soil P was evident only in the Ap horizons. The high concentrations of the total P in the Ap horizons are most likely attributable to cultivation with positive P balances for decades, although some of the P in the Ap horizons has accumulated through natural soil-forming processes. The human impact on the surface soils is most apparent in the results for the degree of P saturation: the results of the Ap horizons ranged from 8% to 36%, while the results for all the subsurface horizons remained below 7%. The contrast in the degree of P saturation between the Ap horizons and the subsurface soils was also reflected in the sorption experiments. The Ap horizons were able to maintain elevated PO₄-P concentrations in the solution phase – the B horizons retained practically all the P added in the sorption experiments. Only the Ap horizons seem to be capable of releasing any significant amounts of P into the soil solution.

Most of the available sorption capacity in the soils is located in the B horizons at depths between 30 and 70 cm. The sorption capacity in the Ap horizons is lower than in the B horizons because of the enrichment of anthropogenic P. The sorption capacity in the C horizons is lower than in the B horizons because insignificant weathering has not created that many sorption sites. Although the sorption affinity in the C horizons seemed lower than in the B horizons, all the subsoil horizons retained P effectively because of their low P saturation. The massive sorption capacity of the B horizons could be utilized in reducing the potential of P losses from the soils having an excessive P status. Because of its great affinity for P, a small amount of sorptive material from the B horizon mixed into the Ap horizon

with deep tillage could reduce the equilibrium P concentration of the surface soil considerably.

Due to the drastic differences in the P characteristics between adjoining soil horizons, soil sampling of the subsoils has to be conducted according to the genetic horizons or at small depth increments. Otherwise contrasting materials are likely to be mixed in one sample. As a consequence, the results of such samples do not represent correctly any material present in the soil profile. In grasslands and in minimum-tilled soils, sampling the old Ap horizon at two separate depths may be justified if the fertilization or cultivation practices have created stratification of the P properties in the surface soil. If soil samples are to be used for analyzing the most labile P forms, storing the samples moist should be considered because air-drying the soil samples was found to alter the results of the sorption experiments and water extractions drastically.

6 References

- Aaltonen, V.T. 1951. Maannostuminen ja maannos. In: *Suomen maantieteen käsikirja* (Editors Granö, J.G. *et al.*), pp. 57-64. Kustannusosakeyhtiö Otava, Helsinki.
- Agbenin, J.O. & Tiessen, H. 1995. Phosphorus sorption at field capacity and soil ionic strength: kinetics and transformation. *Soil Science Society of America Journal* **59**, 998-1005.
- Allaway, W.H. & Rhoades, H.F. 1951. Forms and distribution of phosphorus in horizons of Nebraska soil in relation to profile development. *Soil Science* **72**, 119-128.
- Allen, B.L. & Hajek, B.F. 1989. Mineral occurrence in soil environments. In: *Minerals in Soil Environments*. 2nd edition (Editors Dixon, J.B. & Weed, S.B.), pp. 199-278. Soil Science Society of America Book Series 1.
- American Public Health Organization 1985. *Standard methods for examination of water and wastewater*. 16th edition, p. 31. American Public Health Organization, American Water Works Association & Water Pollution Control Federation, Washington.
- Anderson, B.H. & Magdoff, F.R. 2005. Relative Movement and Soil Fixation of Soluble Organic and Inorganic Phosphorus. *Journal of Environmental Quality* **34**, 2228-2233.
- Anderson, G., Williams, E.G. & Moir, J.O. 1974. A comparison of the sorption of inorganic orthophosphate and inositol hexaphosphate by six acid soils. *Journal of Soil Science* **25**, 51-62.
- Anderson, R. & Xia L. 2001. Agronomic measures of P, *Q/I* parameters and lysimeter-collectable P in subsurface soil horizons of a long-term slurry experiment. *Chemosphere* **42**, 171-178.
- Antikainen, R., Lemola, R., Nousiainen, J., Sokka, L., Huhtanen, P., Esala, M. & Rekolainen, S. 2005. Stocks and flows of nitrogen and phosphorus in the Finnish food production and consumption system. *Agriculture, Ecosystems & Environment* **107**, 287-305.
- Baker, R.T. 1976. Changes in the chemical nature of soil organic phosphate during pedogenesis. *Journal of Soil Science* **27**, 504-512.
- Barberis, E., Ajmone Marsan, F., Scalenghe, R., Lammers, A., Schwertmann, U., Edwards, A.C., Maquire, R., Wilson, M.J., Delgado, A. & Torrent, J. 1996. European soils overfertilized with phosphorus: Part I. Basic properties. *Fertilizer Research* **45**, 199-207.
- Barrow, N.J. 1978. The description of phosphate adsorption curves. *Journal of Soil Science* **29**, 447-462.
- Barrow, N.J. 1983a. Understanding phosphate reaction with soil. In: *Proceedings of the 3rd international congress on phosphorus compounds*, pp. 37-51. October 4-6 1983. Brussels.
- Barrow, N.J. 1983b. A mechanistic model for describing the sorption and desorption of phosphate by soil. *Journal of Soil Science* **34**, 733-750.
- Barrow, N.J. 1985. Reactions of anions and cations with variable-charge soils. *Advances in Agronomy* **38**, 183-230.
- Barrow, N.J. 1989. Surface reactions of phosphate in soils. *Agricultural Science* **2**, 33-37.
- Barrow, N.J. 2000. Towards a single-point method for measuring phosphate sorption by soils. *Australian Journal of Soil Research* **38**, 1099-1113.
