ISSN 1457-263X
Helsinki 2013

Pro Terra

No. 63

ABATEMENT OF PHOSPHORUS- AND LEAD-INDUCED ENVIRONMENTAL RISKS BY MEANS OF APATITE ORE MINE TAILINGS

Salla Venäläinen

ACADEMIC DISSERTATION

To be presented, with the permission of the Faculty of Agriculture and Forestry of the University of Helsinki, for public examination in Walter Hall, Agnes Sjöbergin katu 2, Helsinki, on 31 May 2013, at 12 o'clock.

UNIVERSITY OF HELSINKI
DEPARTMENT OF FOOD AND ENVIRONMENTAL SCIENCES
Helsinki 2013

Supervisor:

Prof. Markku Yli-Halla
Department of Food and Environmental Sciences, University of Helsinki, Finland

Pre-examiners:

Prof. Ole K. Borggaard
University of Copenhagen, Denmark

Prof. Samuel J. Traina
University of California, Merced, USA

Opponent:

Prof. Mark Hodson
Environment Department, University of York, United Kingdom

Custos:

Prof. Maija Tenkanen
Department of Food and Environmental Sciences, University of Helsinki, Finland

Cover photo by Hannu Vallas, Lentokuva Vallas Oy: An aerial view of the Siilinjärvi phosphate mine and the tailings pond

ISBN 978-952-10-8772-1 (pbk.)
ISBN 978-952-10-8773-8 (PDF)
ISSN 1457-263X
Electronic version available at https://ethesis.helsinki.fi/

Salla Venäläinen
Department of Food and Environmental Sciences
P.O. Box 27, FIN-00014 University of Helsinki, Finland

Helsinki University Printing House
Helsinki, 2013

Abstract

Mining of phosphorus (P) and lead (Pb) ores increases their amounts in biogeochemical cycles and, consequently, their environmental risks. Phosphorus is an important nutrient, but P loading from sewage waters and agricultural activities to watercourses may result in eutrophication, a process eventually detrimental to aquatic ecosystems. Lead, on the other hand, poses a direct risk of intoxication to all living organisms. In addition to technical applications, Pb is used in pellets and shots on shooting ranges, which accounts for a large source of Pb loading to the environment. Prevention and abatement of detrimental impacts of P and Pb require large-scale, cost-effective techniques that do not compromise the environment.

This thesis was undertaken to investigate the potential of tailings from apatite ore beneficiation at the Siilinjärvi phosphate mine, Finland, in the dephosphorization of sewage and in the remediation of metal-contaminated areas. The material is a mixture of minerals, mainly phlogopite [$KMg_3(Si_3Al)O_{10}(OH)_2$] and calcite ($CaCO_3$), accompanied by apatite [$Ca_5(PO_4)_3F$] residues. Based on the versatile chemical properties, this geomaterial was hypothesized to act as a sorbent for P and Pb, rendering the tailings a potential agent for environmental remediation. A part of the original tailings material was artificially weathered by treating with a strong acid to create reaction-active aluminium (Al) and iron (Fe) (hydr)oxide sites. Some of the acidified material was further subjected to partial neutralization by treating with a strong base to precipitate any metals dissolved from the mineral structure during the acidification. Furthermore, all of the tailings materials were sieved into two particle-size fractions somewhat differing in their mineralogical composition and investigated as separate amendments.

The ability of the tailings to retain P and Pb from aqueous solutions as well as the tailings-induced changes in the Pb retention capacity of a mineral soil were studied by means of an isotherm technique. A sequential fractionation procedure was undertaken to investigate (a) the distribution of inherent and added P between various chemical pools in the tailings and (b) the tailings-induced changes in the distribution of Pb between various chemical pools in a mineral soil artificially contaminated with Pb as well as in an organic shooting range soil contaminated with pellet-derived Pb. Because the toxicity of dissolved Pb depends on its chemical speciation, the tailings-induces changes in the chemical speciation of water-extractable Pb in contaminated shooting range soil was tested separately by means of a cation exchange resin.

The tailings retained both P and Pb efficiently. The removal of soluble P was primarily due to specific sorption by Al and Fe (hydr)oxides and possibly to retention to calcite. Lead sorption by the untreated tailings was a combination of various sorption mechanisms taking place simultaneously, primarily through precipitation and surface complexation. All tailings materials increased the Pb sorption capacity of a mineral soil and transferred Pb from the NH_4NO_3-extractable pool to the more strongly bound forms. In a contaminated shooting range soil, the pellets were found to undergo continuous weathering processes that released Pb into the soil. Amending the soil with the untreated tailings (a) reduced the solubility of the pellet-derived Pb through the formation of sparingly soluble fluorpyromorphite and cerussite, (b) reduced the bioavailability of Pb by transferring it

from the water-soluble and NH_4NO_3-extractable pools into the NaOH-extractable one and (c) transferred the most toxic cationic Pb species to the less toxic non-cationic form.

The results suggest that the tailings may serve as an agent for dephosphorization of sewage and for Pb immobilization in polluted soil. The sorption properties of the material may be further optimized by chemical and physical pre-treatments. At present, the tailings material represents an uneconomic fraction of the ore deposit, but its components may render it a natural, environmentally sound and cost-effective remediation agent.

Foreword

I was first introduced to the topic of this thesis in 2004, when, as a M.Sc. student, I had the opportunity to visit the apatite mine of Kemira GrowHow Oyj in Siilinjärvi, Eastern Finland. I was impressed by the massive mine and the tailings ponds continuing as far as the eye can see. Environmental chemistry and geology being the areas of my interests throughout my M.Sc. studies eventually led to a thesis dealing with phosphorus sorption by the tailings. It all started with a simple question raised by Dr. Jukka Koski-Vähälä: Why does the tailings material reduce phosphorus content of sewage when passing it through a filter bed? I was fortunate to have Paula Ylinen, Lic.Sc. (Tech.), from Kemira GrowHow Oyj as a contact person and a valuable source of information concerning the tailings material. Together with Professor Markku Yli-Halla she acted as my thesis supervisor. I also gained much appreciated help from Jenni Lybeck, M.Sc. (Tech.), from Kemira GrowHow Oyj. The M.Sc. thesis was funded by Kemira GrowHow Oyj.

The investigations carried out with phosphorus inspired me to continue working with the tailings as a Ph.D. student. During my studies, in 2007, I had an opportunity to fulfill a long-lived dream of travelling to Australia, one of the biggest countries in the mining industry worldwide. In Australia, I studied at the University of Western Australia in Perth for one semester. This broadening and memorable experience was financially enabled by Maa- ja vesitekniikan tuki ry, to which I express my sincere appreciation.

Obtaining the data presented in this thesis required hours of soil sampling and laboratory work. I want to thank Salla Selonen, M.Sc., and Lahden ampumaseura ry for their help and co-operation at the Hälvälä shooting range. I was fortunate to have Martina Metzler, M.Sc., and laboratory technician Miia Collander to help me in sampling the shooting range soil, conduct laboratory analyses and take care of the incubation experiments while I was abroad. I am particularly grateful to Martina for all the after-hours time spent with my laboratory analyses and for her infinitely positive attitude and friendship that gave me joy and energy. I also express my sincere appreciation to the K.H. Renlund Foundation, the Research Foundation of the University of Helsinki, the Maj and Tor Nessling Foundation, the Finnish Society for Soil Investigation and Remediation and Maa- ja vesitekniikan tuki ry for providing me with grants for my Ph.D. work.

The seven-year journey towards a Ph.D. would not have been possible without the valuable guidance and constructive comments that I got from several experts. I hereby acknowledge my supervisor Professor Markku Yli-Halla for his remarks on the manuscript and guidance in my studies. I was fortunate to have the opportunity to combine research with work as a university teacher. I also want to thank the reviewers Professor Jose Torrent, Dr. Wim Chardon and Professor Mark Hodson for their valuable comments on the research articles. Finally, I gratefully acknowledge Professor Ole K. Borggaard and Professor Samuel J. Traina for the thorough and insightful pre-examination of the thesis.

I am grateful to my husband Antti for supporting and believing in me through all of these years. Warm thanks are also due to my obliging parents-in-law, Kikka and Kari, for looking after my little one while I was working on this thesis. Finally, I thank my parents as well as Olli and Hannamari for always being there for me.

Helsinki, April 2013
Salla Venäläinen

Contents

List of original publications and participation

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

I	Hartikainen, S.H. & Hartikainen, H.H. 2008. Phosphorus retention by phlogopite-rich mine tailings. Applied Geochemistry 23, 2716–2723.
II	Venäläinen, S.H. 2012. Sorption of lead by phlogopite-rich mine tailings. Applied Geochemistry 27, 1593–1599.
III	Venäläinen, S.H. 2011. Apatite ore mine tailings as an amendment for remediation of a lead-contaminated shooting range soil. Science of the Total Environment 409, 4628–4634.

Laboratory analyses to obtain data for Article I were conducted by Salla Venäläinen (née, Hartikainen). The manuscript was written under the guidance of Professor Helinä Hartikainen.

Permission to reprint the original articles in this dissertation was granted by the publisher of the journals (Elsevier).

List of abbreviations

ABtT	Acid-base-treated (partly neutralized) tailings
AtT	Acid-treated tailings
CE	Cation exchange
CSA	Critical source area
DOC	Dissolved organic carbon
$DOC_{non-cat}$	Non-cationic DOC
DOC_{tot}	Total DOC
FAP	Fluorapatite
FIA	Flow injection analyser
FPM	Fluorpyromorphite
ICP-MS	Inductively coupled plasma - mass spectrometer
ICP-OES	Inductively coupled plasma - optical emission spectrometer
IM	Initial mass
NH_4-Ox	Ammonium oxalate
Pb_{cat}	Cationic Pb
Pb_{dis}	Dissolved Pb
Pb_{ex}	NH_4NO_3-extractable Pb
$Pb_{non-cat}$	Non-cationic Pb
$Pb_{non-extr}$	Non-extracted Pb
Pb_{org}	NaOH-extractable Pb
Pb_{ox}	Ammonium oxalate (NH_4-Ox)-extractable Pb
Pb_{tot}	Semi-total Pb
Pb_{tot-s}	Total water-soluble Pb
Pb_w	Water-extractable Pb
ΣPb_{pools}	Non-residual Pb
Q_0	Amount of readily mobile phosphorus
Q_{max}	Maximum sorption capacity
SPE	Solid-phase extraction
UtT	Untreated tailings

1 Introduction

1.1 Mineral resources and mining-related environmental problems – A brief overview

Although environmental pollution is generally considered to be an outcome of industrialization and urbanization, it dates far back in history. In Europe, the seed of anthropogenic environmental changes was sewn during the flourishing of the Roman Empire – a progenitor of the civilized Western world. During the peak of its powers maintenance of the high standard of living required large-scale exploitation of natural resources. At the time, large amounts of metals, such as lead (Pb), copper (Cu), zinc (Zn) and mercury (Hg), were mined for various purposes, rendering key roles for mining and metallurgy in the economy (Hong et al., 1994; Nriagu, 1996). As for the valuable metals, Pb became particularly important due to its suitability for various purposes. Lead compounds were used for glazing pottery, and metallic Pb was the raw material for piping and cooking utensils, and it served as an agent for preserving and sweetening wine (Hernberg, 2000; Borsos et al., 2003). Consequently, in their everyday life people were directly exposed to high Pb concentrations by consuming traces of this metal in drinking water, food and wine.

Although Pb toxicity had been recorded already in Egyptian papyrus rolls, it was only in the 1st century that the connection between Pb exposure and toxic manifestations was finally recognized (Hernberg, 2000). Later on, Pb poisoning has been suggested as one of the reasons for the fall of Rome (Hong et al., 1994). For 400 years, the Romans produced 60 000 tonnes of Pb annually (Hernberg, 2000). The extensive smelting of metal ores in open fires for centuries unavoidably led to high metal emissions to the atmosphere. Records of these emissions can nowadays be found in natural deposits such as polar ice caps and aquatic sediments (Renberg et al., 1994).

After the fall of the Roman Empire, Pb production declined significantly, increasing again from the Medieval and Renaissance Ages to the Industrial Revolution. The industrialization from the 18th century onwards brought an unprecedented demand for various natural resources and turned a new page in the history of environmental pollution. The introduction of a steam engine in the 19th century and the later invention of a combustion engine and its use in motorized vehicles not only accelerated efficiency of mining activity, and thereby, the exploitation of natural resources, but also increased the use of fossil fuels. Before the development of end-of-pipe technology, the combustion of coal and the consequent production of fly ash rich in Pb and other metals resulted in notable unintentional Pb emissions. By contrast, lead loading originating from the use of Pb in petrol as an antiknock agent from the 1920s onwards (MacKenzie et al., 1997) was deliberate. This development was later discovered to cause persistent environmental load and to have disastrous health effects.

Replacing animal power with mechanized sources of power also resulted in an accelerated revolution in agriculture. The crucial increase in crop yields, however, took place through the introduction of inorganic fertilizers. Although the fertilizing effects of inorganic salts of phosphorus (P) and nitrogen (N) had been discovered already in the mid-19th century by organic chemist Justus von Liebig (Ashley et al., 2011), for a long time the main source of P used in agriculture was still manure and human excreta (Cordell et al., 2009). The mining of P deposits began in the mid-19th century (Smit et al., 2009), but it was not until the mid-20th century that the use of mineral P resources grew exponentially (Smil, 2000; Ashley et al., 2011). The availability of rock-derived P dramatically increased the use of inorganic P fertilizers in agriculture and eventually led to Green Revolution, the development of high-yielding crop varieties, which – supported by the concomitant invention of high-volume production of artificial nitrogenous fertilizers – resulted in doubled crop yields (IFPRI, 2002). Since the mid-20th century, the consumption of non-fuel minerals has increased continuously and exceeded the total amount of all mineral consumption within the history of mankind (Wellmer and Kürsten, 1992).

As for P mining, the extensive use of non-renewable resources and the P losses from fields to water systems has not only lead to a variety of environmental issues, such as eutrophication of surface waters, but has also raised a question about the sufficiency of this nutrient for feeding the growing population. Several scientists have assumed that the known economically extractable P resources in the world will deplete within the 21st century due to intensive mining of rock phosphate (Herring and Fantel, 1993; Steen, 1998; Smil, 2000). Moreover, control over the remaining global P reserves is concentrated in only a few countries, mainly Morocco, China and the US (Cordell et al., 2009), rendering P valuable not only in monetary but also in strategic respects. While the issue of the sufficiency of P resources is controversial, it is an undisputable fact that more attention needs to be paid to the sustainable use of P resources and the recycling of this valuable nutrient in the future.

Today, the high economic standard of living in developed countries is based on the availability and exploitation of natural resources, leading to environmental problems. As for metal pollution, mining activity is the main source of emissions (Rashed, 2010). Besides emissions of undesired metals in manufacturing processes to air, water and soil environments, mining also produces enormous amounts of by-products known as tailings. This material consists of ground rock and process effluents, i.e. chemicals used in the separation of the desired ore from bulk rock. It is primarily piled in massive ponds. These ponds pose a notable environmental risk because they often have a low pH and are rich in chemicals and metals, including toxic ones. Besides pollution of the surrounding soil and groundwater, the enormous piles of tailings are mainly considered waste with no further use.

1.2 Phosphorus- and lead-induced environmental risks

1.2.1 Phosphorus loading to watercourses

Phosphorus is an essential element for all living organisms. This non-metal is a constituent of DNA, RNA, ATP and phospholipids in cells, therefore playing an important role in protein synthesis and cell metabolism. Together with nitrogen (N) and potassium (K), P is quantitatively the most important plant nutrient. In soil, inorganic P occurs either as soluble phosphates ($H_2PO_4^-$, HPO_4^{2-} or PO_4^{3-}, all denoted as PO_4-P) in soil solution, as labile (i.e. readily exchangeable) P loosely retained by Al and Fe (hydr)oxides on soil particles or as non-labile P strongly bound by the solid phase, e.g. sparingly soluble phosphate minerals, such as apatites [$Ca_5(PO_4)_3OH$, F, Cl)]. Soluble P ending up in soil solution is readily sorbed into the labile pool on the Al and Fe (hydr)oxide surfaces by ligand exchange that controls the solubility. This reaction pattern explains why soil solution is naturally very low in P. As plants take up soluble P and thereby decrease its concentration in the solution phase, the loss tends to be compensated by desorption of P from the labile reserves on the oxide surfaces to maintain an equilibrium between solute and sorbed P. Maintenance of the P equilibrium between the amount of sorbed P (i.e. quantity parameter denoted as Q) and the solute P (i.e. intensity parameter denoted as I) is a specific feature of a soil, and it is controlled by factors such as pH, Al and Fe (hydr)oxides, calcium carbonates ($CaCO_3$), soil organic matter and type and amount of clay (Syers and Curtin, 1989; Frossard et al., 1995).

In many Western European countries, intensive fertilization since the Industrial Revolution has gradually led to a positive P balance (i.e. P import to soil exceeding P export from soil) and caused a considerable P enrichment of soils (Chardon and van Faassen, 1999; Tunney et al., 2003). Besides inorganic fertilizers, a significant amount of surplus P accumulation in agricultural fields also originates from animal husbandry. Between 2005 and 2008, inorganic fertilizers together with manure produced by the livestock accounted for over 95% of the P input to soils in the European Union (EU) (Eurostat, 2012a). In Finland, from 1950 to 1980, P inputs in the form of inorganic fertilizers significantly exceeded P outputs (Granstedt, 2000). Since the 1980's, however, the P balance of Finnish agriculture has decreased by 80%, to a level of 8 kg ha^{-1} reported in 2007 (Uusitalo et al., 2007).