- Barrow, N.J. & Shaw, T.C. 1975. The slow reactions between soil and anions: 2. Effect of time and temperature on the decrease on phosphate concentration in the soil solution. *Soil Science* **119**, 167-177.
- Barrow, N.J. & Shaw, T.C. 1980. Effect of drying soil on the measurement of phosphate adsorption. *Communications in Soil Science and Plant Analysis* **11**, 347-353.
- Beauchemin, S. & Simard, R.R. 1999. Soil phosphorus saturation degree: Review of some indices and their suitability for P management in Québec, Canada. *Canadian Journal of Soil Science* **79**, 615-625.

- Beauchemin, S. & Simard, R.R. 2000. Phosphorus status of intensively cropped soils of St. Lawrence lowlands. *Soil Science Society of America Journal* **64**, 659-669.
- Beaton, J.D., Roberts, T.L., Halstead, E.H. & Cowell, L.E. 1995. Global transfer of P in fertilizer materials and agricultural commodities. In: *Phosphorus in the global environment* (Editor Tiessen, H.), pp. 7-26. John Wiley and Sons, New York.
- Beckett, P.H.T. & White, R.E. 1964. Studies on the phosphate potentials of soils. III. The pool of labile inorganic phosphate. *Plant and Soil* **21**, 253-282.
- Bolan, N.S., Naidu, R., Mahimairaja, S. & Baskaran, S. 1994. Influence of low-molecular-weight organic acids on the solubilization of phosphates. *Biology and Fertility of Soils* **18**, 311-319.
- Borggaard, O.K., Jorgensen, S.S., Moberg, J.P. & Raben-Lange, B. 1990. Influence of organic matter on phosphate adsorption by aluminum and iron oxides in sandy soils. *Journal of Soil Science* **41**, 443-449.
- Borrero, C., Pena, F. & Torrent, J. 1988. Phosphate sorption by calcium carbonate in some soils of the Mediterranean part of Spain. *Geoderma* **42**, 261-269.
- Bouma, J., Finke, P.A., Hoosbeek, M.R. & Breeuwsma, A. 1998. Soil and water quality at different scales: concepts, challenges, conclusions and recommendations. *Nutrient Cycling in Agroecosystems* **50**, 5-11.
- Bowden, J.W., Posner, A.M. & Quirk, J.P. 1973. Generalised model for anion and cation adsorption at oxide surfaces. *Nature* **245**, 81-84.
- Breemen, N. van & Buurman, P. 2002. *Soil formation*. 2nd edition. Kluwer Academic Publishers, Dordrecht.
- Brookes, P.C., Powelson, D.S. & Jenkinson, D.S. 1984. Phosphorus in the soil microbial biomass. *Soil Biology & Biochemistry* **16**, 169-175.
- Burnham, C.P. & Lopez-Hernandez, D. 1982. Phosphate retention in different soil taxonomic classes. *Soil Science* **134**, 376-380.
- Börling, K., Ottabong, E. & Barberis, E. 2001. Phosphorus sorption in relation to soil properties in some cultivated Swedish soils. *Nutrient Cycling in Agroecosystems* **59**, 39-46.
- Börling, K., Barberis, E. & Ottabong, E. 2004. Impact of long-term inorganic phosphorus fertilization on accumulation, sorption and release of phosphorus in five Swedish soil profiles. *Nutrient Cycling in Agroecosystems* **69**, 11-21.
- Carpenter, S.R., Caraco, N.F., Correl, D.L., Howarth, R.W., Sharpley, A.N. & Smith, V.H. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. *Ecological Applications* **8**, 559-568.
- Castro, B. & Torrent, J. 1998. Phosphate sorption by calcareous Vertisols and Inceptisols as evaluated from extended P-sorption curves. *European Journal of Soil Science* **49**, 661-667.
- Catt, J.A., Howse, K.R., Farina, R., Brockie, D., Todd, A., Chambers, B.J., Hodgkinson, R., Harris, G.L. & Quinton, J.N. 1998. Phosphorus losses from arable land in England. *Soil Use and Management* **14**, 168-174.
- Chang, S.C. & Jackson, M.L. 1957. Fractionation of soil phosphorus. *Soil Science* **84**, 133-144.
- Chang, S.C. & Jackson, M.L. 1958. Soil phosphorus fractions in some representative soils. *Journal of Soil Science* **9**, 109-119.
- Cox, J.W., Kirkby, C.A., Chittleborough, D.J., Smythe, L.J. & Fleming, N.K. 2000. Mobility of phosphorus through intact soil cores collected from the Adelaide Hills, South Australia. *Australian Journal of Soil Research* **38**, 973-990.
- Dalal, R.C. 1977. Soil organic phosphorus. *Advances in Agronomy* **29**, 83-115.
- Dalgaard, T., Kyllingsbæk, A., Rubæk, G. & Børgesen, C.D. 2003. Phosphorus surpluses in Danish agriculture. In: *Proceedings of the NJF's 22nd Congress "Nordic Agriculture in Global Perspective"*. July 1-4, 2003, Turku (Editors Niemeläinen, O. & Topi-Hulmi, M.). p. 130. Available at: www.njf.dk/njf/reports/njfreports.htm

- De Smet, J., Hofman, G., Vanderdeelen, J., Meirvenne, M. van & Baert, L. 1996. Phosphate enrichment in the sandy loam soils of West-Flanders, Belgium. *Fertilizer Research* **43**, 209-215.
- Djodjic, F., Ulén, B. & Bergström, L. 2000. Temporal and spatial variations of phosphorus losses and drainage in a structured clay soil. *Water Research* **34**, 1687-1695.
- Donner, J. 1995. *The quaternary history of Scandinavia*. Cambridge University Press, Cambridge.
- Eghball, B., Binford, G.D. & Baltensberger, D.D. 1996. Phosphorus movement and adsorption in a soil receiving long-term manure and fertilizer application. *Journal of Environmental Quality* **25**, 1339-1343.
- Ervio, R. 1970. The importance of soil bulk density in soil testing. *Annales Agriculturae Fenniae* **9**, 278-286.
- Fitter, A.H. & Sutton, C.D. 1975. The use of the Freundlich isotherm for soil phosphate sorption data. *Journal of Soil Science* **26**, 241-246.
- Freese, D., van der Zee, S.E.A.T.M. & van Riemsdijk, W.H.J. 1992. Comparison of different models for phosphate sorption as a function of the iron and aluminum oxides of soils. *Journal of Soil Science* **43**, 729-738.
- Frossard, E., Stewart, J.W.B. & Arnaud, R.J. St. 1989. Distribution and mobility of phosphorus in grassland and forest soils of Saskatchewan. *Canadian Journal of Soil Science* **69**, 401-416.
- Frossard, E., Brossard, M., Hedley, M.J. & Metherell, A. 1995. Reactions controlling the cycle of P in soils. In: *Phosphorus in the global environment* (Editor Tiessen, H.), pp. 107-137. John Wiley & Sons, New York.
- Gallimore, L.E., Basta, N.T., Storm, D.E., Payton, M.E., Huhnke, R.H. & Smolen, M.D. 1999. Water treatment residual to reduce nutrients in surface runoff from agricultural land. *Journal of Environmental Quality* **28**, 1474-1478.
- Gerke, J. & Hermann, R. 1992. Adsorption of orthophosphate to humic-Fe-complexes and to amorphous Fe-oxide. *Zeitschrift für Pflanzenernährung und Bodenkunde* **155**, 233-236.
- Glenworth, R. 1947. Distribution of the total and acetic-acid soluble phosphate in soil profiles having naturally free and impeded drainage. *Nature* **159**, 441-442.
- Goldberg, S. & Sposito, G. 1985. On the mechanism of specific phosphate adsorption by hydroxylated mineral surfaces. A review. *Communications in Soil Science and Plant Analysis* **16**, 801-823.
- Guertal, E.A., Eckert, D.J., Traina, S.J. & Logan, T.J. 1991. Differential phosphorus retention in soil profiles under no-till crop production. *Soil Science Society of America Journal* **55**, 410-413.
- Hannapel, R.J., Filler, W.H., Bosma, S. & Bullock, J.S. 1964. Phosphorus movement in a calcareous soil: I Predominance of organic forms of phosphorus in phosphorus movement. *Soil Science* **97**, 350-357.
- Harrison, A.F. 1987. *Soil organic phosphorus. A review of world literature*. CAB International, Wallingford.
- Hartikainen, H. 1979. Phosphorus and its reactions in terrestrial soils and lake sediments. *Journal of the Scientific Agricultural Society of Finland* **51**, 537-624.
- Hartikainen, H. 1982a. Water soluble phosphorus in Finnish soils and its dependence on soil properties. *Journal of the Scientific Agricultural Society of Finland* **54**, 89-98.
- Hartikainen, H. 1982b. Relationship between phosphorus intensity and capacity parameters in Finnish mineral soils. II. Sorption-desorption isotherms and their relation to soil characteristics. *Journal of the Scientific Agricultural Society of Finland* **54**, 251-262.
- Hartikainen, H. 1989. Effect of cumulative fertilizer dressing on the phosphorus status of mineral soils. I. Changes in inorganic phosphorus fractions. *Journal of Agricultural Science in Finland* **61**, 55-59.
- Hartikainen, H. 1991. Potential mobility of accumulated phosphorus in soil as estimated by the indices of *Q/I* plots and by extractant. *Soil Science* **152**, 204-209.

- Haygarth, P.M., Condron, L.M., Heathwaite, A.L., Turner, B.L. & Harris, G.P. 2005. The phosphorus transfer continuum: Linking source to impact with an interdisciplinary and multi-scaled approach. *Science of the Total Environment* **344**, 5-14.
- Haynes, R.J. & Swift, R.S. 1985. Effects of air-drying on the adsorption and desorption of phosphate and levels of extractable phosphate in a group of acid soils, New Zealand. *Geoderma* **35**, 145-157.
- Hedley, M.J., Stewart, J.W.B. & Chauban, B.S. 1982. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Science Society of America Journal* **46**, 970-976.
- Hibbard, P.L. 1935. Factors influencing phosphate fixation in soils. *Soil Science* **39**, 337-358.
- Hingston, F.J., Atkinson, R.J., Posner, A.M. & Quirk, J.P. 1967. Specific adsorption of anions. *Nature* **215**, 1459-1461.
- Hooda, P.S., Rendell, A.R., Edwards, A.C., Withers, P.J.A., Aitken, M.N. & Truesdale, V.W. 2000. Relating soil phosphorus indices to potential phosphorus release to water. *Journal of Environmental Quality* **29**, 1166-1171.
- Hountin, J.A., Karam, A., Couillard, D. & Cescas, M.P. 2000. Use of fractionation procedure to assess the potential for P movement in a soil profile after 14 years of liquid pig manure fertilization. *Agriculture, Ecosystems & Environment* **78**, 77-84.