A high P surplus in soil increases the risk of P loss to nearby water bodies by surface runoff, erosion and drainage. Runoff waters originating from so-called critical source areas (CSAs) (Sharpley and Rekolainen, 1997; Chardon and van Faassen, 1999) in agricultural fields, such as feeding and queuing areas in pastures and fields repeatedly manured with dung from chicken houses or fur ranches, are particularly problematic. Even if a CSA on a given land area only covers 5% of a catchment, P loss from such an area may account for over 75% of the catchment's total annual P loss (Sharpley and Rekolainen, 1997). Owing to soils' ability to maintain a given P concentration in soil solution, when a soil particle ends up in conditions where the soil-to-solution ratio decreases, P will be released from the particle surfaces to the solution phase to counteract the decrease in the solution P concentration. The tendency of soil to maintain a given equilibrium P concentration in the ambient solution means that the P loading potential of eroded material increases with increasing P saturation on the particle surfaces. An extreme case of such conditions may arise from erosion transferring soil particles from catchments to watercourses and further to larger recipient waters.

A water body receiving eroded material from farmlands amended with manure and fertilizers may become enriched with soluble P, which is usually the growth limiting factor. The subsequent enhanced primary production increases the amount of decomposing plant material, and thus, may eventually lead to the depletion of dissolved oxygen in the hypolimnion of the water system. The anoxic conditions lead to microbially mediated reduction of Fe (III) oxides, which will dissolve and lose their ability to retain P. The subsequent release of P from Fe oxides in the sediments to overlying water causes a vicious cycle known as internal loading. Furthermore, conditions where P no longer is the limiting nutrient favour the growth of cyanobacteria, which are able to fix molecular N (i.e. atmospheric N_2), some also producing toxins.

Besides non-point sources, such as drainage and runoff waters from watersheds, a significant amount of P loading to watercourses originates from point sources, such as industrial and municipal wastewaters. In general, nutrient discharge from sewage waters directed to wastewater treatment plants is fairly easy to control by using modern techniques. In Finland, the level of P recovery by municipal wastewater treatment is about 95% (The Finnish Environment Institute, 2012). Nevertheless, large amounts of soluble P are released to the watercourses also from diffuse sources other than agriculture and forestry. In Finland, a marked P load originates in sewage produced by households outside the sewer network (Hallanaro and Kujala-Räty, 2011). In 2009, only 81% of the population in Finland was connected to urban wastewater treatment (Eurostat, 2012b), leaving one-fifth of the population discharging their wastewaters elsewhere. Moreover, besides the 300 000 year-round households in sparsely populated areas (Hallanaro and Kujala-Räty, 2011), in 2011 there were nearly 500 000 free-time residences or summer cottages also located outside the municipal sewer network (Official Statistics of Finland, 2012). Consequently, P loading to watercourses from rural areas is estimated to be 6-fold that from population centres within the sewer network in Finland (Hallanaro and Kujala-Räty, 2011).

The Finnish authorities have responded to the acknowledged problem by legislation. The Environmental Protection Act (86/2000) stipulating that wastewaters produced outside sewer networks must not cause a risk of pollution to the nearby waterworks came into force in 2000. In 2003, the act was amended with a Government Decree on Treating Domestic Wastewater in Areas Outside Sewer Networks (542/2003). In 2011, this decree was replaced with an updated version (Onsite Wastewater System Decree 209/2011) that sets the minimum standards for wastewater treatment as well as the planning, construction, use and maintenance of treatment systems. The latest decree (209/2011) stipulates that P loading from domestic sewage must be reduced by at least 70% before discharge to the environment. While municipal wastewater treatment plants dephosphorize sewage by large-scale chemical precipitation with iron (Fe) and aluminium (Al) salts (e.g. $Al_2(SO_4)_3$, $AlCl_3$) (Galarneau and Gehr, 1997; Omoike and vanLoon, 1999; Henze et al., 2002, p. 331; Yang et al., 2006; Mortula and Gagnon, 2007), private households require small-scale purification systems that are inexpensive and convenient. For this purpose, several onsite wastewater treatment systems, such as septic tanks combined with filter beds, have been developed. As for black waters (wastewaters including excreta), however, filtering the water through a soil or sand bed does not sufficiently reduce the total P content of the water, and additional P removal with pure chemicals or other manufactured sorbents is often required.

An evaluation of the onsite wastewater treatment systems on the Finnish market was carried out between 2003 and 2004 by the Finnish Environment Institute. Among other solutions, this project studied the applicability of tailings from the Siilinjärvi phosphate mine in two different wastewater purification systems (Vilpas et al., 2005). In one application, the tailings were used as a middle layer in a conventional sand filter bed to improve P sorption. In another application, the tailings material was used as an additional P sorbent in a cesspool receiving sewage water from a conventional sand filter bed. The results revealed that tailings material used as an adsorbing layer in a conventional sand filter bed enhanced P retention, whereas in a cesspool, the tailings did not work as desired. However, the chemical reactions explaining the findings were not studied and the theoretical basis for functioning of the tailings material as a sorbent remained unclear.

1.2.2 Lead as an environmental contaminant

The principal ore mineral for Pb is galena (PbS). Besides primary PbS, weathering products of this unstable mineral, cerussite ($PbCO_3$) and anglesite ($PbSO_4$), are also mined to some extent. Lead is a metal widely used in the metal and chemical industries. Due to the high corrosion tolerance and tendency to mould and shape easily, it is suitable for a wide variety of applications. The primary use for this metal are lead-acid storage batteries, but it is also a common component of pigments, cable sheathing and ammunition. In Finland, as in many other countries, for decades a significant part of Pb emissions to the environment originated from exhaust gases. Since the use of leaded petrol in Finland ended in 1993 (Pietarila et al., 2001), the nationwide Pb emissions dropped from an annual level of 326 tonnes in 1990 to 18 tonnes in 2009 (The Finnish Environment Institute, 2012). Today, one of the main sources of soil pollution is shooting activity (Sorvari et al., 2006). Although the Finnish government decree on hunting (Hunting Act 615/93) prohibits the use of Pb pellets in waterfowl hunting, this metal is still, due to its superior ballistic properties, the main constituent of shots and pellets used in shooting ranges. There are approximately 2000–2500 outdoor shooting ranges in Finland, with almost one-third of the ranges posing a pollution risk to groundwater. Of the total number of 20 000 potentially contaminated sites in the country, shooting ranges comprise 5% of the sites (Sorvari et al., 2006). Considering that the annual site-specific Pb discharge in shotgun pellets may vary from 120 to 15000 kg (Sorvari et al., 2006), the relatively high percentage is not surprising.

Despite the high corrosion tolerance of Pb, a chemically versatile soil environment may expose Pb pellets to various weathering processes such as oxidation, hydration and carbonation (Jørgensen and Willems, 1987; Hardison et al., 2004). The transformation of the pellet-derived Pb into soluble secondary minerals enables the transition of the metal into soil water. In natural conditions, Pb primarily displays the oxidation state +II. While the hydration of Pb^{2+} in an aqueous solution is weak due to the low charge density of the ion (Persson et al., 2011), depending on the pH, the dissolved Pb^{2+} may undergo hydrolysis to form a mononuclear $PbOH^+$ complex (Powell et al., 2009). As the soluble Pb species come into contact with various soil components, such as clay minerals, organic matter, aluminium (Al) and iron (Fe) (hydr)oxides and calcium carbonates ($CaCO_3$), the metal undergoes reactions that largely dictate its bioavailability and ecotoxicity.

Lead is highly toxic to all living organisms. In soil, it decreases the abundance and activity of microorganisms (Kuperman and Carreiro, 1997), disturbs litter decomposition and nutrient mineralization (Tuomela et al., 2005; Rantalainen et al., 2006) and adversely affects various functionally important soil organisms (Rantalainen et al., 2006). Furthermore, Pb inhibits the growth and metabolism of plants (Singh et al., 1997). If leached to the groundwater, it may even threaten public health. As for health effects on humans, it is known to harm the nervous system and to have adverse effects on childhood development of intelligence and academic achievement (e.g. Grandjean, 1978; Lockitch, 1993; Wang et al., 2002; Needleman, 2009). Thus, there is a great demand for environmentally sound and cost-effective ways of reducing the risk of Pb exposure.

The most commonly employed remediation technique is excavation and disposal of contaminated soil (Sorvari et al., 2006; Isoyama and Wada, 2007; Jaakkonen, 2008). Other techniques include containment of the metal by using physical barriers, encapsulation or vitrification, various ex situ methods such as physical separation and soil washing, and in situ methods such as electrokinetics and soil flushing (e.g. Mulligan et al., 2001; Khan et al., 2004). Despite the variety of available techniques, the complexity of the reactions that Pb undergoes in highly versatile soil environments renders their site-specific remediation demanding. Furthermore, many of the remediation techniques are unfeasible in large-scale applications due to their high cost and undesirable secondary environmental impacts. For instance, methods that require extensive use of electricity are very expensive and inconvenient in practice. Moreover, the use of synthesized chemicals, such as soil washing agents, have the disadvantage of causing the risk of further environmental hazard.

1.3 Geological materials as potential agents for environmental remediation

Due to financial and environmental issues related to many sophisticated remediation techniques of contaminated soils and water systems, scientists have explored the potential of various low-cost geological materials in solving environmental problems. Depending on the mineral composition and the consequent chemical characteristics, various geomaterials may be able to act as remediation agents through ion exchange, precipitation and sorption reactions taking place between the contaminant and the mineral components. A review by Yamada et al. (2011) presents the application of smectites, layered doubled hydroxides and zeolites as remediation agents based on their cation- and anion-exchange properties. The utilization of Leca® (Light Expanded Clay Aggregates) (Johansson, 1997) and Filtralite P® (Leca® with lime included) (Jenssen et al., 2005, 2010) has been investigated for their ability to act as P sorbents in wastewater applications and as heavy metal sorbents in the purification of runoff waters originating from metal-contaminated shooting ranges (Strømseng et al., 2008). Moreover, several researchers have studied the immobilization of Pb and other metals using sparingly soluble phosphate minerals, such as phosphate rock (e.g. Ma et al., 1995; Cao et al., 2004; Lin et al., 2005; Elouear et al., 2008; Cao et al., 2009), natural or synthesized hydroxyapatite (HAP) [$Ca_5(PO_4)_3OH$)] (e.g. Ma et al., 1993; Davies et al., 2002; Ioannidis and Zouboulis, 2003; Sandrine et al., 2007; Dybowska et al., 2009; Kaludjerovic-Radoicic and Raicevic, 2010) and synthesized phosphate glass (Jin and Heo, 1998). However, the problem with many of the artificial materials is that even if they successfully mimic naturally occurring minerals and, in that respect, may be considered environmentally friendly, the manufacturing of the chemicals required in the synthesis of the substances often involves extensive use of energy and discharge of other harmful substances to the environment. Thus, the application of such materials for remediation purposes may eventually compromise the environment.

1.3.1 Mineralogical and chemical properties of tailings of Siilinjärvi apatite ore

Siilinjärvi carbonatite complex (described in detail by Puustinen, 1971) is the most substantial phosphate mine in Western Europe and the largest open pit in Finland. The deposit mainly consists of three rocks: phlogopite- and apatite-rich glimmerite, granite-like syenite and carbonate-rich carbonatite. Due to the rock composition, the complex has been mined since 1980 for apatite, a phosphate mineral used as a source of phosphoric acid and P fertilizers, and it is still in operation. The annual production of 795 000 tonnes of apatite concentrate requires the mining of 8.5 million tonnes of apatite ore (Stén et al., 2003). In the beneficiation process, the raw rock material goes through crushing, wet grinding and flotation to separate the desired apatite ore from the tailings by-product. From the total annual volume (150 000 tonnes) of tailings produced, a small part is subjected to carbonate removal, particle-size fractionation and dewatering to produce soil amendment suitable for K, Mg and Ca fertilization. However, the bulk of the tailings material is discharged and pumped into the tailings ponds of Musti, Raasio and Jaakonlampi in the nearby area (Stén et al., 2003). After settling of the tailings material in the pond, most of the water used in the beneficiation process, together with the drainage water from the open pit, is recirculated to the concentration plant (Stén et al., 2003). The surplus water is treated with water purification chemicals and adjusted to pH 7 before release to the nearby lake.

The tailings material from apatite ore beneficiation mainly consists of a trioctahedral phyllosilicate mineral, phlogopite [$KMg_3(Si_3Al)O_{10}(OH)_2$] (ca. 75%), carbonate minerals (mainly calcite, $CaCO_3$) (ca. 16%) and water as well as fluorapatite (FAP) [$Ca_5(PO_4)_3F$)] residues from the beneficiation process. In addition to the mineral components and water, the material contains unidentified flotation chemical residues. Based on the composition of the tailings, the material is not considered toxic. The versatile mineralogy renders the tailings a multicomponent material, allowing a variety of chemical reactions to take place between the solid and dissolved substances. As for the phlogopite component, the sorption properties are largely dictated by the high content of Al and Fe derived from the isomorphic substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and of Fe^{2+} for Al^{3+} in the octahedral layer of the mineral structure. Numerous studies have proved that P has a high affinity for Al^{3+} and Fe^{3+} on the edges of secondary minerals or in hydrated oxides (Muljadi et al., 1966; Hingston et al., 1967; Parfitt et al., 1975; Ryden et al., 1977; Borggaard, 1983; Beck et al., 1999; Borggaard et al., 2004; Peltovuori, 2006). The same components are also able to retain Pb (Bargar et al., 1997; Dong et al., 2000; Bradl, 2004; Helal, 2006; Xu et al., 2006).

The retention of ions onto metal (hydr)oxides takes place either through the formation of an outer-sphere or an inner-sphere complex between the adsorbate and the metal. An outer-sphere complex is formed through electrostatic forces. Due to the amphotheric nature of Al and Fe (hydr)oxides, depending on the pH, these surfaces possess either a negative, positive or neutral surface charge. Thus, it is theoretically possible that at pH below the point of zero charge (p.z.c.), the retention of anions, such as PO_4-P, may take place electrostatically, whereas that of cations (e.g. Pb^{2+}) may take place at pH above the p.z.c. However, it is more probable that these adsorbates form an inner-sphere complex via a ligand exchange mechanism, which involves the substitution of a hydroxy (OH^-) or an aqua (H_2O) group in the co-ordination sphere of the metal on the adsorbate surface. Since the H_2O group is more prone to substitution than the deprotonated OH^- group, a decrease in pH favours the reaction. The covalent bond formed in the reaction is very strong by nature, thus efficiently protecting the adsorbate from leaching.

In addition to the Al and Fe (hydr)oxides in phlogopite, there is evidence that Pb may also be adsorbed by amorphous silica emerging on the fracture edges and edge-faces of weathered silicate minerals through the formation of inner-sphere surface complexes (Schindler et al., 1976; Elzinga and Sparks, 2002; Chen et al., 2006). This mechanism may partly contribute to the sorption properties of the phlogopite component in the tailings. Furthermore, $CaCO_3$ has been reported to retain both PO_4-P (Cole et al., 1953; Freeman and Rowell, 1981; Borrero et al., 1988) and Pb (Rouff et al., 2002, 2005). The retention of PO_4-P by calcite occurs through monolayer surface sorption or through precipitation of P as dicalcium phosphate (Cole et al., 1953). As for the retention of Pb, the sorption may occur through surface complexation (Rouff et al., 2005) or through the formation of sparingly soluble cerussite ($PbCO_3$) (Taylor and Lopata, 1984; Godelitsas et al., 2003; Al-Degs et al., 2006).

As for the fluorapatite component in the tailings, it may significantly contribute to Pb retention. A number of researchers have demonstrated that phosphates, particularly primary igneous apatites [$Ca_5(PO_4)_3OH$, F, Cl)], together with secondary sedimentary phosphate rocks, play a significant role in Pb retention. Pb^{2+} may substitute for apatitic Ca^{2+} through an ion exchange mechanism (Suzuki et al., 1982; Chen et al., 1997; Zhu et al., 2010) due to its high value of electronegativity (2.33) and ionic radius (0.118 nm) close to that of Ca^{2+} (0.09–0.13 nm) (Suzuki et al., 1982). Apatites may also retain Pb^{2+} through surface adsorption and complexation by the functional groups of the mineral

(Forsling and Wu, 1993; Ma et al., 1995; Mavropoulos et al., 2002; Hashimoto and Sato, 2007; Sandrine et al., 2007). Furthermore, provided that the conditions are sufficiently acidic, the reaction between Pb^{2+} and apatites may result in the formation of sparingly soluble pyromorphites (PM) [$Pb_5(PO_4)_3(OH, F, Cl)$] through dissolution of the parent apatite mineral and subsequent precipitation of PM (e.g. Ma et al., 1993, 1995; Chen et al., 1997; Cao et al., 2003, 2004; Mavropoulos et al., 2002, 2004).

1.4 Objectives of the work

While the mining industry produces metals and non-metal elements for various purposes, it also produces large quantities of tailings considered to be waste material. Mining of bedrock-derived elements inevitably increases their concentrations in the biogeochemical cycles, and thus, increases the risk of contamination or pollution of various environmental compartments. By contrast, some tailings materials may have potential to be utilized in an environmentally sound way for various purposes or even to abate the deterioration of soil and water ecosystems. Based on its versatile mineralogy, the tailings from Siilinjärvi apatite ore beneficiation can be taken as a multicomponent geomaterial with the potential to act as a remediation agent to counteract P- and Pb-related environmental risks.