- Howard, D.D., Essington, M.E. & Tyler, D.D. 1999. Vertical phosphorus and potassium stratification in no-till cotton soils. *Agronomy Journal* **91**, 266-269.
- Humphreys, J., Tunney, H. & Duggan, P. 1998. Soil phosphorus determination using three extraction procedures, the effect of sampling depth and comparison of phosphorus fertilizer recommendations for grassland. *Irish Journal of Agricultural and Food Research* **37**, 29-38.
- International Fertilizer Industry Association. 2005. *Nitrogen, phosphate and potash statistics 1973-1973/74 to 2002-2002/03*. IFADATA statistics online. Available at: <http://www.fertilizer.org/ifa/statistics.asp> [30.12.2005].
- Jaakkola, A., Hartikainen, H. & Lemola, R. 1997. Effect of fertilization on soil phosphorus in a long-term field experiment in southern Finland. *Agricultural and Food Science in Finland* **6**, 313-322.
- Jokinen, R. 1984. Comparison of and correlation between the characteristics of agricultural topsoil and subsoil at the southern coast of Finland. *Journal of Agricultural Science in Finland* **56**, 245-254.
- Jones, R.C. & Uehara, G. 1973. Amorphous Coatings on Mineral Surfaces. *Soil Science Society of America Proceedings* **37**, 792-798.
- Kaila, A. 1948. Viljelymaan orgaanisesta fosforista. (Summary: On the organic phosphorus in cultivated soils). *Valtion maatalouskoetoimikunnan julkaisuja* **129**.
- Kaila, A. 1956. Phosphorus in various depths of some virgin peat lands. *Journal of the Scientific Agricultural Society of Finland* **28**, 90-104.
- Kaila, A. 1963a. Phosphorus conditions at various depths in some mineral soils. *Journal of the Scientific Agricultural Society of Finland* **35**, 69-79.
- Kaila, A. 1963b. Organic phosphorus in Finnish soils. *Soil Science* **95**, 38-44.
- Kaila, A. 1963c. Total content of phosphorus in some Finnish soils. *Journal of the Scientific Agricultural Society of Finland* **35**, 19-26.
- Kaila, A. 1963d. Fertilizer phosphorus in various fractions of soil phosphorus. *Journal of the Scientific Agricultural Society of Finland* **35**, 36-46.
- Kaila, A. 1964a. Fractions of inorganic phosphorus in Finnish mineral soils. *Journal of the Scientific Agricultural Society of Finland* **36**, 1-13.

- Kaila, A. 1964b. Forms of newly retained phosphorus in mineral soils. *Journal of the Scientific Agricultural Society of Finland* **36**, 65-76.
- Kaila, A. 1965. The fate of water-soluble phosphate applied to some mineral soils. *Journal of the Scientific Agricultural Society of Finland* **37**, 104-115.
- Kao, C.W. & Blanchar, R.W. 1973. Distribution and chemistry of phosphorus in an Albaqualf soil after 82 years of phosphate fertilization. *Journal of Environmental Quality* **2**, 237-240.
- Kivinen, 1934. Über die Pflanzennährstoffverhältnisse der Mineralböden in Finnland. *The Journal of the Scientific Agricultural Society of Finland* **6**, 85-96.
- Kleinman, P.J.A., Needelman, B.A., Sharpley, A.N. & McDowell, R.W. 2003. Using soil phosphorus profile data to assess phosphorus leaching potential in manured soils. *Soil Science Society of America Journal* **67**, 215-224.
- Koljonen, T. 1992. *The geochemical atlas of Finland. Part 2: Till*. Geological Survey of Finland, Espoo.
- Koopmans, G.F., McDowell, R.W., Chardon, W.J., Oenema, O. & Dolfing, J. 2002. Soil phosphorus quantity-intensity relationships to predict increased soil phosphorus loss to overland and subsurface flow. *Chemosphere* **48**, 679-687.
- Koritnig, S. 1965. Geochemistry of phosphorus, I. The replacement of Si^{4+} by P^{5+} in rock-forming silicate minerals. *Geochimica et Cosmochimica Acta* **29**, 361-371.
- Kuo, S. 1996. Phosphorus. In: *Methods of Soil Analysis. Part 3. Chemical Methods* (Editor Sparks, D.L.), pp 869-919. Soil Science Society of America, American Society of Agronomy, Madison.
- Kähäri, J., Mäntylähti, V. & Rannikko, M. 1987. *Suomen peltojen viljavuus 1981-1985*. (Summary: Soil Fertility of Finnish Cultivated Soils in 1981-1985). Viljavuuspalvelu Oy. Helsinki.
- Lachat Instruments. 1994. Orthophosphate in waters 1.00 to 200 $\mu\text{g P/L}$. QuikChem Method 10-115-01-1-B. Lachat Instruments, 6645 West Mill Road, Milwaukee, WI 53218-1239, USA.
- Larsen, S. 1967. Soil phosphorus. *Advances in Agronomy* **19**, 151-210.
- Letkeman, L.P., Tiessen, H. & Campbell, C.A. 1996. Phosphorus transformations and redistribution during pedogenesis of western Canadian soils. *Geoderma* **71**, 201-218.
- Li, L. & Stanforth, R. 2000. Distinguishing adsorption and surface precipitation of phosphate on goethite ($\alpha\text{-FeOOH}$). *Journal of Colloid and Interface Science* **230**, 12-21.
- Linquist, B.A., Singleton, P.W., Yost, R.S. & Cassman, K.G. 1997. Aggregate size effects on the sorption and release of phosphorus in an ultisol. *Soil Science Society of America Journal* **61**, 160-166.
- Lookman, R., Freese, D., Merckx, R., Vlassak, K. & van Riemsdijk, W.H. 1995a. Long-term kinetics of phosphate release from soil. *Environmental Science & Technology* **29**, 1569-1575.
- Lookman, R., Vandeweert, N., Merckx, R. & Vlassak, K. 1995b. Geostatistical assesment of the regional distribution of phosphate sorption capacity parameters (Fe_{ox} and Al_{ox}) in northern Belgium. *Geoderma* **66**, 285-296.
- McGechan, M.B. 2002. Sorption of phosphorus by soil, Part 2: Measurement methods, results and model parameter values. *Biosystems Engineering* **82**, 115-130.
- McLaughlin, J.R., Ryden, J.C. & Syers, J.K. 1981. Sorption of inorganic phosphate by iron- and aluminum-containing components. *Journal of Soil Science* **32**, 365-377.
- Mattingly, G.E.G. 1975. Labile phosphate in soils. *Soil Science* **119**, 369-375.
- Mokma, D.L., Yli-Halla, M. & Hartikainen, H. 2000. Soils in a young landscape on the coast of southern Finland. *Agricultural and Food Science in Finland* **9**, 291-302.
- Mokma, D.L., Yli-Halla, M. & Lindqvist, K. 2004. Podzol formation in sandy soils of Finland. *Geoderma* **120**, 259-272.

- Mount, H.R., Newton, D.L., Räisänen, M.-L. & Lee, S.E. 1995. Morphology of the soils in Central Finland. *Soil Survey Horizons* **36**, 142-154.
- Mozaffari, M. & Sims, J.T. 1994. Phosphorus availability and sorption in an Atlantic coastal plain watershed dominated by animal-based agriculture. *Soil Science* **157**, 97-107.
- Mustonen, S. 1992. *SURVO. An integrated environment for statistical computing and related areas*. Survo Systems, Ltd, Helsinki.
- Nair, V.D., Portier, K.M., Graetz, D.A. & Walker, M.L. 2004. An environmental threshold for degree of phosphorus saturation in sandy soils. *Journal of Environmental Quality* **33**, 107-113.
- Nguyen, B.T. & Marchner, P. 2005. Effect of drying and rewetting on phosphorus transformations in red brown soils with different soil organic matter content. *Soil Biology & Biochemistry* **37**, 1573-1576.
- Niskanen, R. 1989. Extractable aluminium, iron and manganese in mineral soils I Dependence of extractability on the pH of oxalate, pyrophosphate and EDTA extractants. *Journal of Agricultural Science in Finland* **61**, 73-77.
- Novak, J.M., & Watts, D.W. 2004. Increasing the phosphorus sorption capacity of southeastern coastal plain soils using water treatment residuals. *Soil Science* **169**, 206-214.
- Ognalaga, M., Frossard, E. & Thomas, F. 1994. Glucose-1-phosphate and myo-inositol hexaphosphate adsorption mechanisms on goethite. *Soil Science Society of America Journal* **58**, 332-337.
- Olsen, R. & Court, M.N. 1982. Effect of wetting and drying of soils on phosphate adsorption and resin extraction of soil phosphate. *Journal of Soil Science* **33**, 709-717.
- Olsen, S.R. & Khasawneh, F.E. 1980. Use and limitations of physical-chemical criteria for assessing the status of phosphorus in soils. In: *The role of phosphorus in agriculture* (Editors Khasawneh, F.E. et al.), pp. 361-410. American Society of Agronomy, Crop Science Society of America and Soil Science Society of America, Madison.
- Oloya, T.O. & Logan, T.J. 1980. Phosphate desorption from soils and sediments with varying levels of extractable phosphate. *Journal of Environmental Quality* **9**, 526-531.
- Parfitt, R.L. 1978. Anion adsorption by soils and soil materials. *Advances in Agronomy* **30**, 1-50.
- Parfitt, R.L., Atkinson, R.J. & Smart, R.S.C. 1975. The mechanism of phosphate fixation by iron oxides. *Soil Science Society of America Proceedings* **39**, 837-841.
- Pearson, R.W., Spry, R. & Pierre, W.H. 1940. The vertical distribution of total and dilute acid-soluble phosphorus in twelve Iowa soil profiles. *Journal of American Society of Agronomy* **32**, 683-696.
- Pierzynski, G.M., Logan, T.J., Traina, S.J. & Bigham, J.M. 1990. Phosphorus chemistry and mineralogy in excessively fertilized soils: Description of phosphorus-rich particles. *Soil Science Society of America Journal* **54**, 1583-1589.
- Posner, A.M. & Barrow, N.J. 1982. Simplification of a model for ion adsorption on oxide surfaces. *Journal of Soil Science* **33**, 211-217.
- Pote, D.H., Daniel, T.C., Sharpley, A.N., Moore, P.A., Edwards, D.R. & Nichols, D.J. 1996. Relating extractable soil phosphorus to phosphorus losses in runoff. *Soil Science Society of America Journal* **60**, 855-859.
- Puustinen, M., Merilä, E., Palko, J. & Seuna, P. 1994. Kuivatustila, viljelykäytäntö ja vesistökuormitukseen vaikuttavat ominaisuudet Suomen pelloilla (Abstract: Drainage level, cultivation practices and factors affecting load on waterways in Finnish farmland). *Vesi- ja ympäristöhallituksen julkaisu - sarja A* **198**. 319 p.