This study was undertaken to unravel the chemical reactions of P and Pb with the apatite ore tailings in order to create a theoretical basis for potential practical applications. The aim was to investigate the potential of the tailings to act as a multifunctional remediation agent in the dephosphorization of domestic wastewaters and in the reduction of P discharge from CSAs (Article I) and in the remediation of shooting ranges and other areas contaminated with Pb (Articles II and III). Systematic experiments were carried out to evaluate the ability of the tailings material (a) to retain P and Pb from pure aqueous solutions (Articles I and II), (b) to immobilize Pb in a chemically versatile soil environment (Article III), (c) to understand the sorption mechanisms of P and Pb (Articles I-III) and (d) to reveal the potential of the material to reduce the bioavailability and ecotoxicity of pellet-derived Pb in contaminated soil (Article III). Attempts were also made to determine whether the sorption capacity of the material could be further enhanced (a) by sieving the tailings into small (ø < 0.2 mm) and large (ø > 0.2 mm) particle-size fractions differing to some extent in their mineralogy (Articles I–III) or (b) by artificially manipulating the quantity of reaction-active sites through acid (Articles I–II) or acid-base (Article I) pre-treatment. Since the material consists of natural soil components, its use in environmental applications would be ecologically justified. Besides finding a way to abate the P loading problems in watercourses and the Pb pollution of soils, the research also aims at finding sound and economically justified use for the untapped tailings, thereby reducing the enormous amount of tailings discharge primarily piled as waste.

2 Materials and methods

The experimental designs and methodologies applied in this thesis are described here in brief. The main research subjects covered in the original articles (Articles I–III) and the experiments carried out to investigate the research subjects (Experiments 1–6) as well as the number of replicates used in each of the experiments are compiled in Table 1. Detailed descriptions of the procedures are given in the original publications.

***Table 1**. Summary of the main research subjects, the experiments conducted and the number of replicates analysed in each experiment*

	Research subject	Experiment		No. of replicates
		No.	Description	
Article I	P sorption by tailings	1	Chemical fractionation of intrinsic and added P between various chemical pools in tailings	3
		2	P desorption-sorption isotherms (*Q/I* plot) of tailings	4
		3	P desorption-sorption isotherm (*Q/I* plot) of acid-treated tailings after the removal of Al and Fe (hydr)oxides	3
Article II	Pb sorption by tailings	4	Pb sorption isotherms of untreated tailings	4
		5a	Pb sorption isotherms of tailings-amended mineral soil	4
		5b	Chemical fractionation of added Pb between various chemical pools in uncontaminated mineral soil	4
Article III	Tailings as a remediation agent for Pb-contaminated shooting range soil	6a	Chemical fractionation of Pb-contaminated shooting range soil	4
		6b	Chemical speciation of water-extractable Pb from Pb-contaminated shooting range soil	4

2.1 Tailings samples

The tailings provided by Kemira GrowHow Oyj (company purchased by Yara in 2007) originated from the Siilinjärvi phosphate mine (for details, see Puustinen, 1971) located in Eastern Finland (63˚08´N, 27˚44´E). A part of the tailings material was treated with 70% H_2SO_4 (Articles I and II) in the research centre of the company to simulate weathering that produces reactive Al and Fe (hydr)oxides. A portion of the acidified tailings was also partly neutralized with NH_4OH (Article I) to precipitate any metals dissolved from the mineral structure during the acidification. The acid-treated tailings (AtT), the acid-base-treated tailings (ABtT) and the untreated material (UtT) were passed through a 0.2-mm sieve to divide the materials into small (ø < 0.2 mm) and large (ø > 0.2 mm) particle-size fractions, which were studied as separate remediation agents. A portion of the material was also investigated without subjecting it to any preliminary physical or chemical treatments (Article III).

The tailings samples were dried at 60°C overnight to remove any adsorbed moisture and stored at room temperature in tight plastic containers. The unsieved tailings materials were analysed for electrical conductivity (EC) in a water suspension (V:V 1:2.5) and classified for colour according to the Munsell Color (1994) soil colour chart. All of the tailings samples, except for the small- and the large-sized fractions of the ABtT were analysed for pH in de-ionized H_2O (V:V 1:2.5). Furthermore, all of the tailings samples, except for the unsieved ABtT, were analysed for poorly crystalline Al and Fe (hydr)oxides by extracting twice with 0.05 M acidic ammonium oxalate (NH_4-Ox) (($(NH_4)_2C_2O_4 \cdot H_2O$, pH 3.3, 1:50 g:mL, 2 h shaking in the dark) with a method modified from Niskanen (1989). Prior to the proper oxalate extraction, calcite residues in the UtT were removed with a method modified by Loeppert and Inskeep (1996) from those of Schwertmann (1964) and McKeague and Day (1966). In the removal of calcite, 1.5 g UtT samples were extracted with 90 mL of 1 M ammonium acetate (CH_3COONH_4) (pH 5.5). During the extraction, pH of the suspensions was controlled and readjusted to 5.5 with acetic acid (CH_3COOH) until it remained unchanged. Next, the acid was discarded and the samples were washed twice with 50 mL of de-ionized H_2O before drying at 50°C. Extraction of the samples with acid ammonium acetate revealed that the consumption of acid was higher for the small-sized than the large-sized UtT, suggesting that the small-sized material was richer in calcite than the large-sized one. The physico-chemical properties of the tailings materials are given in Table 2.

Table 2. *Properties of tailings materials*

Tailings	**Mesh Ø**	**pH[a] H_2O**	**EC[a] µS cm^{-1}**	**Poorly crystalline oxides[b] mmol kg^{-1} ± SD**		**Colour[c]**
				Al	**Fe**	
Untreated tailings (UtT)	Unsieved	9.3	$1.5\cdot10^2$	0.8 ± 0.07	8.7 ± 0.7	10 YR 4/2 (greyish brown)
	> 0.2 mm	9.4	n.a.	0.6 ± 0.04	6.8 ± 0.5	
	< 0.2 mm	9.1	n.a.	1.5 ± 0.05	17.8 ± 2.1	
Acid-treated tailings (AtT)	Unsieved	3.2	$2.6\cdot10^4$	240 ± 11	184 ± 9	7.5 YR 6/2 (pinkish grey)
	> 0.2 mm	4.0	n.a.	196 ± 8	150 ± 7	
	< 0.2 mm	3.1	n.a.	388 ± 6	299 ± 4	
Acid-base-treated tailings (ABtT)	Unsieved	4.6	$3.2\cdot10^4$	n.a.	n.a.	10 YR 6/6 (brownish yellow)
	> 0.2 mm	n.a.	n.a.	203 ± 5	158 ± 2	
	< 0.2 mm	n.a.	n.a.	288 ± 4	247 ± 5	

[a] Measured from water suspension 1:2.5 (V:V)

[b] Extracted twice with 0.05 M ammonium oxalate (pH 3.3, 1 g : 50 mL, shaking for 2 h in the dark) (method modified from Niskanen, 1989).

[c] Munsell (1994)

n.a. = Not analysed

2.2 Analytical approaches to studying the sorption properties of tailings

2.2.1 Chemical fractionation

To distinguish between the different sorption sites responsible for the retention of P and Pb, the tailings samples were subjected to sequential fractionation procedures. In these procedures, the samples are subjected to sequential extraction with solutions of increasing extraction power assumed to extract P or Pb from various chemical pools. However, it should be noted that these pools are operationally defined and strongly dependent on the solutions and conditions used in the extraction. Nevertheless, in this thesis the fractionation approach was considered to give an idea of the primary sorption sites and to reveal the principal differences in sorption properties of the different tailings materials.

2.2.2 Desorption-sorption isotherms (*Q/I* plots)

In the determination of a desorption-sorption isotherm, a series of sorbent material is allowed to equilibrate at a constant temperature with solutions of increasing concentrations of the adsorbate, and the final concentrations of the adsorbate in the ambient solutions are analysed. Sorption to or desorption from the sorbent surface (quantity parameter Q, mg kg^{-1}) is calculated from the change of the adsorbate concentration. The intensity parameter I, on the other hand, represents the final adsorbate concentrations in the equilibrium solutions (mg L^{-1}). Plotting the equilibrium concentration against the desorption from or sorption by the solid surface constitutes a quantity/intensity plot i.e. a *Q/I* plot (Beckett and White, 1964). The *Q/I* graph can be used to estimate the quantity of sorption or desorption needed to reach a given adsorbate concentration in the ambient solution. Plotting the initial solution concentration against the parameter Q constitutes another type of graph. This type of isotherm describes the desorption or sorption when the sorbent is subjected to a solution of a given adsorbate concentration (Hartikainen, 1982). This type of graph is termed the initial mass (IM) isotherm by Nodvin et al. (1986).

In this thesis, the *Q/I* approach was chosen to describe the ability of the tailings to maintain given adsorbate concentrations in the solution phase. The *Q/I* isotherms were used to estimate the P and Pb sorption capacities of the different tailings materials and to reveal different stages of P and Pb sorption, such as specific sorption by Al and Fe (hydr)oxide surfaces, precipitation, possible re-release of sorbed P and Pb, or reaching of a sorption maximum (Articles I and II). Furthermore, the *Q/I* technique was applied to estimate the ability of the different tailings materials to lower solute P concentration, e.g. in purification systems to an allowable level (Article I), as well as to estimate the impact of tailings amendment on the Pb sorption properties of a mineral soil, i.e. on the risk of Pb leaching from soil (Article II).

2.3 Phosphorus sorption by tailings

Prior to the actual experiments described below, preliminary experiments were carried out to get a general idea of the P sorption capacity of the tailings and to define the enrichment solution concentrations to be used in the experiments. The results from the preliminary tests indicated that the P sorption capacity of the AtT and the ABtT largely exceeded that of the UtT. Therefore, when preparing the *Q/I* isotherms higher P additions were needed for the AtT and the ABtT than for the UtT. The large variation in the sorption properties of the different tailings materials also explains the different tailings-to-solution ratios used for them.

2.3.1 Distribution of intrinsic and sorbed phosphorus between various chemical pools in tailings materials (Experiment 1)

As a premise for the investigation of P sorption capacity of tailings, the materials were analysed for the occurrence of intrinsic P. To obtain information about the different chemical forms of innate P rather than to simply analyse the total P content of the material, the tailings were subjected to a sequential fractionation using a modified version of the Chang and Jackson (1957) method (Hartikainen, 1979). Despite the widely used Chang and Jackson method is known to have shortcomings (e.g. ambiguous segregation between Al and Fe bound P, possible transition of P from one pool to another, formation of new components able to retain P during the extraction), it was, however, considered to provide sufficient information about the apparent P pools in the different tailings materials. In this procedure, the samples were extracted with a selection of solutions assumed to extract P from various chemical pools as follows:

1) 1 M NH_4Cl replaces exchangeable Ca by NH_4^+ ions and removes water-soluble and loosely bound P (NH_4Cl-P)

2) 0.5 M NH_4F (pH 8.5) removes Al-bound P (NH_4F-P) through ligand exchange of PO_4-P for F^--ions. Fluoride is known to have a higher affinity for Al^{3+} than for Fe^{3+} (Lindsay, 1979, pp. 36, 130).

3) 0.1 M NaOH removes Fe-bound P (NaOH-P) on oxide surfaces through substitution of PO_4-P by OH^-- ions

4) 2.5 M H_2SO_4 dissolves P from the residues of the apatite ore that passed the beneficiation process (H_2SO_4-P)

Contrary to the original method of Chang and Jackson (1957), in the modified version of Hartikainen (1979) the pH of the NH_4F solution was adjusted to 8.5 (instead of 7.0) to minimize the dissolution of Fe-bound P during the extraction, as suggested by Fife (1959).

After the second and third steps, the samples were washed twice with saturated NaCl solution to remove the P residues of the preceding extract in the interstitial water.

To distinguish between the initially occupied and the still available P sorption sites, another set of tailings samples was first enriched with KH_2PO_4 solutions and then re-subjected to a sequential fractionation. In the P addition procedure, 1-g UtT samples received 50 mL of a solution containing 1 mg P L^{-1}, and 0.5-g AtT and ABtT samples received 50 mL of a solution containing 50 mg P L^{-1}. The suspensions were shaken for 1 h, allowed to equilibrate for 23 h at room temperature, and re-shaken for 10 min before passing through a 0.2-µm membrane filter (Nuclepore ® polycarbonate). All extracts were analysed for P with a spectrophotometer. The DPS (degree of phosphorus saturation) of the Al and Fe (hydr)oxides (denoted as Al_{ox} and Fe_{ox}) in both unenriched and enriched tailings was calculated according to Peltovuori et al. (2002) (Eq. 1):

$$\mathrm{DPS} = (\mathrm{NH_4Cl\text{-}P+NH_4F\text{-}P+NaOH\text{-}P}) / (0.5\times(\mathrm{Al_{ox}+Fe_{ox}})) \times 100(\%) \qquad \text{(Eq. 1)}$$

where NH_4Cl-P, NH_4F-P, NaOH-P, Al_{ox} and Fe_{ox} are given in mmol kg^{-1}. According to the original procedure for DPS determination, the calculation is based on NH_4-Ox-extractable P (van der Zee and van Riemsdijk, 1988; Lookman et al., 1995). However, since acid oxalate solution is able to extract primary P resulting in erroneously high DPS values for materials high in apatitic P (Peltovuori et al., 2002), the sum of Chang and Jackson's (1957) NH_4Cl-P, NH_4F-P and NaOH-P fractions was used instead. The coefficient 0.5 employed in the equation is a value for a parameter that represents the fraction of Al and Fe presumably able to bind P. The parameter value used here is a mean of those determined by Breeuwsma and Schoumans (1986) and van der Zee and van Riemsdijk (1988).

2.3.2 Phosphorus desorption-sorption isotherms (*Q/I* plots) (Experiment 2)

To obtain further information about the ability of small- and large-sized UtT, AtT and ABtT to release and retain P as well as about the dependency of P reactions on contact time, the tailings samples were subjected to analysis for their P exchange properties by means of an isotherm technique (method modified from Hartikainen, 1982). In the procedure, two sets of tailings samples were allowed to react with aqueous KH_2PO_4 solutions of eight increasing P concentrations for either 23 h or 7 d at 20°C (details about equilibration times, solid-to-solution ratios and concentrations of the enrichment solutions used for the different tailings samples are given in Table 3). After equilibration, the suspensions were shaken for 10 min before passing through a 0.2-µm membrane filter (Nuclepore® polycarbonate). The filtrates were analysed for P with a flow injection analyser (FIA) and their pH was measured. The P concentrations were employed to calculate the parameters Q and I to construct a Q/I plot. The amount of readily mobile P (Q_0, point of intersection on the y-axis) and the maximum quantity of P that the material is able to retain (Q_{max}) were interpreted from the Q/I graph. During the equilibration, the formation of a white milky precipitate was observed in all suspensions containing P solution, especially in those containing AtT and ABtT. A subsequent chemical analysis of the collected precipitate by XRD technique (analysis carried out in the research centre of Kemira Growhow Oyj) revealed that it mainly consisted of P, Si, Fe and Al, listed in order of decreasing abundance.

Table 3. *Equilibration times, solid-to-solution ratios and P concentrations of enrichment solutions used in the Q/I experiments conducted with different tailings materials*

Tailings	**Mesh**	**Equilibration time**	**Solid-to-solution ratio**	**P enrichment solution concentrations**
	Ø mm		**w:V**	**mg L^{-1}**
Untreated tailings (UtT)	> 0.2	24 h	1:50	0, 0.05, 0.1, 0.3, 0.5, 1.0, 2.0 and 4.0
	< 0.2	24 h		
	> 0.2	7 d	1:50	0, 0.1, 0.3, 0.5, 1.0, 2.0, 4.0 and 5.0
	< 0.2	7 d		
Acid-treated tailings (AtT)	> 0.2	24 h	1:100	0, 25, 50, 100, 200, 300, 400 and 500
	< 0.2	24 h		
	> 0.2	7 d	1:100	0, 25, 50, 100, 200, 300, 400 and 500
	< 0.2	7 d		
Acid-base-treated tailings (ABtT)	> 0.2	24 h	1:100	0, 25, 50, 100, 200, 300, 400 and 500
	< 0.2	24 h		
	> 0.2	7 d	1:100	0, 50, 100, 200, 300, 400, 500 and 600
	< 0.2	7 d		
AtT (oxides removed)	< 0.2	24 h	1:50	0, 0.05, 0.1, 0.2, 0.5, 1.0, 2.0 and 3.0

2.3.3 Contribution of Al and Fe (hydr)oxides to phosphorus sorption (Experiment 3)

To substantiate the contribution of Al and Fe (hydr)oxides to P sorption, the small-sized AtT material that had the highest Al and Fe (hydr)oxide contents out of all tailings (Table 2) was examined in more detail. It was subjected to removal of oxides by using the modified acid ammonium oxalate method of Niskanen (1989), but using a larger extraction ratio of 100:1 (V:w) to ascertain a thorough removal of the (hydr)oxides. After the oxalate extraction, the samples were washed with saturated NaCl solution and with water to remove soluble ions, and the material was dried overnight. Next, the small-sized AtT material free of NH_4-Ox-extractable Al and Fe was subjected to a 23-h equilibration with KH_2PO_4 solutions of eight increasing P concentrations (Table 3) at 20°C before a 10-min shaking, filtration through a 0.2-µm membrane filter (Nuclepore® polycarbonate) and analysis for P with a flow injection analyser. The desorption-sorption results were depicted as a function of the P concentration in the solution.

2.4 Lead sorption by tailings

After confirming the ability of the tailings to retain P in Article I, the focus of the research shifted to Pb sorption (Article II). To obtain an overview of the Pb sorption capacity of the material, a series of preliminary tests were carried out by means of isotherm technique. Besides studying the impact of acid and acid-base treatments (At and ABt) and assorting (see Article I) on the Pb sorption properties of the tailings material, preliminary experiments were undertaken to investigate the contribution of thermal treatment (combustion at 550°C) and reaction time (24 h and 7 d) on the Pb retention by the tailings.

However, the isotherms obtained with the AtT were practically upright in shape and the Pb additions required to obtain any curvilinear sorption graphs were unrealistically large and irrelevant in practice. Therefore, the AtT material was excluded in the further sorption experiment carried out with pure aqueous solutions (Experiment 4). Nevertheless, the AtT material was included in Experiments 5a and 5b (Article II), where the impact of tailings-derived Al and Fe (hydr)oxides to Pb sorption by an uncontaminated mineral soil was investigated. On the basis of the results of the preliminary experiments, in the sorption tests higher Pb additions were used for the AtT-amended soil samples than for the control soil or the UtT-amended soil samples.

As for the acidified tailings that were partially neutralized (i.e. acid-base-treated tailings, ABtT), extension of the reaction time from 24 h to 7 d or thermal treatment of the tailings material did not notably affect the Pb sorption results. Therefore, the ABtT material was entirely excluded from the experiments described below.

2.4.1 Lead sorption by untreated tailings (Experiment 4)

To obtain a general picture of the Pb retention ability of the tailings, sorption isotherms were produced for the small- and the large-sized UtT by shaking the samples for 1 h with aqueous $Pb(NO_3)_2$ solutions of 11 increasing Pb concentrations (Table 4). The suspensions were allowed to equilibrate for 23 h at room temperature before a 10-min shaking and then passed through a filter paper (Schleicher & Schüll type 5893). The filtrates were analysed for Pb with ICP-MS and their pH was measured. The final Pb concentrations were employed to calculate the parameters Q and I to construct a Q/I plot. Details about the concentrations of the enrichment solutions and the solid-to-solution ratios are given in Table 4.

2.4.2 Impact of tailings materials on lead sorption by soil (Experiment 5)

The tailings-induced changes in the Pb sorption ability of mineral soils and the different reaction mechanisms attributable to Pb removal were investigated in an incubation experiment with uncontaminated sandy loam soil (soil described in detail by Simojoki, 2000). The soil contained 2.5% organic carbon and had a pH of 5.8 (measured in water, V:V 1:2.5). The effective cation exchange capacity (CEC_{ef}) of the soil was 7.6 cmol(+)

kg^{-1} (unpublished data). One set of 125-g soil samples was amended with 5 or 10 g of small- or large-sized UtT. Another set of samples received 5 or 10 g of small- or large-sized AtT rich in Al and Fe (hydr)oxides to reveal their contribution to Pb retention. Soil samples without tailings amendment served as controls. Each of the experimental units received 30 mL of mQ-H_2O to obtain field capacity and were covered with cling film. During the 3-month incubation at 20°C, the experimental units were watered according to weight loss to replace evaporated moisture.

2.4.2.1 Lead sorption isotherms of tailings-amended soil (Experiment 5a)

After the incubation, subsamples from the experimental units were shaken for 1 h with aqueous $Pb(NO_3)_2$ solutions of eight increasing Pb concentrations (Table 4) and allowed to react for 23 h at 20°C before a 10-min shaking and passing through a filter paper (Schleicher & Schüll type 5893). The filtrates were analysed for Pb with an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) and their pH was measured. The Pb concentrations were employed to calculate the parameters Q and I to construct a Q/I plot. The following Langmuir adsorption equation (Eq. 2, Essington, 2004, p. 339) was fitted to the Q/I data points obtained by a least squares fit using MS Excel 2007 Solver Tool:

$$Q = Q_{max}*K*I \,/\, I+K*I \qquad \text{(Eq. 2),}$$

where Q_{max} is the maximum Pb sorption and K is a sorption equilibrium constant. Details about the sorption experiment are given in Table 4.

Table 4. *Tailings dosages used in the incubation experiment conducted with 125 g of mineral soil with and without tailings amendment and Pb concentrations of the enrichment solutions used in the Q/I experiments carried out with and without soil at a solid-to-solution ratio of 1:50 (w:V).*

Sample	**Tailings**		**Pb enrichment solution concentrations**
	Mesh Ø mm	**Addition to soil g**	**mg L^{-1}**
Untreated tailings (UtT)	> 0.2	-	0, 2.5, 5, 7.5, 10, 12.5, 15, 20, 25, 30 and 35
	< 0.2	-	
Soil	-	-	0, 50, 75, 100, 250, 500, 750 and 1000
Soil + UtT	> 0.2	5	0, 50, 75, 100, 250, 500, 750 and 1000
	> 0.2	10	
	< 0.2	5	
	< 0.2	10	
Soil + Acid-treated tailings (AtT)	> 0.2	5	0, 100, 250, 500, 750, 1000, 1500 and 2000
	> 0.2	10	
	< 0.2	5	
	< 0.2	10	

2.4.2.2 Tailings-induced changes in the distribution of sorbed lead between various chemical pools (Experiment 5b)

The tailings-induced changes in the distribution of sorbed Pb between various chemical pools were investigated in a subsequent study. The samples that had received a Pb addition of 100 mg L^{-1} and retained an average of 5286 ± 113 mg Pb kg^{-1} in the preceding isotherm experiment were carefully collected from the filter papers and dried. The dry Pb-enriched samples were subjected to a sequential extraction using a method modified from Venäläinen (2011, Article III). In the procedure, the soil samples were extracted with a selection of solutions (soil-to-solution ratio of 1:100 dw:V, 2-h shaking, filtration through a Schleicher & Schüll type 5893 filter paper) assumed to extract Pb from various chemical pools as follows:

1) mQ-H_2O to remove water-soluble Pb (Pb_w)

2) 1 M NH_4NO_3 to remove exchangeable Pb (Pb_{ex}) through the replacement of Pb^{2+} with NH_4^+

3) 0.5 M NaOH to remove Pb retained by organic substances (Pb_{org}) through the dissolution of humic substances

4) 0.05 M ammonium oxalate (NH_4-Ox) (pH 3.3) (Niskanen, 1989) to remove Pb retained by poorly crystalline Al and Fe (hydr)oxides (Pb_{ox}) through the dissolution of the oxides

The second step of the extraction procedure was repeated to ascertain the complete removal of Pb_{ex}. Furthermore, the second and third steps of the extraction were followed by washing the samples twice with mQ-H_2O to remove any soluble salts remaining from the NH_4NO_3 and NaOH extraction. The extracts were analysed for Pb with ICP-OES and their pH was measured. The Pb not extracted in the sequential extraction ($Pb_{non\text{-}extr}$) was calculated as the difference between the total amount of sorbed Pb (Pb_{sorbed}) and the sum of Pb_w, Pb_{ex}, Pb_{org} and Pb_{ox} ($\sum Pb_{pools}$), i.e. non-residual Pb.

2.5 Impact of tailings on lead in shooting range soil

While the Pb sorption experiments in Article II were conducted with pure chemicals and uncontaminated soil, the experiments in Article III were undertaken to simulate the tailings-induced changes in a real contaminated soil environment. Soil material collected from a shooting range soil area was incubated with and without tailings amendment (Experiment 6). The small-sized fraction, the large-sized fraction and the unsieved material were investigated as separate amendments. Originally, the experiment was carried out with both the UtT and the AtT. However, the results revealed that the AtT of very low pH significantly increased the water-extractable Pb, rendering the material unsuitable as a remediation agent. Therefore, the AtT amendment was omitted from Article III.

2.5.1 Soil samples and sample preparation

The soil samples used in Article III were collected from the Hälvälä shooting range (61°00.644′ N, 025°28.406′ E) located in Hollola, southern Finland. The area is described in detail by Hartikainen and Kerko (2009). The soil in the area, classified as Haplic Regosol (Humic, Dystric, Arenic) (FAO, 2006), consists of a sandy mineral horizon overlaid by a 0- to 7-cm-thick humus layer and is typical of a boreal forest. The soil sampling at the shooting range was carried out by first removing the ground cover and then collecting a composite sample from the underneath organic horizon, where the majority of the pellets are accumulated (Hartikainen and Kerko, 2009). In the laboratory, the soil was passed through a 1-cm sieve to remove the coarsest plant parts and then worked through in small amounts to carefully extract all of the visible shotgun pellets with a pair of tweezers. Finally, the pellet-free material was homogenized by passing through a 2-mm sieve and stored at 5°C in a tight plastic container.

The fresh soil was analysed for pH in water (V:V 1:2.5), for water content as weight loss on drying for 1.5 h at 105°C and for organic matter (OM) content as loss of weight on ignition for 2 h at 550°C after the drying. The water holding capacity (WHC) of the soil was determined by saturating 20-g soil samples with water overnight and calculating the amount of water held by the samples as a weight loss after drying the saturated samples at 105°C overnight. Furthermore, the soil was analysed for its effective cation exchange capacity (CEC_{ef}) as the sum of cations (extracted four times with 1 M CH_3COONH_4, pH 7, soil-to-solution ratio 1:20 w:V, measurement with ICP-OES) and exchangeable acidity (extracted four times with 1 M KCl, soil-to-solution ratio 1:20 w:V, titration with NaOH solution). The soil properties are given in Table 5.

Table 5. *Properties (mean ± SD) of Hälvälä shooting range soil (modified from Venäläinen, 2011)*

Water content (% of fresh weight)	49.6 ± 0.1
Organic matter content (% of dry weight)	56.5 ± 0.3
WHC[a] (% of dry weight)	546 ± 24
pH in H_2O	5.3 ± 0.0
CEC_{ef} (cmol(+) kg^{-1})	17.3 ± 1.0

[a]WHC = Water holding capacity

2.5.2 Design of the incubation experiment (Experiment 6)

A set of 50-g samples of fresh homogenized shooting range soil was placed in tared plastic vessels and then amended with 9-g dosages of the small-sized, large-sized or unsieved UtT material by spreading it over the samples. The 9-g tailings dosage was chosen to correspond to an application rate of 10 t ha^{-1} to the surface soil. This was considered a realistic application rate in an in situ remediation situation. Samples not receiving a tailings addition served as controls. The samples were carefully moistened with 25 mL of mQ-H_2O to adjust the soil moisture to 33% of the WHC and weighed for their total mass before covering with cling film. The experimental units were stored at a constant temperature of 20°C and watered weekly according to weight loss to replace evaporated water.

2.5.3 Chemical fractionation of pellet-derived lead (Experiment 6a)

The experimental units of the shooting range soils were sampled after a 9-, 10-, 14- and 21-month incubation for the chemical analyses and for the determination of the exact water content in the samples to allow the calculation of the results per dry weight of soil. The tailings-induced changes in the distribution of pellet-derived Pb among various chemical pools in the contaminated shooting range soil were determined by means of a sequential extraction procedure described in Section 2.4.2.2 and in detail in Article III. In addition, the soil samples were analysed for the semi-total Pb content (Pb_{tot}) by microwave digestion in 70% HNO_3 according to the Environmental Protection Agency (EPA) 3051 protocol (EPA, 1994). The extracts were analysed for Pb with an Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The amount of Pb not extracted with the sequential extraction ($Pb_{non\text{-}extr}$) was calculated by subtracting the sum of Pb_w, Pb_{ex}, Pb_{org} and Pb_{ox} ($\sum Pb_{pools}$) from Pb_{tot}.

2.5.4 Speciation of water-extractable lead (Pb_w) (Experiment 6b)

Following the incubation, the water-extractable fraction, i.e. the most readily bioavailable Pb fraction (Pb_w), was subjected to a novel chemical speciation analysis to elucidate the tailings-induced changes in the occurrence of the most ecotoxic Pb species, Pb^{2+} and $PbOH^+$. The use of geochemical thermodynamic equilibrium modelling programs (e.g. Visual MINTEQ, Gustafsson, 2000) commonly applied to predict metal speciation and sorption on geomedia (e.g. Cao et al., 2008; Kaludjerovic-Radoicic and Raicevic, 2010) was not considered convenient due to the high complexity of the soil-tailings-metal system where precipitation reactions are expected to take place. Instead, for the speciation analysis, all of the experimental units were extracted with water (1:200 dw:V, 2-h shaking). A part of the suspension was filtered through a coarse (12–25 µm) filter paper (Schleicher & Schüll type 5891), retaining the largest plant parts, while allowing the total water-soluble Pb ($Pb_{tot\text{-}s}$), likely including Pb^{2+} and $PbOH^+$ ions, and Pb bound to large-molecular humic substances or particular organic matter to pass through. The filtrate was then subjected to microwave digestion in 70% HNO_3, followed by analysis for Pb with ICP-OES. The rest of the suspension was filtered through a 0.2-µm membrane filter (Nuclepore® polycarbonate), retaining the large-molecular humic substances and particular organic matter, while allowing only the actual dissolved Pb (Pb_{dis}) to pass through.

To further distinguish between the dissolved cationic Pb (Pb^{2+}, $PbOH^{+}$ and possible organic cationic Pb species) and the neutral low-molecular organic Pb complexes in the Pb_{dis} fraction, the membrane filtrate was subjected to cation exchange (CE) by passing it through a solid-phase extraction (SPE) tube (Strata-X-C 33 µm, 12 mL/1 g), retaining the cationic Pb species, while allowing the non-cationic Pb species ($Pb_{non\text{-}cat}$) to pass through. Prior to CE, the SPE tubes were preconditioned with 0.4 M KH_2PO_4 of pH 5 to prevent disintegration of any dissolved organic Pb complexes. The membrane filtrates were analysed for Pb with ICP-OES before and after the CE. The relative proportion of the less toxic non-cationic Pb to the actual dissolved Pb was calculated as $Pb_{non\text{-}cat}/Pb_{dis} * 100\%$. Furthermore, to distinguish between the most toxic inorganic cationic Pb species (Pb^{2+} and $PbOH^{+}$) and the organic Pb species of lower toxicity, the membrane filtrates were also analysed for dissolved organic carbon (DOC) with a carbon analyser before and after the CE. The abundance of possible organic cationic Pb species in each solution was estimated as the proportion of DOC after the CE to DOC before the CE (i.e. $DOC_{non\text{-}cat}/DOC_{tot}$). A schematic description of the speciation analysis procedure is given in Figure 1.

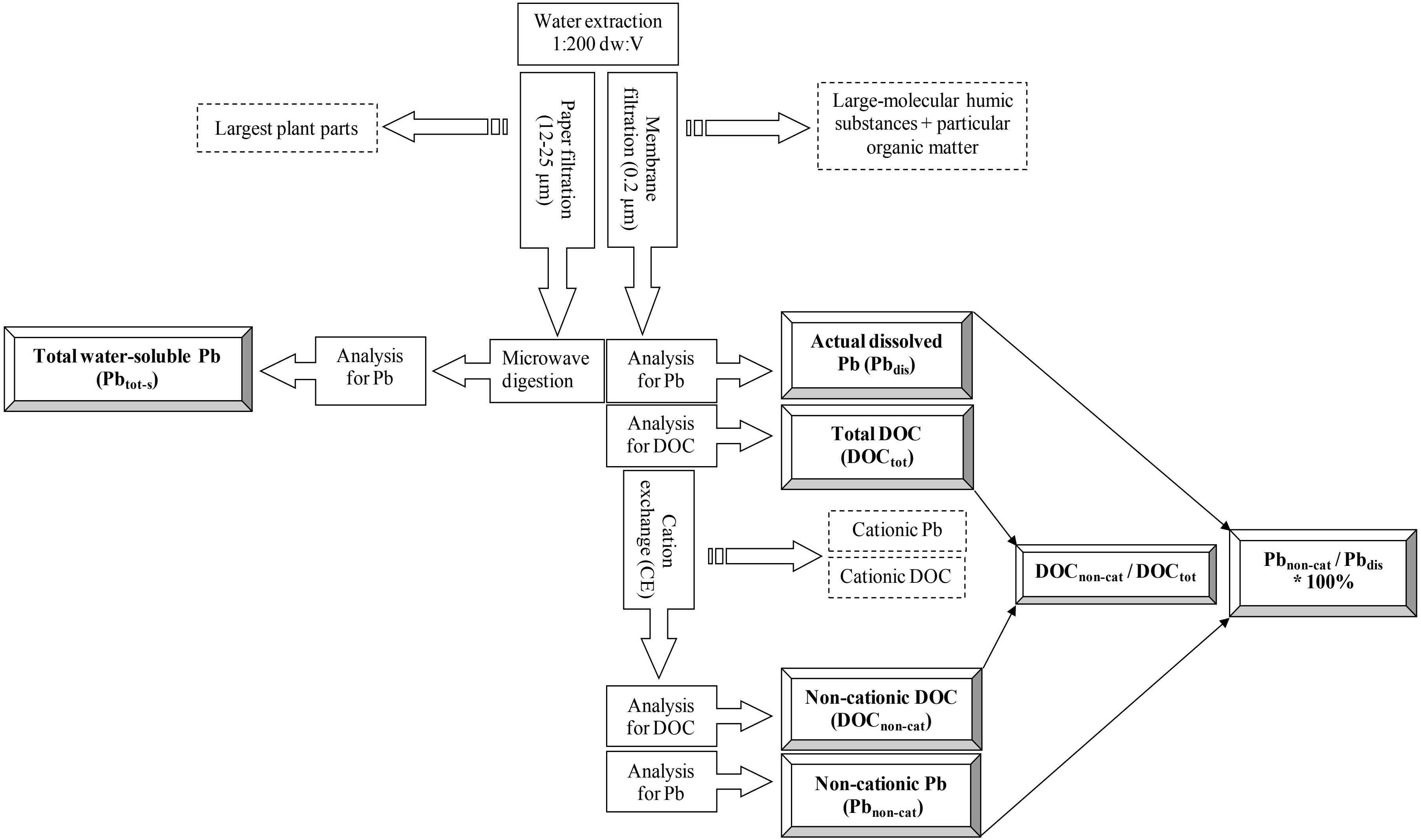

Figure 1. *Schematic description of speciation analysis of water-extractable Pb (Pb_w)*

2.6 Quality control of chemical analyses

The chemical analyses were primarily carried out in the laboratories of the Soil and Environmental Sciences Division at the Department of Food and Environmental Sciences, University of Helsinki. All analyses were carried out in 3–4 replicates (Table 1). Blank samples were included in all sample series. All of the devices used in the measurements were calibrated according to the manufacturers' instructions before use. The reference material used in controlling the quality of the microwave digestion procedure (Article III) was NIST SRM® 2711 Montana Soil (National Institute of Standards and Technology, U.S. Department of Commerce). The operation of ICP-MS (Article III), ICP-OES (Articles II and III), carbon analyser (Article III) and flow injection analyser (Article I) was confirmed by running external standards of known concentrations every 20 samples. According to the SFS standard (SFS-EN ISO 3696), the water used in the P experiments (Article I) was at least of Grade 2 (de-ionized water) and in the Pb experiments (Articles II and III) of Grade 1 (mQ-H_2O, Millipore, Billerica, MA, USA). The quality of the waters was controlled by routine measurements of their electrical conductivities. All chemicals used in the experiments were of analytical grade. All dishes were machine-washed, followed by soaking in acid (2% HNO_3) and five rinses in running mQ-H_2O.