- Rehm, G.W., Randall, G.W., Scobbie, A.J. & Vetsch, J.A. 1995. Impact of fertilizer placement and tillage system on phosphorus distribution in soil. *Soil Science Society of America Journal* **59**, 1661-1665.
- Rekolainen, S. 1989. Phosphorus and nitrogen load from forest and agricultural areas in Finland. *Aqua Fennica* **19**, 95-107.

- Rolston, D.E., Rauschkolb, R.S. & Hoffman, D.L. 1975. Infiltration of organic phosphate compounds in soil. *Soil Science Society of America Proceedings* **39**, 1089-1094.
- Ron Vaz, M.D., Edwards, A.C., Shand, C.A. & Cresser, M.S. 1993. Phosphorus fractions in soil solution: Influence of soil acidity and fertilizer additions. *Plant and Soil* **148**, 175-183.
- Russel, E.J. & Prescott, J.A. 1916. The reaction between dilute acids and the phosphorus compounds of the soil. *Journal of Agricultural Science* **8**, 65-110.
- Ryden, J.C. & Syers, J.K. 1975. Rationalization of ionic strength and cation effects on phosphate sorption by soils. *Journal of Soil Science* **26**, 395-406.
- Ryden, J.C., McLaughlin, J.R. & Syers, J.K. 1977. Time-dependent sorption of phosphate by soils and hydrous ferric oxides. *Journal of Soil Science* **28**, 585-595.
- Saarela, I. 2002. Phosphorus in Finnish soils in the 1900s with particular reference to the acid ammonium acetate soil test. *Agricultural and Food Science in Finland* **11**, 257-271.
- Saarela, I., Järvi, A., Hakkola, H. & Rinne, K. 2003. Phosphorus status of diverse soils in Finland as influenced by long-term P fertilisation I. Native and previously applied P at 24 experimental sites. *Agricultural and Food Science in Finland* **12**, 117-132.
- Salonen, M. 1941. Fosforin esiintymismuodoista Suomen maalajeissa (The forms of phosphorus in soils of Finland). *Acta Agralia Fennica* **48**. 120 p.
- Sample, E.C., Soper, R.J. & Racz, G.J. 1980. Reactions of phosphate fertilizers in soils. In: *The role of phosphorus in agriculture* (Editors Khasawneh, F.E. *et al.*), pp. 263-310. American Society of Agronomy, Crop Science Society of America and Soil Science Society of America, Madison.
- Sanyal, S.K. & De Datta, S.K. 1991. Chemistry of phosphorus transformations in soil. *Advances in Soil Science* **16**, 1-120.
- Schoenau, J.J., Stewart, J.W.B. & Bettany, J.R. 1989. Forms and cycling of phosphorus in prairie and boreal forest soils. *Biogeochemistry* **8**, 223-237.
- Schoeneberger, P.J., Wysocki, D.A., Benham, E.C. & Broderon, W.D. 1998. *Field book for describing and sampling soils*. Natural Resources Conservation Service, United States Department of Agriculture, National Soil Survey Center, Lincoln.
- Schofield, R.K. 1955. Can a precise meaning be given to 'available' phosphorus? *Soils and Fertilizers* **18**, 373-375.
- Schwertmann, U. 1964. Differenzierung der Eisenoxide des Bodens durch photochemische Extraktion mit saurer Ammoniumoxalat-Lösung. *Zeitschrift für Pflanzenernährung und Bodenkunde* **105**, 194-202.
- Schwertmann, U. 1966. Inhibitory effect of soil organic matter on the crystallization of amorphous ferric hydroxide. *Nature* **212**, 645-646.
- Schwertmann, U. 1985. The effect of pedogenic environments on iron oxide minerals. *Advances in Soil Science* **1**, 172-200.
- SFS-ISO 3696. *Vesi analyttisen laboratorion käyttöön. Laatuvaatimukset ja testimenetelmät* (Water for analytical laboratory use. Specification and test methods). 1992. Suomen Standardoimisliitto, Helsinki.
- Sharpley, A.N. 1985a. The selective erosion of plant nutrients in runoff. *Soil Science Society of America Journal* **49**, 1527-1534.
- Sharpley, A.N. 1985b. Depth of surface soil-runoff interaction as affected by rainfall, soil, slope, and management. *Soil Science Society of America Journal* **49**, 1010-1015.
- Sharpley, A.N. 1995. Dependence of runoff phosphorus on extractable soil phosphorus. *Journal of Environmental Quality* **24**, 920-926.
- Sharpley, A.N. 2003. Soil mixing to decrease surface stratification of phosphorus in manured soils. *Journal of Environmental Quality* **32**, 1375-1384.

- Sharpley, A.N. & Menzel, R.G. 1987. The impact of soil and fertilizer phosphorus on the environment. *Advances in Agronomy* **41**, 297-324.
- Sharpley, A.N. & Withers, P.J.A. 1994. The environmentally-sound management of agricultural phosphorus. *Fertilizer Research* **39**, 133-146.
- Sharpley, A.N., Tillman, R.W. & Syers, J.K. 1977. Use of laboratory extraction data to predict losses of dissolved inorganic phosphate in surface runoff and tile drainage. *Journal of Environmental Quality* **6**, 33-36.
- Shipitalo, M.J., Nuutinen, V. & Butt, K.R. 2004. Interaction of earthworm burrows and cracks in a clayey, subsurface drained, soil. *Applied Soil Ecology* **26**, 209-217.