To avoid the adsorption of Pb onto the dishes, practically all Pb experiments were carried out using plastic dishes (polypropylene) because Pb is more prone to adsorption by borosilicate than polypropylene surfaces (Issaq and Zielinski, 1974). To ensure that Pb is not adsorbed to the plastic centrifuge tubes during the equilibration, the UtT and AtT were equilibrated in 50 mL of $PbNO_3$ solutions containing 15, 35, 400 and 1000 mg Pb L^{-1} for 24 h. After the equilibration, the samples were discarded and the tubes were rinsed with 50 mL of mQ-H_2O to remove any Pb solution residues. Next, the tubes were shaken with 20 mL portions of 2% HNO_3 for 16 h before filtration and analysis for Pb with ICP-MS. The test revealed that at a maximum 0.3% of the added Pb was adsorbed to walls of the centrifuge tubes.

The validity of the cation exchange procedure in Article III was ascertained by a recovery test. The resin in the SPE tubes used was extracted with 10 mL of 15% HNO_3 and the eluates were analysed for Pb with ICP-OES. The recovery of Pb retained by the tubes varied between 112% and 123%.

2.7 Statistical analyses

The results of the replicate samples were used to calculate averages and standard deviations (SDs). The limit of quantification assessed as 10 * SD of the blank samples was 0.04 mg P L^{-1} for the FIA measurements, 0.03 mg Pb L^{-1} for the ICP-MS measurements and 0.007 mg Pb L^{-1} for the ICP-OES measurements. In addition, the statistical significance of differences in certain variables between various tailings samples was tested with Student's t-test and one-way ANOVA. Statistical significance was set at $p \leq 0.05$.

The principal statistical analyses carried out with references to the original papers are listed in Table 6.

Table 6. *Statistical analyses carried out for the results from Experiments 1-6*

Article **No.**	**Experiment** **No.**	**Description**	**Statistically tested variable**	**Statistical analysis**
I	1	Distribution of intrinsic and enriched P between various chemical pools in tailings	Enrichment-induced changes in P recovery from various chemical pools between various tailings	Student's t-test
I	2	P sorption-desorption isotherms (*Q/I* plot) of tailings	Differences in Q_{max} between various tailings	One-way ANOVA with Tukey's test for paired comparisons
	2		Differences in Q_{max} between tailings of different particle sizes and after different reaction times	Student's t-test
II	5b	Distribution of enriched Pb between various chemical pools in uncontaminated mineral soil	Tailings-induced changes in relative proportions of various Pb pools to the Pb_{sorbed}	Student's t-test
III	6b	Chemical speciation of water-extractable Pb (Pb_w) from Pb-contaminated shooting range soil	Differences in Pb_{tot-s}, $Pb_{non-cat}$ and Pb_{dis} between control and tailings-treated soils	Student's t-test

3 Results and discussion

3.1 Tailings materials as phosphorus sorbents

The isotherm test (Experiment 2) revealed that all tailings retained P efficiently. However, due to the strong fluctuation in the desorption-sorption curves with increasing levels of P addition, no actual plateau was reached with any of the tailings materials (Figure 2). Thus, the peak sorption was taken to represent the Q_{max} value. It was used in the comparison of the P sorption capacities. In all tailings materials, the Q_{max} value obtained within the 24-h equilibration was higher for the small-sized than for the large-sized fraction. This can be attributable to a larger surface area, but also to differences in the mineralogical composition. In all tailings materials, the small-sized fraction was substantially higher in Al and Fe (hydr)oxides than the large-sized one (Table 2).

Acid treatment of the tailings drastically increased the Q_{max} values obtained within 24 h for of both particle-size fractions. In the large-sized AtT, Q_{max} increased from 5.7 to 8890 mg kg^{-1}, whereas in the small-sized AtT the corresponding increase was from 7.6 to 14420 mg kg^{-1}. The partial neutralization of the AtT reduced the Q_{max} value. In the ABtT, the peak value was 8460 mg kg^{-1} for the large-sized fraction and 11420 mg kg^{-1} for the small-sized one. As for the small-sized material, the partial neutralization of the acidified material diminished the amount of extractable Al and Fe (hydr)oxides (Table 2). This decrease may be due to possible loss of some of the oxidic material during the neutralization process.

Extension of the equilibration time to 7 days substantially increased the Q_{max} values. As for the AtT, the peak value for the large-sized fraction was 10900 mg kg^{-1} and 17110 mg kg^{-1} for the small-sized one. The Q_{max} value for the large-sized ABtT was 15400 mg kg^{-1} and for the small-sized one 13000 mg kg^{-1}. Thus, Q_{max} of the large-sized fraction of the ABtT was substantially higher than that of the AtT. This reaction pattern may be attributable to the formation of Al and Fe hydroxypolymers offering reactive sites within their porous structure. On the contrary, in the UtT, no significant time-dependent change in Q_{max} was observed, the peak value for the large-sized fraction being 4.5 mg kg^{-1} and for the small-sized fraction 7.2 mg kg^{-1}. However, in the UtT and the ABtT equilibrated for 7 days at high P addition, the P sorption plunged with the tail ends of the curves showing desorption of P. It is noteworthy that the removal of NH_4-Ox-extractable metal oxides from the AtT (Experiment 3) resulted in a 300-fold drop in Q_{max} values, from the initial level of 14400 mg kg^{-1} to 45 mg kg^{-1}.

At different stages of sorption, pH of the equilibrium solutions fluctuated to some extent (Figure 2). Overall, the changes in pH values seemed to reflect the nature of the components in the different tailings materials and their reactions rather than P sorption. The UtT elevated pH of the initial P solution from 5.4–6.3 to 7.3–7.6 in the equilibrium P solution. This increase was presumably due to the calcite compartment but also to the residuals of unidentified flotation chemicals. The latter factor can explain pH of the UtT (9.1–9.3) (Table 2) being much higher than calcite alone could maintain. The AtT and the

ABtT in turn, lowered the pH of the initial P solutions from 4.6–5.1 to 3.5–4.1. This reaction pattern was undoubtedly due to the residuals of acids left from the artificial weathering of the material.

The chemical fractionation of the P-unenriched tailings (Experiment 1) revealed that the main part of P was in the H_2SO_4-extractable pool, which predominated especially in the large-sized fraction (Table 7). This indicates that plenty of apatite residues were left in the tailings after the beneficiation process. As expected, the H_2SO_4-extractable fraction was highest in the UtT, whereas the pre-treatment with acid had transferred some of apatitic P primarily to the NaOH- and NH_4F-extractable fractions assumed to represent Fe- and Al-associated P, respectively (Table 7). This conclusion is supported by the drastic concomitant increase in the poorly crystalline Al and Fe oxides found in the AtT material (Table 2).

In the AtT and the ABtT, enriching the samples with P significantly increased all P fractions, whereas in the UtT the increase was statistically significant only in the H_2SO_4- and NaOH-extractable ones (Table 7). In the AtT and the ABtT, most of the sorbed P was recovered in the NaOH- and NH_4F-extractable fractions. The retention being strikingly higher by Al-oxides is consistent with the dominance of this sorption component (Table 2). In all tailings subjected to the acidification step, a significant amount of the added P remained in the salt-soluble pool (NH_4Cl-P). As expected, the added P markedly increased DPS of the Al and Fe (hydr)oxides in all tailings, except for UtT (Table 7), where P was primarily retained in a sparingly soluble form in the H_2SO_4-extractable fraction.

The finding that in the AtT and the ABtT the sorbed P was primarily allocated to the NaOH- and NH_4F-extractable pools supports the hypothesis that the high P sorption (Figure 2) was primarily due to the Al and Fe (hydr)oxides formed as a result of artificial weathering of the material (Table 2). This was further ascertained by the fact that in the AtT the apparent Q_{max} decisively dropped after the removal of metal oxides by NH_4-Ox-extraction. Being the conjugate bases of moderately weak acids, phosphate anions have a high affinity for Al and Fe (hydr)oxides (Hingston et al., 1967; Parfitt et al., 1975; Ryden et al., 1987; Beck et al., 1999), rendering the artificially weathered tailings material an ideal adsorbent for P. The long-term retention being higher in the ABtT and in the AtT is likely attributable to the diffusion of P into the porous oxides produced by the base treatment of the acidified material. Similarly, the scarcity of reaction active sites explains why the extension of the equilibration time from 24 h to 7 d did not enhance P sorption by the UtT (Table 2).

While in the AtT and the ABtT the P sorption took place on the Al and Fe (hydr)oxide surfaces, it is likely that in the UtT a combination of various sorption reactions occurred simultaneously (Figures 2a and 2b). Calcite is known to retain P to some extent (Cole et al., 1953; Wang et al., 1995). Despite the fact that its contribution to P sorption is probably minor in the presence of Fe (hydr)oxides and other P sorbents (Borrero et al., 1988), calcite may have to some extent contributed to P sorption by the UtT low in the reaction-active Al and Fe (hydr)oxides. According to Cole et al. (1953), at low P concentrations the reaction between calcite and P occurs via rapid monolayer sorption, whereas at higher concentrations P may be precipitated as dicalcium phosphate ($CaHPO_4$). Thus, the gradual P sorption at the low P addition levels may be due to saturation of the few oxide and calcite surfaces, whereas the rapid peak sorption observed thereafter may represent precipitation of P as calcium phosphates. According to Lindsay (1979, p.195), however, increased P activity eventually leads to the formation of soluble calcium phosphate species ($CaPO_4^-$ and $CaH_2PO_4^+$), which may explain the desorption of P by the UtT observed with the highest added P concentrations after the 7-d equilibration. Because the rather radical pre-treatment by strong acid would have dissolved any calcite present in the AtT and the ABtT, its contribution to P sorption by these materials can be ignored.

Table 7. *P in various pools before ($P_{unenriched}$) and after ($P_{enriched}$) the addition of P and the increment of P fractions in various types of tailings materials (modified from Hartikainen and Hartikainen, 2008)*

	Mesh	**Added P**		**P mg kg^{-1} in various pools**				**DPS**[a]
	Ø mm	mg kg^{-1}		NH_4Cl-P Salt-soluble P	NH_4F-P "Al-P"	NaOH-P "Fe-P"	H_2SO_4-P Apatitic P	%
Untreated tailings (UtT)	> 0.2	50	Unenriched	0.2	7.6	0.3	695	6.2
			Enriched	0.2	2.1	3.9	709	4.7
			Increment	**± 0**	**- 5.5**	**3.6**	**14**	
	< 0.2	50	Unenriched	0.2	4.5	1.2	204	1.6
			Enriched	0.7	4.1	3.1	1111	2.2
			Increment	**0.5**	**- 0.4**	**1.9***	**907*****	
Acid-treated tailings (AtT)	> 0.2	5000	Unenriched	1.4	29	38	591	1.1
			Enriched	69	2212	762	1045	50
			Increment	**68****	**2183*****	**724*****	**454*****	
	< 0.2	5000	Unenriched	8.0	28	65	153	0.9
			Enriched	62	2847	1106	430	40
			Increment	**54****	**2820*****	**1042****	**277*****	
Acid-base-treated tailings (ABtT)	> 0.2	5000	Unenriched	0	20	55	442	1.3
			Enriched	71	2276	773	1076	56
			Increment	**71***	**2256*****	**719*****	**634****	
	< 0.2	5000	Unenriched	0	21	83	141	1.3
			Enriched	55	2640	1442	288	50
			Increment	**55*****	**2619*****	**1359*****	**147****	

* $\alpha \leq 95\%$

** $\alpha \leq 99\%$

*** $\alpha \leq 99.9\%$

[a] DPS = Degree of P saturation

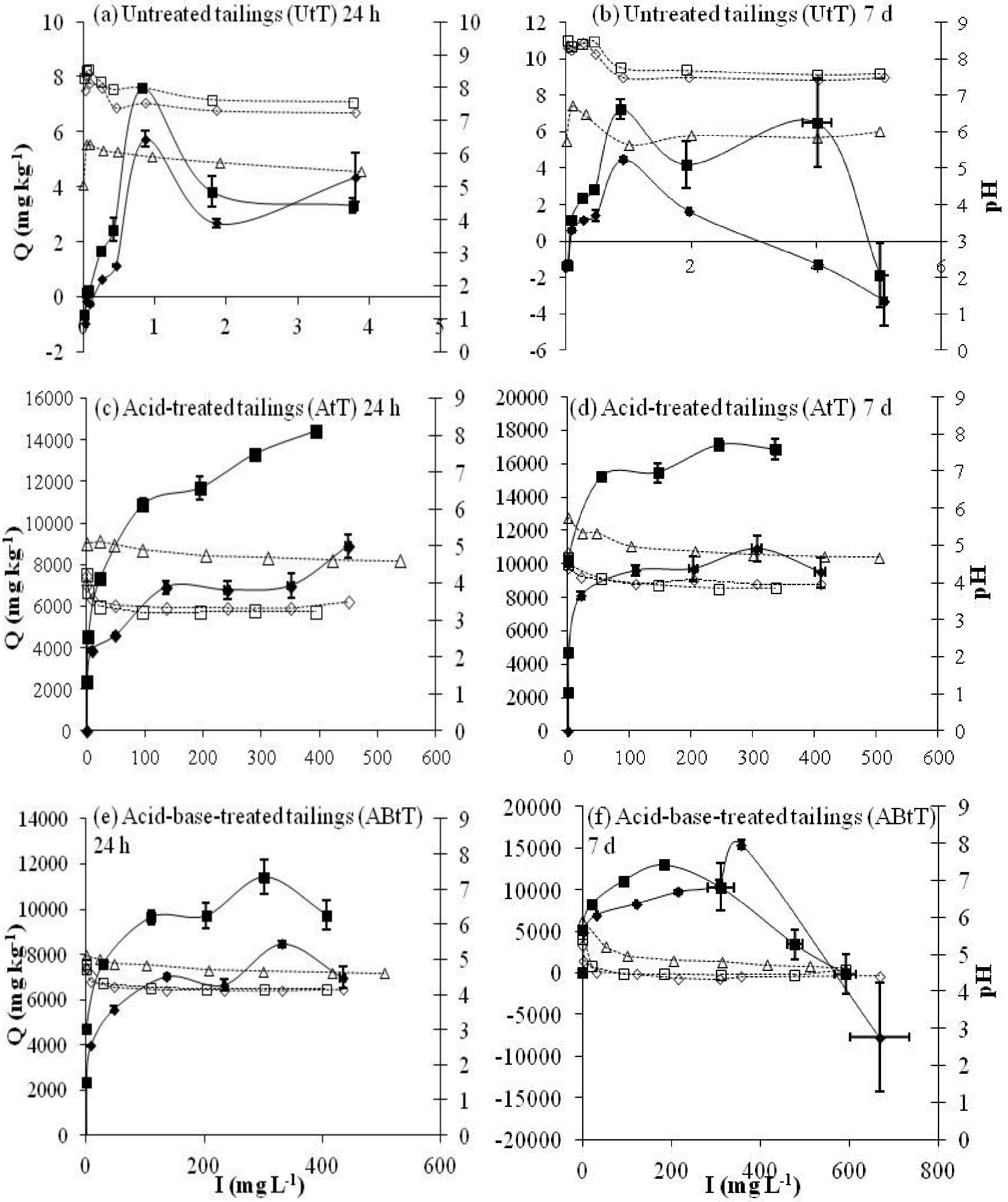

Figure 2. *P sorption-desorption isotherms of tailings samples (solid lines) and pHs of equilibrium solutions (dashed lines) with different reaction times. (♦) Tailings Ø > 0.2 mm; (■) Tailings Ø < 0.2 mm; (◊) pH Tailings Ø > 0.2 mm; (□) pH Tailings < 0.2 mm; (Δ) pH P enrichment solution. Error bars indicate the standard deviations of Q and I (modified from Hartikainen and Hartikainen, 2008). The original measured Q/I data is given in Appendices 1–3.*

3.2 Tailings as sorbent for lead

3.2.1 Sorption and its mechanisms in untreated tailings

The Pb sorption isotherms obtained with the UtT in Experiment 4 (Figure 3) revealed that both size fractions of the material retain Pb efficiently. Similarly to P, the curves fluctuated strongly upon increasing Pb additions, reflecting the multiplicity of the reactions taking place at various steps. The sorption curves obtained with the small- and large-sized UtT were of similar shapes, but the small-sized material showed a more intensive retention of Pb. Since no sorption maxima were reached, the comparison of the particle size fractions was based on the Pb concentration in the equilibrium solution at the upper limit value of soil Pb specified in the Sewage Sludge Directive of the European Council (86/278/EEC). According to this directive, the total Pb concentration of soil should not exceed 0.3 g kg^{-1}. This was taken as the reference Pb concentration in the solid phase. The comparison showed that the equilibrium Pb concentration in the solution obtained with the large-sized UtT (0.2 mg L^{-1}) was 10-fold that obtained with the small-sized material (0.02 mg L^{-1}).

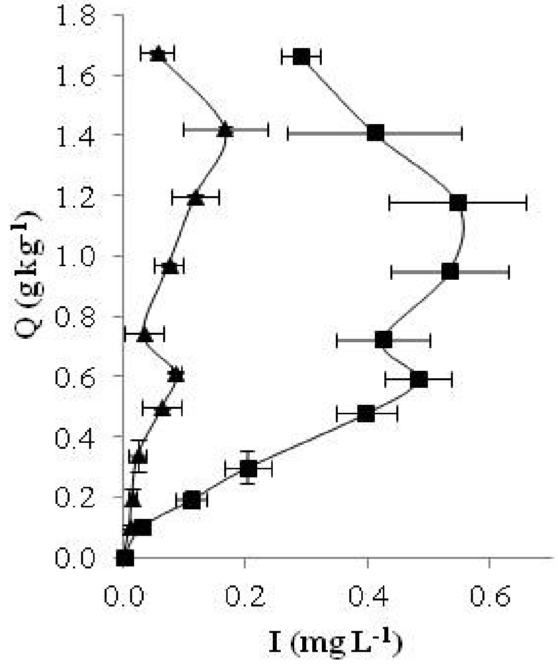

Figure 3. Pb sorption isotherm for the small- (▲) and the large-sized (■) UtT. Error bars indicate the standard deviations of I and Q (Venäläinen, 2012). The original measured Q/I data is given in Appendix 4.

As for the chemical reactions taking place with increasing Pb additions, their mechanisms depend on the chemical speciation of Pb. The pK_a value of Pb^{2+} being 7.7 (Lindsay, 1979, p.331), Pb undergoes hydrolysis in weak acidic aqueous solution:

$$Pb^{2+} + H_2O \rightleftharpoons PbOH^{+} + H^{+} \qquad \text{(Eq. 3)}$$

At pH up to 6, Pb is primarily found as Pb^{2+}, whereas at higher pH its hydroxy species ($PbOH^{+}$) becomes more significant. In the UtT, both size fractions elevated the pH of the initial enrichment solution by more than 2 units (from 3.9–4.8 to 6.4–6.9), rendering Pb^{2+} and $PbOH^{+}$ the predominant Pb species in the solution. The foreparts of the sorption curves resembled the L-type sorption (see Giles et al., 1960) up to equilibrium solution concentration of 0.1 mg L^{-1} in the small-sized fraction and up to 0.5 mg L^{-1} in the large-sized one (Figure 3). The initial retention was obviously attributable to retention of Pb^{2+} to possible cation exchange sites and that of $PbOH^{+}$ to the few Al and Fe (hydr)oxide surfaces in the phlogopite compartment of the tailings (Figure 3). The relatively high pH of the equilibrium solutions (6.4–6.9) probably favoured the Pb hydrolysis and the formation of $PbOH^{+}$ species able to be chemisorbed on Al and Fe (hydr)oxide surfaces. At the low Pb additions, the retention was more intensive by the small-sized material, presumably due to its higher content of Al and Fe (hydr)oxides (Table 2).

After the L-type forepart of the sorption curves, the equilibrium Pb concentrations sharply decreased to 0.03 and 0.4 mg L^{-1} for the small- and the large-sized tailings, respectively, even though the amount of sorbed Pb still increased. Upon further addition of Pb, the solute Pb concentration relapsed to the level prior to the sharp drop. At the highest Pb addition level, the equilibrium concentrations eventually decreased to 0.06 and 0.3 mg Pb L^{-1} for the small- and the large-sized tailings, respectively. The sharp drop in the equilibrium Pb concentration after the L-type forepart of the retention curve indicates the precipitation of Pb. In the UtT material, the constituents able to precipitate Pb are calcite and fluorapatite (FAP), which may react with soluble Pb to form sparingly soluble cerussite and fluorpyromorphite (FPM). The formation of cerussite is assumed to involve the dissolution of calcite (Eq. 4, Plummer et al., 1978; Chou et al., 1989), followed by the interaction between solute Pb^{2+} and CO_3^{2-} (Eq. 5, Al-Degs et al., 2006) or the deposition of $PbCO_3$ on the calcite surface (–S–$CaCO_3$) (Eq. 6, Al-Degs et al., 2006):

$$CaCO_3\ (s) \rightleftharpoons Ca^{2+}\ (aq) + CO_3^{2-}\ (aq) \qquad \text{(Eq. 4)}$$
$$Pb^{2+}\ (aq) + CO_3^{2-}\ (aq) \rightleftharpoons PbCO_3\ (s) \qquad \text{(Eq. 5)}$$
$$\text{–S–}CaCO_3\ (s) + PbCO_3\ (s) \rightarrow [\text{–S–}CaCO_3\text{–}PbCO_3]\ (s) \qquad \text{(Eq. 6)}$$

Similarly, the formation of fluorpyromorphite is initiated by the dissolution of the parent FAP mineral (log K_{sp} -12.98, Lindsay, 1979, p. 331) (Eq. 7) and followed by the interaction between the soluble $H_2PO_4^{-}$ and Pb^{2+} (Eq. 8) (Cao et al., 2004):

$$Ca_{10}(PO_4)_6F_2\ (s) + 12H^{+} \rightleftharpoons 10Ca^{2+}\ (aq) + 6H_2PO_4^{-}\ (aq) + 2F^{-}\ (aq) \qquad \text{(Eq. 7)}$$
$$10Pb^{2+}\ (aq) + 6H_2PO_4^{-}\ (aq) + 2F^{-}\ (aq) \rightleftharpoons Pb_{10}(PO_4)_6F_2\ (s) + 12H^{+} \qquad \text{(Eq. 8)}$$

The relatively high pH of the solutions, however, presumably restrained the dissolution of FAP, and consequently, the formation of FPM. Nevertheless, the apatite compartment in the tailings may still have partly contributed to Pb sorption through surface adsorption by the functional groups of FAP. Based on the acid-base properties of the FAP-water interfaces and the pH of the equilibrium solutions (Forsling and Wu, 1993), the principal functional groups occurring on the FAP surfaces of the UtT would be $\equiv PO^-$, $\equiv POH$ and $\equiv CaOH_2^+$ in the pH range (6.4–6.9) detected in this thesis. These surfaces may adsorb Pb^{2+} as follows (Eqs. 9–11, Mavropoulos et al., 2002):

$$\equiv PO^- + Pb^{2+} \rightarrow \equiv POPb^+ \quad \text{(Eq. 9)}$$

$$\equiv POH + Pb^{2+} \rightarrow \equiv POPb^+ + H^+ \quad \text{(Eq. 10)}$$

$$\equiv CaOH_2^+ + Pb^{2+} \rightarrow \equiv CaOPb^+ + 2H^+ \quad \text{(Eq. 11)}$$

Due to the versatility of the tailings material, it is possible that reaction mechanisms other than those given above also contributed to Pb sorption. Such reactions may involve the formation of some meta-stable intermediate Pb compounds before the development of the actual precipitates. This may partly explain the abrupt changes in the equilibrium Pb concentrations upon increasing Pb addition levels.

3.2.2 Impact of various tailings amendments on lead retention by mineral soil

3.2.2.1 Lead sorption by amended soil samples

Lead sorption experiments conducted with the uncontaminated mineral soil with and without tailings amendments (Experiment 5a) yielded isotherms of the H-type (see Giles et al., 1960) (Figure 4). The experimental data obtained with the AtT-amended soil samples fit the Langmuir model, whereas those obtained with the control soil and the UtT-amended soil did not follow the model equally well. The Langmuir model was still used to calculate the sorption parameters Q_{max} and K for all materials, allowing comparison of the isotherms.

Based on the Q_{max} values (Table 8), all tailings materials significantly increased the Pb sorption capacity of the control soil, the AtT-evoked increases in Q_{max} values being substantially higher than those obtained with the UtT. Irrespective of the amendment, Q_{max} increased with decreasing particle size and increasing tailings dosage. In other words, in the UtT-amended samples, the Q_{max} values obtained with the small-sized tailings were higher than those obtained with the large-sized material, and the 10-g dosages were more efficient than the 5-g ones. This outcome suggests that with the UtT the particle size holds larger significance for Pb sorption than does the dosage. In the AtT-amended samples, on the contrary, the highest Q_{max} values were obtained with the 10-g dosages irrespective of particle size, but also in this treatment the small-sized material was superior to the large-sized one. Thus, with the AtT, the dosage proved to hold more significance for Pb sorption than did the particle size. The sorption affinity assessed as the slopes of the isotherms (1/*K*, Table 8), tended to increase with increasing Q_{max} values. The small-sized UtT elevated pH of the equilibrium solution in the control soil (3.7–4.8) to 3.9–6.3, whereas the large-sized UtT elevated it to 3.8–5.8. However, the small-sized AtT slightly decreased pH of the equilibrium solution to 3.8–4.2, whereas the large-sized fraction had no effect on the equilibrium solution pH.

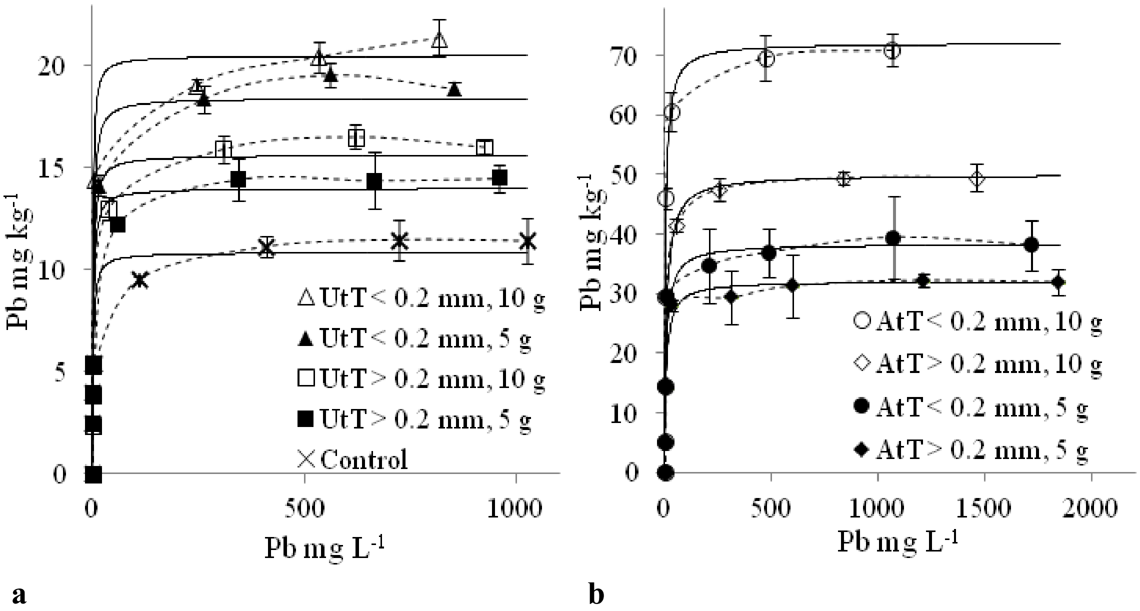

***Figure 4**. Experimental data (dashed lines) and Langmuir Pb sorption isotherms (solid lines) for (a) the control soil and the soil amended with the different dosages of the small- (< 0.2 mm) or the large-sized (> 0.2 mm) UtT and (b) the soil amended with different dosages of the small- or the large-sized AtT. Error bars indicate the standard deviations of the sorbed Pb (Venäläinen, 2012). The original measured Q/I data is given in Appendix 5.*

***Table 8.** Pb sorption parameters of control soil and UtT- and AtT-amended soils (modified from Venäläinen, 2012)*

Amendment	**Tailings**		**Sorption parameter**	
	Mesh (ø mm)	**Dosage (g)**	Q_{max}[a] **(g kg^{-1})**	**1/*K***[b]
Control			10.8	1.8
Untreated tailings (UtT)	> 0.2	5	14.0	1.9
		10	15.6	1.9
	< 0.2	5	18.4	2.0
		10	20.5	1.2
Acid-treated tailings (AtT)	> 0.2	5	32.1	9.1
		10	50.0	11.1
	< 0.2	5	38.4	9.1
		10	72.1	5.9

[a] Q_{max} = Maximum Pb sorption
[b] 1/*K* = Slope of the isotherm

3.2.2.2 Distribution of retained lead between various pools

At the addition level of 100 mg Pb L^{-1}, all soil samples incubated with various tailings materials retained approximately the same amount of Pb (average 5286 ± 113 mg kg^{-1}) (Experiment 5b, Figure 5). The fractionation analysis carried out to unravel the distribution of the sorbed Pb between various chemical pools showed that in all samples the relative proportion of water-extractable Pb (Pb_w) to the total sorbed Pb (Pb_{sorbed}) was negligible ($\leq$ 0.1%). In the control soil, most of the Pb_{sorbed} was found in the NH_4NO_3-exchangeable pool (Pb_{ex}) (51%), covering 34% of the CEC_{ef}, whereas the relative proportions of NaOH-extractable Pb (Pb_{org}) and NH_4-Ox-extractable Pb (Pb_{ox}) were 4% and 9%, respectively. The overall recovery of the sorbed Pb in the control soil was approximately 64%, leaving 36% in the non-extracted pool ($Pb_{non\text{-}extr}$) representing more strongly bound Pb. This approximation is, however, only computational and, unfortunately, is not confirmed by a chemical analysis of the residual fraction by a microwave digestion and the subsequent measurement of acid-extractable Pb.

All tailings decreased the total non-residual Pb (ΣPb_{pools}) and increased the non-extracted pool ($Pb_{non\text{-}extr}$) (Figure 5). This was primarily due to the transfer of Pb_{ex} to the non-extracted pool. The 10-g dosage of the small-sized UtT diminished the relative proportion of Pb_{ex} to Pb_{sorbed} most efficiently. Furthermore, the UtT and the 10-g dosage of the large-sized AtT transferred some of the NH_4NO_3-extractable Pb (Pb_{ex}) to the NaOH-extractable (Pb_{org}) pool. On the contrary, the small-sized AtT practically eliminated Pb_{org} at both addition levels.

The UtT elevated pH of the water extracts [pH(H_2O)] from 4.5 in the control soil to 4.6–5.1 and pH of the NH_4NO_3 extracts from 4.1 to 5.7–6.3 (Figure 5). This reaction pattern is similar to that found in the sorption tests in Experiment 4, where the UtT efficiently elevated the pH of the equilibrium solutions. An increase in pH promotes the formation of organo-Pb complexes (see Sauvé et al., 1997; Klucakova and Pekar, 2008), which may partly explain the finding that the ratio of Pb_{org} to Pb_{sorbed} increased in all UtT-amended samples. This conclusion is supported by the abundance of calcite. It can be ascribed to the fact that the liming effect was more notable for the small particle-size fraction higher in calcite than the large-sized one. Moreover, the marked increase in the relative proportion of $Pb_{non\text{-}extr}$ to Pb_{sorbed} in the UtT-amended samples suggests calcite-induced formation of cerussite during the short-term (24-h) reaction.

Despite the fact that both the large- and small-sized AtT materials were very acidic (pHs 4.0 and 3.1, respectively, Table 2), the 5-g dosages of both materials slightly increased the pH of the water extracts [pH(H_2O)], from 4.5 to 4.6 (Figure 5). On the contrary, the 10-g dosages decreased it to 4.4 and 4.2. Despite the acidity of the At-promoted weathering reactions in the mineral soil and the significantly increased content of Al and Fe (hydr)oxide surfaces, no increase in Pb_{ox} was observed in any of the AtT-amended samples. In fact, only the 10-g dosage of the small-sized AtT slightly decreased the relative proportion of Pb_{ox} to Pb_{sorbed}. This outcome suggests that Fe and Al (hydr)oxides were not the key factors in the AtT-induced increase in Q_{max} values observed in Experiment 5a. Furthermore, the severe acid pre-treatment that the material underwent also excluded the contribution of calcite in the retention. Thus, the AtT-induced Pb immobilization was most likely attributable to the fluorapatite (FAP) compartment in the tailings.