- Shreve, B.R., Moore, P.A. Jr, Daniel, T.C., Edwards, D.R. & Miller, D.M. 1995. Reduction of phosphorus runoff from field-applied poultry litter using chemical amendments. *Journal of Environmental Quality* **24**, 106-111.
- Sibanda, H.M. & Young, S.D. 1986. Competitive adsorption of humus acids and phosphate on goethite, gibbsite and two tropical soils. *Journal of Soil Science* **37**, 197-204.
- Sibbesen, E. 1978. An investigation of the anion-exchange resin method for soil phosphate extraction. *Plant and Soil* **50**, 305-321.
- Sibbesen, E. & Runge-Metzger, A. 1995. Phosphorus balance in European agriculture - status and policy options. In: *Phosphorus in the global environment* (Editor Tiessen, H.), pp. 43-57. John Wiley and Sons, New York.
- Simard, R.R., Cluis, D., Ganbazo, G. & Beauchemin, S. 1995. Phosphorus status of forest and agricultural soils from a watershed of high animal density. *Journal of Environmental Quality* **24**, 1010-1017.
- Simard, R.R., Beauchemin, S. & Haygarth, P.M. 2000. Potential for preferential pathways of phosphorus transport. *Journal of Environmental Quality* **29**, 97-105.
- Sippola, J. & Saarela, I. 1992. Suomen maalaajien fosforinpidätysominaisuudet ja niiden merkitys vesien kuormituksen kannalta (Phosphorus retention properties in soils of Finland and their effects on phosphorus loading of surface waters). Yhteistutkimusprojektin tutkimusraportit. *Vesi- ja ympäristöhallituksen monistesarja* **359**, 27-36.
- Smeck, N.E. 1973. Phosphorus: An indicator of pedogenetic weathering process. *Soil Science* **115**, 199-206.
- Smeck, N.E. 1985. Phosphorus dynamics in soils and landscapes. *Geoderma* **36**, 185-189.
- Smeck, N.E. & Runge, E.C.A. 1971. Phosphorus availability and redistribution in relation to soil profile development in an Illinois landscape segment. *Soil Science Society of America Proceedings* **35**, 952-959.
- Soil Survey Staff, 1998. *Keys to soil taxonomy*. 8th edition. United States Department of Agriculture. Natural Resources Conservation Service. U.S. Government Printing Office, Washington, DC.
- Soinne, H. & Peltovuori, T. 2005. Extractability of slurry and fertilizer phosphorus in soil after repeated freezing. *Agricultural and Food Science* **14**, 181-188.
- Speter, M. 1935. Final summary of the research into the origin of superphosphate. *Superphosphate* **8**, 141-151.
- St. Arnaud, R.J., Stewart, J.W.B. & Frossard, E. 1988. Application of the pedogenic index to soil fertility studies, Saskatchewan. *Geoderma* **43**, 21-32.
- Tate, K.R. 1984. The biological transformations of P in soil. *Plant and Soil* **76**, 245-256.
- Tiessen, H., Stewart, J.W.B. & Cole, C.V. 1984. Pathways of phosphorus transformations in soils of differing pedogenesis. *Soil Science Society of America Journal* **48**, 853-858.
- Torbert, H.A., Daniel, T.C., Lemunyon, J.L. & Jones, R.M. 2002. Relationship of soil test phosphorus and sampling depth to runoff phosphorus in calcareous and noncalcareous soils. *Journal of Environmental Quality* **31**, 1380-1387.

- Torbert, H.A., King, K.W. & Harmel, R.D. 2005. Impact of soil amendments on reducing phosphorus losses from runoff in sod. *Journal of Environmental Quality* **34**, 1415-1421.
- Torrent, J. 1987. Rapid and slow sorption by mediterranean soils: effect of iron oxides. *Soil Science Society of America Journal* **51**, 78-82.
- Turner, B.L. 2005. Storage-induced changes in phosphorus solubility of air-dried soils. *Soil Science Society of America Journal* **69**, 630-633.
- Turner, B.L. & Haygarth, P.M. 2003. Changes in bicarbonate-extractable inorganic and organic phosphorus by drying pasture soils. *Soil Science Society of America Journal* **67**, 344-350.
- Turtola, E. 1999. *Phosphorus in surface runoff and drainage water affected by cultivation practices*. Doctoral dissertation. Agricultural Research Centre of Finland. Institute of Crop and Soil Science. Jokioinen. 108 p.
- Turtola, E. & Kempainen, E. 1998. Nitrogen and phosphorus losses in surface runoff and drainage water after application of slurry and mineral fertilizer to perennial grass ley. *Agricultural and Food Science in Finland* **7**, 596-581.
- Turtola, E. & Yli-Halla, M. 1999. Fate of phosphorus applied in slurry and mineral fertilizer: accumulation in soil and release into surface runoff water. *Nutrient Cycling in Agroecosystems* **55**, 165-174.
- Uusitalo, R. 2004. Potential bioavailability of particulate phosphorus in runoff from arable clayey soils. Doctoral dissertation. Agricultural Research Centre of Finland. *Agrifood Research Reports* **53**. 95 p.
- Vadas, P.A., Kleinman, P.J.A., Sharpley, A.N. & Turner, B.L. 2005. Relating soil phosphorus to dissolved phosphorus in runoff. *Journal of Environmental Quality* **34**, 572-580.
- Vagstad, N., Stålnacke, P., Andersen, H.E., Deelstra, J., Gustafson, A., Iital, A., Jansons, V., Kyllmar, K., Loigu, E., Rekolainen, S., Tumas, R. & Vuorenmaa, J. 2001. Nutrient losses from agriculture in Nordic and Baltic countries. Measurement in small agricultural catchments and national agro-environmental statistics. *TemaNord 2001* **591**. 74 p.
- van der Molen, D.T., Breeuwsma, A. & Boers, P.C.M. 1998. Agricultural Nutrient losses to Surface Water in the Netherlands: Impact, Strategies, and Perspectives. *Journal of Environmental Quality* **27**, 4-11.
- van der Zee, S.E.A.T.M. & van Riemsdijk, W.H.J. 1988. Model for long-term phosphate reaction kinetics in soil. *Journal of Environmental Quality* **17**, 35-41.
- van der Zee, S.E.A.T.M., Fokkink, L.G.T. & van Riemsdijk, W.H. 1995. A new technique for assesment of reversibly adsorbed phosphate. *Soil Science Society of America Journal* **51**, 599-604.
- van Riemsdijk, W. M., Boumans, L.J.M. & de Haan, F.A.M. 1984. Phosphate sorption by soils. I: A diffusion precipitation model for the reaction of phosphates with metal oxides. *Soil Science Society of America Journal* **48**, 537 - 540.
- Vuorenmaa, J., Rekolainen, S., Lepistö, A., Kenttämies, K. & Kauppila, P. 2002. Losses of nitrogen and phosphorus from agricultural and forest areas in Finland during the 1980s and 1990s. *Environmental Monitoring and Assessment* **76**, 213-248.
- Vuorinen, J. & Mäkitie, O. 1955. The method of soil testing in use in Finland. *Agrogeological Publications* **63**, 1-44.
- Walker, T.W. & Adams, A.F. 1959. Studies on soil organic matter: 2. Influence of increased leaching at various stages of weathering on levels of carbon, nitrogen, sulfur, and organic and total phosphorus. *Soil Science* **87**, 1-10.
- Walker, W. & Syers, J.K. 1976. The fate of phosphorus during pedogenesis. *Geoderma* **15**, 1-19.
- Wiklander, L. & Koutler-Andersson, E. 1966. Effect of air-drying on the solubility of soil phosphate. *Lantbrukshögskolans Annaler* **32**, 309-317.
- Wild, A. 1950. The retention of phosphate by soils. A review. *Journal of Soil Science* **1**, 221-238.
- Willet, I.R., Chatres, C.J. & Nguyen, T.T. 1988. Migration of phosphate into aggregated particles of ferrihydrate. *Journal of Soil Science* **39**, 275-282.

- Williams, E.G. & Saunders, W.M.H. 1956. Distribution of phosphorus in profiles and particle size fractions of some Scottish soils. *Journal of Soil Science* **7**, 90-108.
- Whalen, J.K. & Chang, C. 2001. Phosphorus accumulation in cultivated soils from long-term annual applications of cattle feedlot manure. *Journal of Environmental Quality* **30**, 229-237.
- Wood, T., Bormann, F.H. & Voigt, G.K. 1984. Phosphorus cycling in a northern hardwood forest: Biological and chemical control. *Science* **223**, 391-393.
- Yli-Halla, M. 1989. Effect of different rates of P fertilization on the yield and P status of the soil in two long term field experiments. *Journal of Agricultural Science in Finland* **61**, 361-370.
- Yli-Halla, M. 1997. Classification of acid sulphate soils of Finland according to Soil Taxonomy and FAO/Unesco legend. *Agricultural and Food Science in Finland* **6**, 247-258.
- Yli-Halla, M. & Mokma, D. 1998. Soil temperature regimes in Finland. *Agricultural and Food Science in Finland* **7**, 507-512.
- Yli-Halla, M. & Mokma, D. 2001. Soils in an agricultural landscape of Jokioinen, south-western Finland. *Agricultural and Food Science in Finland* **10**, 33-43.
- Yli-Halla, M., Hartikainen, H., Ekholm, P., Turtola, E., Puustinen, M. & Kallio, K. 1995. Assessment of soluble phosphorus load in surface runoff by soil analysis. *Agriculture, Ecosystems & Environment* **56**, 53-62.
- Yli-Halla, M., Sippola, J. & Saarela, I. 1998. Increase of potential phosphorus leaching in soils with high test concentrations. *Kunglige Skogs- och Lantbruksakademiens Tidskrift* **137**, 187-189.
- Yli-Halla, M., Puustinen, M. & Koskiahho, J. 1999. Area of cultivated acid sulphate soils in Finland. *Soil Use and Management* **15**, 1-6.
- Yli-Halla, M., Mokma, D., Peltovuori, T. & Sippola, J. 2000. Suomalaisia maaprofiileja (Abstract: Agricultural soil profiles in Finland and their classification). *Maatalouden Tutkimuskeskuksen Julkaisuja, Sarja A* **78**. 104 p.
- Yli-Halla, M., Nykänen, A., Siimes, K. & Tuhkanen, H.-R. 2001. Ympäristötuen ehdot ja maan helpoliukoisen fosforin pitoisuus (Abstract: Agri-Environmental Programme regulations and the easily soluble phosphorus concentration in soil). *Maatalouden Tutkimuskeskuksen Julkaisuja, Sarja A* **77**. 45 p.
- Zheng, Z., MacLeod, J.A. & Lafond, J. 2004. Phosphorus status of a Humic Cryaquept profile in a frigid continental climate as influenced by cropping practices. *Biology and Fertility of Soils* **39**, 467-473