The artificial weathering procedure dissolved the sparingly soluble FAP mineral compartment and released $H_2PO_4^-$ anions according to Eq. 7. The released anions are susceptible to specific sorption by hydrous Al and Fe (hydr)oxides, as shown in Article I by Hartikainen and Hartikainen (2008). The phosphate surfaces formed, in turn, are able to retain Pb^{2+} according to Eqs. 9 and 10. Moreover, the acid-induced dissolution of the FAP compartment also enabled the formation of sparingly soluble fluorpyromorphite (FPM) when Pb was added to the system (Eq. 8). This reaction can explain the increased ratio of $Pb_{non\text{-}extr}$ to Pb_{sorbed} in all AtT-amended samples. The large-sized AtT fraction was richer in H_2SO_4-extractable FAP than the small-sized one (Table 7). However, because the specific surface area of minerals increases with decreasing particle size, the small-sized tailings material was presumably higher in reactive FAP surfaces than the large-sized one. This may explain the outcome that the Q_{max} obtained in the sorption test for the small-sized AtT was higher than that for the same dosage of the large-sized material (Figure 4). The formation of FPM and cerussite is largely dictated by the solubility of the parent FAP and calcite minerals. The theoretical solubility of FAP (log K_{sp} -0.21, Lindsay, 1979, p.165) being substantially lower than that of calcite (log K_{sp} 9.74, Lindsay, 1979, p.88) explains why the relative proportion of $Pb_{non\text{-}extr}$ to Pb_{sorbed} increased more in the UtT-amended than in the AtT-amended soil.

Pb_{sorbed} mg kg^{-1}	5337	5349	5324	5411	5336	5258	5156	5054	5351
pH (H_2O)	4.5	4.6	4.7	4.7	5.1	4.6	4.4	4.6	4.2
pH (NH_4NO_3)	4.1	5.7	6.0	6.1	6.3	4.7	4.3	5.6	4.3

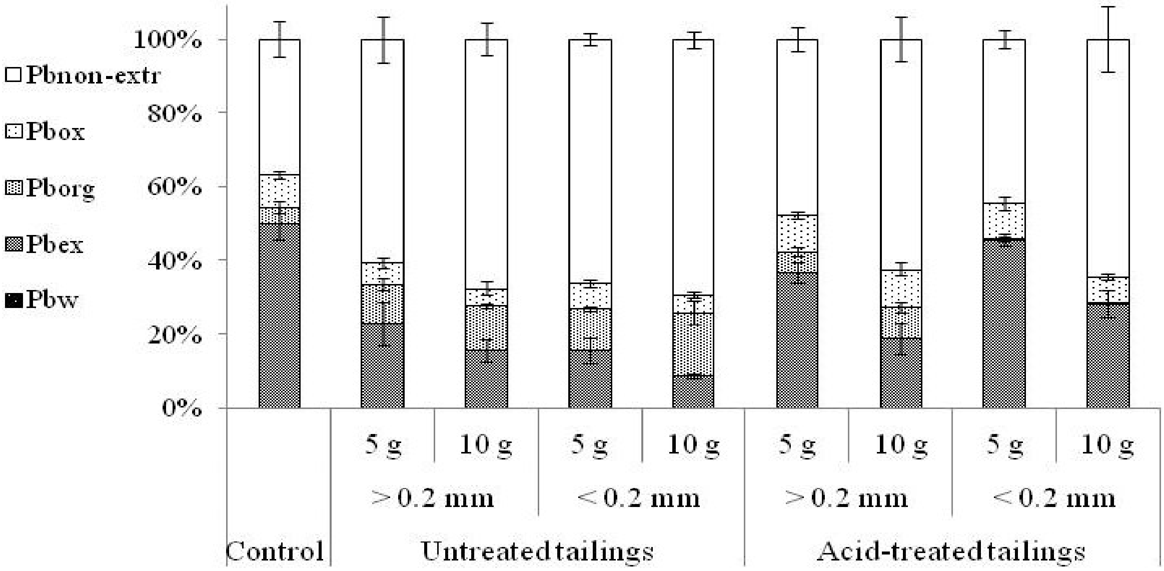

Figure 5. *Relative proportion of water-soluble Pb (Pb_w) (quantity negligible), NH_4NO_3-extractable Pb (Pb_{ex}), NaOH-extractable Pb (Pb_{org}), NH_4-Ox-extractable Pb (Pb_{ox}) and residual Pb ($Pb_{non\text{-}extr}$) to the total enriched Pb ($Pb_{tot\text{-}sorb}$) in the soil with and without tailings treatment and the pHs as measured from the water extracts [pH(H_2O)] and the NH_4NO_3 extracts [pH(NH_4NO_3)] (Venäläinen, 2012).*

3.3 Remediation of lead-contaminated shooting range soil with tailings

3.3.1 Tailings-induced changes in the distribution of lead between various chemical pools

The shooting range soil used in the incubation experiment conducted with and without UtT amendment (Experiment 6) was highly contaminated, with Pb_{tot} in the control soil (33.5 g kg^{-1}) largely exceeding the average background level of Pb in Finnish soils (17 mg kg^{-1}) (Koljonen, 1992). In all samples, the sum of Pb_w, Pb_{ex}, Pb_{org} and Pb_{ox} ($\sum Pb_{pools}$), i.e. non-residual Pb recovered in the fractionation analysis, significantly increased over the incubation time of 9-21 months (Figure 6). At the first sampling time (i.e. after a 9-month incubation), $\sum Pb_{pools}$ in the control sample covered 21% of the Pb_{tot}, whereas at the last sampling time (i.e. after the 21-month incubation), the proportion increased to 72%. As for the large-sized UtT-amended sample, extending the incubation from 9 to 21 months increased the Pb recovery from 29% to 80%. However, in the samples amended with the unsieved and the small-sized UtT, the corresponding proportions increased from 24–29% to 47–50%. In the small-sized UtT-amended sample, the 50% Pb recovery was obtained already at the third sampling time (after a 14-month incubation), with no further change in the $\sum Pb_{pools}$ observed thereafter.

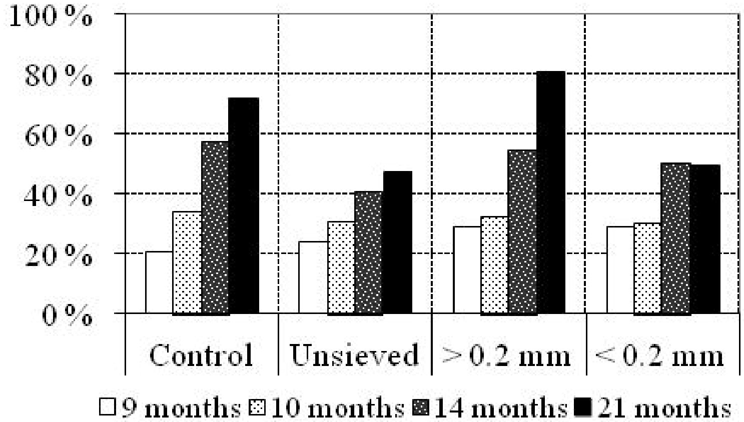

Figure 6. *Proportion (%) of non-residual Pb ($\sum Pb_{pools}$) to semitotal Pb (Pb_{tot}) in the control soil and in the UtT-amended soils as a function of incubation time (Venäläinen, 2011).*

The substantial increase in the $\sum Pb_{pools}$ indicates that Pb was released to the soil during the incubation. The probable source of the released Pb was the tiny, undetectable pellet fragments that went unnoticed when picking pellets from the soil samples. Such fragments may be released to the soil as a result of weathering, making the pellets brittle and susceptible to crumbling. The continuing dissolution of these fragments explains the increased Pb recovery by the sequential fractionation over the course of the incubation. A significant increase in $\sum Pb_{pools}$ within a relatively short period (21 months) indicates that, under conditions favouring the dissolution of pellets (suitable temperature, moisture, pH), the release of pellet-derived Pb to the soil can be considerable. This phenomenon highlights the significance of incubation time when assessing the behaviour and pellet-derived risks of Pb in soil, as also suggested by Levonmäki and Hartikainen (2007).

The dissimilarities in the ability of the different size fractions to lower the Pb recovery can be explained by differences in their mineralogy. In the samples amended with the small-sized UtT rich in calcite, the solubility of Pb was presumably hindered by the relatively fast formation of cerussite taking place in the reaction between Pb^{2+} and the dissolution products of calcite (see Eq. 5). The formation of this sparingly soluble precipitate is supported by the finding that in the small-sized UtT-amended sample the maximum in $\sum Pb_{pools}$ (50%) was reached already within a 14-month incubation (Figure 6). In the samples amended with the unsieved and the large-sized UtT richer in FAP than the small-sized fraction, the formation of cerussite was likely to take place simultaneously with the formation of an intermediate phase solid solution of Ca and Pb, such as $(Ca,Pb)_{10}(PO_4,CO_3)_6(F)_{2.56} \cdot 1.5H_2O$ (Mavropoulos et al., 2002) and the FPM end-product (Chen et al., 1997; Cao et al., 2003, 2004). The solubility of FAP being much lower than that of calcite, the precipitation reactions between FAP and Pb are less likely to take place than the formation of cerussite. However, FPM has been reported to occur within the pH range of 2–7 (Valsami-Jones et al., 1998).

Furthermore, organic acids typically abundant in boreal forest soil environments have been reported to promote the dissolution of FAP (Cerezine et al., 1988; Welch et al., 2002). Thus, they may also have encouraged the formation of FPM in the shooting range soil used in this study. However, due to the higher solubility of calcite than of FAP, in the presence of both minerals the formation of cerussite becomes more important in controlling Pb solubility, as also reported by Mavropoulos et al. (2005). Consequently, in the small-sized UtT-amended samples, the solubility of Pb was mainly restricted by the formation of cerussite, whereas in the soil amended with the unsieved material the gradual formation of FPM or FPM-like minerals may also have taken place. Nevertheless, due to the lower stability of cerussite (log K_{sp} 4.65, Lindsay, 1979, p. 331) than of FPM (log K_{sp} -12.98, Lindsay, 1979, p. 331), the apatite compartment in the tailings has more potential to act as a long-term sink for Pb than does calcite.

As for the extracts from the shooting range samples, a more extensive analysis of their chemical composition may have allowed the calculation of the degree of saturation of solution phase with respect to P and Pb solids. This information may have provided further support for the precipitation reactions that were predicted to take place in the system. Unfortunately, however, the extracts were only analyzed for their Pb concentrations. Thus, the solution data was insufficient to allow the estimation of the degree of saturation.

As for the individual pellet-derived Pb pools in the shooting range soil, the results obtained with the uppermost organic soil layer were quite different from those obtained with the mineral soil in Experiment 5b. In the control sample, Pb_w remained low (20–25 mg kg^{-1}) throughout the 21-month experiment (Figure 7a). In the samples amended with the unsieved UtT, this Pb pool was either slightly reduced or remained unchanged over the course of the incubation. Similarly, at the first two sampling times (after the 9- and 10-month incubations), no change in Pb_w was observed in the samples amended with the large- and the small-sized UtT, but by the end of the experiment (after a 21-month incubation) these tailings materials elevated Pb_w to 40 and 51 mg kg^{-1}, respectively. Throughout the experiment, pH of the water extracts varied between 4.1 and 4.5 (Figure 7a). In all samples, Pb_w remained rather low during the incubation, even though Pb was regularly released from the pellet fragments (Figure 6). This was presumably attributable to the abundance of various sorption components that efficiently retained dissolved Pb. In the control samples, for instance, Pb_{ex} increased from 2.6 to 16.1 g kg^{-1} (Figure 7b). Amending the soil with the UtT drastically lowered this pool to 0.9–1.5 g kg^{-1}, while elevating pH of the NH_4NO_3 extracts from 3.7–3.9 in the control to 5.2–6.3 (Figure 7b). The increased pH favours the formation of exchange sites on variable-charge surfaces.

Similarly to the Pb_{ex} pool, Pb_{org} in the control sample increased throughout the experiment from 3.1 to 6.2 g kg^{-1} (Figure 7c). After the 10-month incubation, the control sample showed a slight temporary drop in Pb_{org}, but, after 14 and 21 months, this Pb pool yet again exceeded the level observed at the first (9-month) sampling time. The unpredictable variation in Pb_{org} was probably due to the fact that from the 10-month incubation onwards the NH_4NO_3-extractable pool was removed more efficiently by repeating the NH_4NO_3 extraction, leaving less Pb susceptible to extraction with NaOH. Amending the soil with the UtT further increased Pb_{org}, which reached 9.0–15.4 g kg^{-1} by the end of the experiment. The large-sized material increased this Pb pool most efficiently. The pH of the NaOH extracts ranged between 13.1 and 13.7, with no substantial variations between the control and the tailings-amended soils. The increase in Pb_{ex} and Pb_{org} in the control soil suggests that the Pb dissolved from the pellet fragments ended up in the cation exchange sites or it formed complexes with organic matter. In the UtT-amended samples, the calcite-induced increase in pH resulted in a marked reduction in Pb_{ex} and a notable concomitant increase in Pb_{org}, suggesting the transfer of exchangeable Pb^{2+} to the organic pool, where the stability of the complexes is favoured by elevated pH.

In the incubated shooting range samples, no significant time- or tailings-related changes were detected in the NH_4-Ox-extractable Pb pool (Pb_{ox}) (Figure 7d). The Pb content of this pool within the samples varied between 0.9 and 2.1 g kg^{-1}, with all of the extracts having a pH of approximately 3.5 throughout the experiment. Despite the increase in pH in the NH_4NO_3 extracts, which might enhance the abundance of $PbOH^+$ susceptible to specific sorption on Al and Fe (hydr)oxide surfaces, this reaction pattern seemed to be insignificant in the samples representing the organic soil layer.

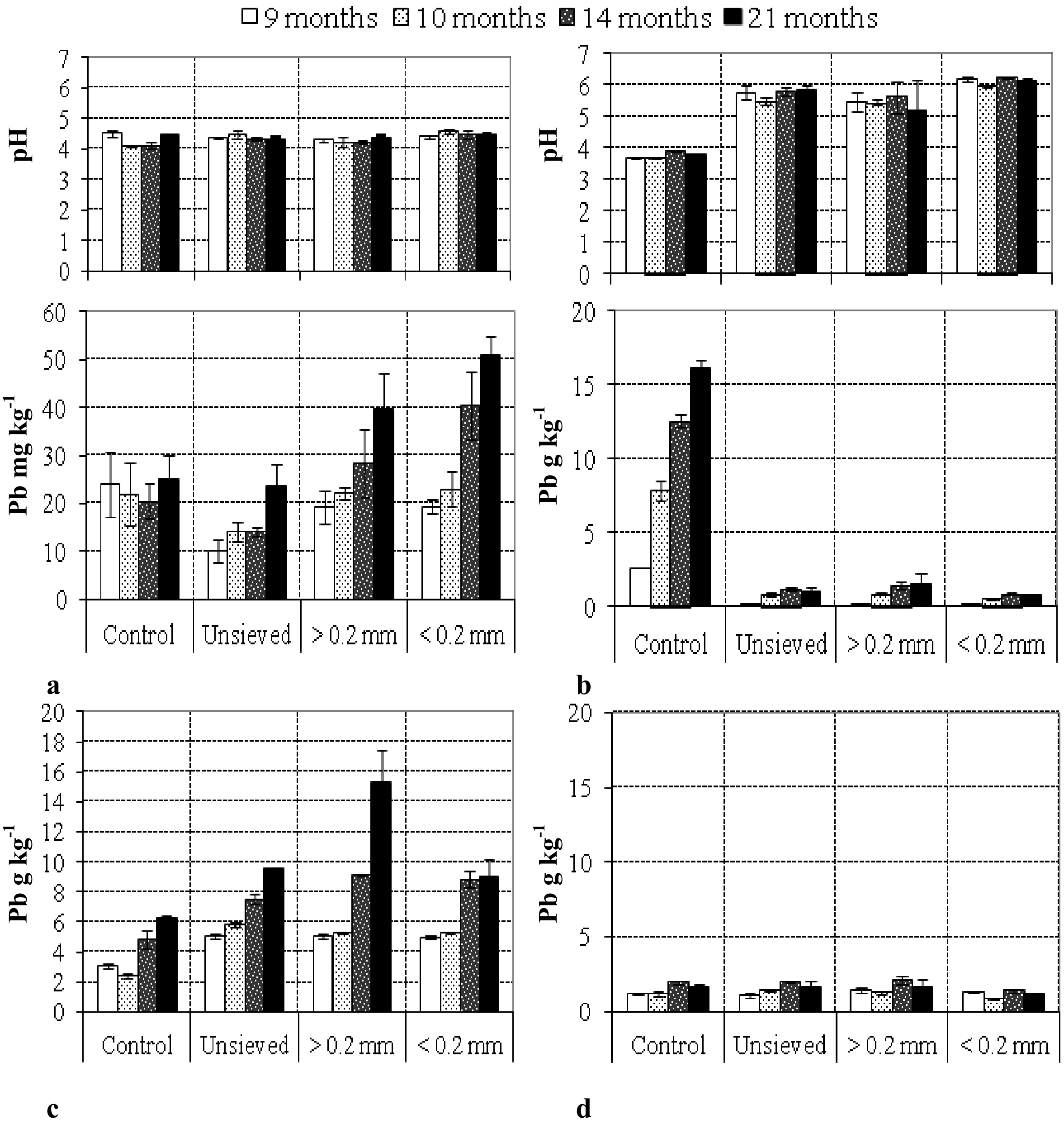

Figure 7. *(a) Water-soluble Pb (Pb$_w$) and pH of the water extract, (b) NH$_4$NO$_3$-extractable Pb (Pb$_{ex}$) and pH of the NH$_4$NO$_3$ extract, (c) NaOH-extractable Pb (Pb$_{org}$) and (d) NH$_4$-Ox-extractable Pb (Pb$_{ox}$) in various treatments as a function of incubation time. Error bars indicate the standard deviations of Pb. Note the dissimilar scales and dimensions for Pb fractions (Venäläinen, 2011).*

3.3.2 Tailings-induced changes in the speciation of water-extractable lead (Pb_w)

Because the ecotoxicity of soluble Pb is dependent on the species present, the Pb_w fraction was further subjected to speciation analysis. The analysis was carried out with separate water extracts from the shooting range samples with and without UtT amendments (the small-sized fraction, the large-sized fraction and the unsieved material) (Experiment 6b). The results revealed that in the control sample all particle size fractions decreased the total water-soluble Pb (Pb_{tot-s}) from 0.72 mg L^{-1} to 0.25–0.20 mg L^{-1} and the actual dissolved Pb (Pb_{dis}) from 0.36 mg L^{-1} to 0.04–0.08 mg L^{-1}. Moreover, the UtT amendments notably elevated pH of the water extracts from 5.0 in the control sample to 5.9–6.2. Regardless of the sample, Pb_{tot-s} largely exceeded Pb_{dis}, suggesting that a large proportion of the water-extractable Pb was bound in particulate form that failed to pass the 0.2-μm membrane filter. Passing the actual dissolved Pb through a cation exchange resin did not affect DOC notably. The proportion of the non-cationic DOC ($DOC_{non-cat}$) to the total DOC (DOC_{tot}) ranged between 81% and 97%. This outcome indicates that only a minor part of cationic Pb was in organically bound form. In the control soil, the subsequent cation exchange (CE) procedure decreased Pb_{dis} by 95%, leaving 5% of the actual dissolved Pb in the less toxic non-cationic pool. Thus, almost all of the actual dissolved Pb was in inorganic cationic form (i.e. Pb^{2+} or $PbOH^{+}$), representing the most ecotoxic Pb species.

In the UtT-amended samples, the relative proportions of non-cationic Pb species were much higher than in the control, being 10%, 12% and 9% for the unsieved, large-sized and small-sized materials, respectively. This finding provides evidence that tailings amendments diminished the proportion of the more toxic cationic species and converted them to the less toxic non-cationic form. This outcome can be ascribed to the calcite compartment and possible alkaline chemical residues in the tailings material that elevated pH of the water extracts, and thus, most likely favoured the formation of stable organo-Pb complexes (see Sauvé et al., 1997; Klucakova and Pekar, 2008).

4 General discussion

Phosphorus loading from non-point and point sources on the watershed not only causes a risk of eutrophication of surface waters but also dissipates non-renewable natural P resources. Theoretically, P losses from soil as well as removal of P from household sewage waters can be attained by means of Al and Fe salts. However, the precipitation chemicals are not safe for use on agricultural land, and in wastewater treatment they form P compounds of low bioavailability. Thus, there is need for introducing sustainable measures to control P losses to watercourses and, simultaneously, to keep P in the biogeochemical cycle. On the other hand, to control the environmental risks caused by detrimental heavy metals, such as Pb in soil, it is important to immobilize them into sparingly soluble forms. The prerequisite for the on-site remediation is, however, that the adopted measure has no negative secondary effects. The apatite ore mine tailings representing a natural geomaterial consist of a mixture of components relevant in reactions with both P and Pb. This study was undertaken to unravel the applicability of the tailings material as a sorption and remediation agent to be used in abatement of P- and Pb-evoked environmental risks.

4.1 Reducing phosphorus in domestic wastewaters

An evaluation of different on-site wastewater treatment systems supplemented with tailings from the Siilinjärvi phosphate mine revealed that when used as a middle layer material of a conventional sand filter bed, the tailings efficiently lowered P concentration of the sewage water. By contrast, when used as a sorbent material in a cesspool receiving sewage water from a conventional sand filter bed, the tailings did not dephosphorize the sewage equally well (Vilpas et al., 2005). The results here provide explanations for the differences in P retention between the two applications. The *Q/I* experiment (Experiment 2) revealed that the UtT material is able to retain P when its concentration in water is relatively low. As for the sand filter bed, the uppermost soil layers reduce the P concentration of the sewage to a level where the tailings material is able to retain P efficiently. Furthermore, in a sand filter bed the infiltration proceeds gradually and over a large area. This means that a relatively high tailings-to-solution ratio can be maintained, favouring the sorption reactions. On the contrary, a closed cesspool system connected to a conventional sand filter bed (without additional sorption components) may receive sewage water relatively high in P. Under these conditions, the ability of the UtT material to retain P is rather quickly used up or the material is even subjected to desorption of P, as observed in the *Q/I* experiment (Experiment 2).

However, the results obtained with the AtT indicate that the tailings very high in Al and Fe (hydr)oxides may function as an efficient P sorbent even at extremely high P concentrations. In Finland, the average total P concentration of unpurified sewage from sparsely populated areas is 17 mg L^{-1} (Vilpas et al., 2005). Treating such sewage water with the artificially weathered tailings at a tailings-to-solution ratio of 1:100 would reduce the P concentration of the sewage water by 98% and 99.9% within 24-h and 7-d periods (Experiment 2). The P concentration of the output water being less than 0.5 mg L^{-1} and 0.005 mg L^{-1}, respectively, would clearly exceed the 70% purification requirement set for total P in the Onsite Wastewater System Decree (209/2011). However, a notable disadvantage related to the AtT material is that its preparation requires the use of strong acid, rendering production of the material less economic and environmentally friendly.

4.2 Reducing phosphorus losses from agricultural land

The ability of the UtT and AtT materials to retain P makes their utilization in abatement of P loading to watercourses from agricultural land, especially CSAs, worth considering. In a 2-month incubation test conducted by Venäläinen (2009), the UtT and AtT materials significantly elevated the P sorption maximum (Q_{max}), even though the tailings dosage was relatively low. The AtT also increased the P affinity of the soil, as estimated by the increase in the slope of the isotherm (parameter K). The acid-treated material also significantly decreased the potentially labile, i.e. easily desorbable, P (Q_0), considered to provide an estimate for the direct risk of P loading (see e.g. Koski-Vähälä et al., 2001). Despite the low pH, the AtT did not decrease soil pH significantly. The tailings-induced changes in the DPS values of the soil were not analysed.

In the present study, the innate DPS values of the tailings materials were 6.2% and 1.6% in the UtT and 1.1% and 0.9% in the AtT for large- and small-sized fractions, respectively (Table 7). These values were very low relative to soil DPS values of 25–40%, commonly considered to cause an increased risk of P loss in leaching or with surface runoff (Pautler and Sims, 2000). Mixing the tailings with a soil most likely reduces DPS of the soil.

4.3 Tailings as a means of decreasing lead leaching to groundwater from contaminated sites

In shooting ranges, one of the highest environmental risks is leaching of Pb to the groundwater. The susceptibility of pellet-derived Pb to vertical movement within the soil profile largely depends on the physico-chemical properties of the soil. The Hälvälä shooting range investigated here is located in a typical boreal forest where the plant residues in soil are acidic by nature, rendering fulvic acids (FAs) more abundant than humic acids (HAs) (Stevenson, 1982, p. 46). Hartikainen and Kerko (2009) reported that in the Hälvälä shooting range, the pellets are accumulated in the organic horizon of the topsoil. This horizon is rich in FAs and HAs that are likely to form organo-metal compounds with Pb. The organic ligands not only reduce the ecotoxicity of Pb compared with its free cationic species ($Pb^{2+}$and $PbOH^{+}$) (Shanmukhappa and Neelakantan, 1990; Mager et al., 2011) but may also affect the solubility of the metal. FAs being lower in molecular weight and higher in acidity than HAs, their complexes with metals are less likely to be precipitated than those formed with HAs (Kerndorff and Schnizer, 1979; Christl and Kretzschmar, 2001).

Amending the contaminated shooting range soil with the UtT was observed to promote the formation of organo-Pb complexes (Pb_{org}) (Experiment 6a). This phenomenon was presumably due to the liming effect of the calcite compartment of the UtT, which favours the formation and stability of organic metal complexes (Sauvé et al., 1997; Klucakova and Pekar, 2008). Although the increase in Pb_{org} took place at the expense of the more bioavailable NH_4NO_3-extractable Pb pool (Pb_{ex}), in certain conditions the liming effect of the UtT may be undesired. Liming may increase the risk of leaching of Pb as soluble organic complexes to the deeper soil layers, towards the groundwater. This feature of the UtT material becomes particularly significant if the soil in the shooting range area is peaty (e.g. Histosols), as also shown by Deiss et al. (2004). In the Hälvälä shooting range, amending the soil with the UtT may to some extent decrease the abundance of Pb in the biologically active top soil layer and transfer the toxic metal to the deeper soil layers of lower biological activity.

In the experimental site of this study, the organic top soil is underlayed by a sandy mineral soil horizon rich in Al and Fe (hydr)oxides. These (hydr)oxide surfaces are able to retain FA-metal complexes through the formation of inner-sphere or outer-sphere complexes with the functional groups of the organic ligand (McBride, 1989; Weng et al. 2005; Vreysen and Maes, 2006; Perelomov et al., 2011). Thus, they may further reduce the leaching of the organically bound Pb. This became evident in Experiment 5, where the retention of Pb by uncontaminated mineral soil was investigated. The retention of organically bound Pb by oxide surfaces is particularly efficient in conditions where the soil is podzolic by nature (e.g. in forests of Nordic countries, Mokma et al., 2004) with an illuvial horizon enriched with Al and Fe (hydr)oxides (Borggaard et al., 1990). Furthermore, in organic soil the UtT material reduces the abundance of the most toxic Pb species (Experiment 6b), rendering the utilization of the material justified despite the risk of increased leaching of Pb to the mineral soil layers.

The reactions between Pb and the tailings-amended soil largely depend on the nature of the soil. In uncontaminated mineral soil, both the UtT and the AtT tailings efficiently increased the Pb retention capacity of the soil and the relative abundance of non-extracted Pb ($Pb_{non\text{-}extr}$), i.e. Pb retained in sparingly soluble forms (Experiment 5). This reaction pattern is contrary to that obtained with the organic soil, where the UtT enhanced the Pb_w and Pb_{org}, i.e. the solubility of Pb (Experiment 6a). In mineral soil, the increase in $Pb_{non\text{-}extr}$ was predicted to be attributable to cerussite and FPM formation in the reaction between added Pb and UtT or AtT. The immobilization of Pb through the formation of sparingly soluble compounds may be significant, especially in the remediation of contaminated areas low in organic matter such as major roads, metalliferous mines (Fonseca et al., 2011) or shooting ranges located in barren landscapes or even in sand pits. For this purpose, the UtT material would probably exhibit the most efficient remedial effects due to its superior ability to reduce the quantity of Pb_{ex} and to increase the quantity of $Pb_{non\text{-}extr}$ without increasing the acidity of the soil.

4.4 Tailings as a multifunctional remediation agent

Contaminated soils and aqueous waste streams often contain a variety of undesired substances. Based on the results obtained with P and Pb, the tailings material can be assumed to be able to retain also other harmful substances chemically resembling P, such as arsenate, chromate and possibly antimonite, and metal cations with a pK_a value similar to that of Pb, such as Cu (pK_a 7.95, Powell et al., 2007) and Zn (pK_a 7.69, Lindsay, 1979, p. 213). The multifunctionality of the tailings would be particularly advantageous in the remediation of areas contaminated with chemicals like chromated-copper-arsenate (CCA), commonly used as a wood preservative (Girouard and Zagury, 2009). Furthermore, the *Q/I* experiment carried out with the UtT without soil (Experiment 4) revealed that the UtT retains Pb efficiently from aqueous solutions. Thus, the material may be suitable for the purification of aqueous waste streams of industrial and shooting range origins. As for runoff waters from shooting ranges, the solutions are not only rich in Pb but may also contain significant amounts of Sb and Cu (Heier et al., 2009, 2010; Mariussen et al., 2012); thus, the tailings show potential for multipurpose remediation of such waste.

4.5 Recovery of used tailings

Utilization of the untapped tailings material from the Siilinjärvi apatite ore in environmental applications may provide a sound and cost-effective way of recycling the waste produced by the mining industry. Since the UtT material consists of natural and harmless geological components, the material applied to, for instance, CSAs or shooting ranges may be left in the soil. However, tailings material used in more controlled systems, such as wastewater purification applications, may have the potential to be further recycled. As the tailings material in a conventional sand filter eventually becomes enriched with P, and thus, loses its P sorption ability, the sorbent needs to be replaced by unenriched material. Fortunately, the P-enriched tailings material has the potential to serve as a P fertilizer in agricultural fields. As for the fertilizer use of the tailings, the Siilinjärvi complex has the advantage of being internationally exceptionally low in cadmium (Cd), a toxic element often associated with phosphate deposits (Louekari et al., 2000).

However, the use of the tailings material as a P fertilizer has some restrictions. First, the prerequisite for the utilization of the material as a fertilizer is that P retained will be released in the soil. Decomposable organic matter may produce organic acids able to release precipitated P through dissolution reactions. As for sorbed P, desorption reactions can be promoted by elevating pH through liming. Furthermore, organic ligands may enhance the desorption by competing with P for sorption sites (Bhatti et al., 1998). The efficiency of the latter reaction pattern is, however, controversial since the organic ligands are more relevant in reducing sorption than in inducing desorption (Violante et al., 2002). Second, toilet waste associated with the black waters from households poses a high risk of pathogens (Vinnerås, 2007). This limitation may, however, be overcome by composting the tailings. Besides sanitation, exposing the material to microbial activity in a compost may offer other advantages. Several studies have shown that a range of bacteria and fungi are able to solubilize phosphate minerals (e.g. Harris et al., 2006; Chatli et al., 2008; Kang et al., 2009; Feng et al., 2011). Subjecting the tailings to such microbes may promote the release of P from the sparingly soluble apatite fragments, thus further increasing the fertilizer value of the material.

Yet another theoretical possibility for the re-use of the tailings enriched with P lies in the chemistry between Pb and PO_4-P. Due to the high affinity of Pb for the PO_4^{3-} ligand, the P-enriched tailings may have the potential to be used as an improved Pb sorbent, e.g. in the remediation of Pb-contaminated wastewater or even at Pb-contaminated sites. The re-use of the P-enriched tailings material would further increase its ecological and economic value and support the recycling of P. However, all of the suggested applications should be carefully studied before being put into practice.

5 Concluding remarks

Mine tailings from apatite ore beneficiation consist of phlogopite, calcite and apatite residues that are able to retain P and Pb from aqueous solutions. The tailings also increase the Pb retention capacity of uncontaminated mineral soil and decrease the ecotoxicological risk of pellet-derived Pb in contaminated shooting range soil by reducing its most bioavailable and most toxic Pb species (i.e. water-soluble and NH_4NO_3-extractable Pb). The results obtained here suggest that the tailings may act as a P sorbent in the purification of wastewaters and as a remediation agent in Pb-contaminated sites. Depending on the purpose of use, the sorption properties of the tailings may be further optimized by sieving and treating with strong acid. However, utilization of acid-treated material of very low pH in environmental applications should be carefully considered before being put into practice.

The naturalness of the untreated tailings material may allow its utilization in various applications even after serving as a P sorbent in wastewater treatment. Provided that the sorbed P can be re-released from the tailings, e.g. by liming or addition of organic matter, the material may have the potential to be used as a P fertilizer in agricultural land. Because Pb has high affinity for phosphate, the tailings used in P retention may be suitable for removing Pb from wastewater and immobilizing it in contaminated soil.

The results showing that the tailings are able to retain P and Pb give reason to suggest that the tailings may also be able to retain other elements with similar chemical behaviour such as toxic As, Sb or Cu. This feature would further increase the value of the material as a remediation agent. The introduction of the tailings could offer an environmentally sound and cost-effective remediation or stabilization technique for various potentially harmful substances in the environment. Furthermore, it would also decrease the amount of untapped by-products produced by the mining industry, without further compromising the environment, and support the recycling of P.

6 References

Al-Degs, Y.S., El-Barghouthi, M.I., Issa, A.A., Khraisheh, M.A. & Walker, G.M. 2006. Sorption of Zn(II), Pb(II), and Co(II) using natural sorbents: Equilibrium and kinetic studies. *Water Research* **40**, 2645–2658.

Ashley, K., Cordell, D. & Mavinic, D. 2011. A brief history of phosphorus: From the philosopher's stone to nutrient recovery and reuse. *Chemosphere* **84**, 737–746.

Bargar, J.R., Brown Jr., G.E. & Parks, G.A. 1997. Surface complexation of Pb (II) at oxide-water interfaces: II. XAFS and bond-valence determination of mononuclear Pb(II) sorption products and surface functional groups on iron oxides. *Geochimica et Cosmochimica Acta* **61**, 2639–2652.

Beck, M.A., Robarge, W.P. & Buol, S.W. 1999. Phosphorus retention and release of anions and organic carbon by two andisols. *European Journal of Soil Science* **50**, 157–164.

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.

Bhatti, J.S., Comerford, N.B. & Johnston, C.T. 1998. Influence of oxalate and soil organic matter on sorption and desorption of phosphate onto a spodic horizon. *Soil Science Society of America Journal* **62**, 1089–1095.

Borggaard, O.K. 1983. The influence of iron oxides on phosphate adsorption by soil. *Journal of Soil Science* **34**, 333–341.

Borggaard, O.K., Jørgensen, S.S., Møberg, J.P. & Raben-Lange, B. 1990. Influence of organic matter on phosphate adrsorption by aluminium and iron oxides in sandy soils. *Journal of Soil Science* **41**, 443–449.

Borggaard, O.K., Szilas, C., Gimsing, A.L. & Rasmussen, L.H. 2004. Estimation of soil phosphate adsorption capacity by means of a pedotransfer function. *Geoderma* **118**, 55–61.

Borrero, C., Peña, F. & Torrent, J. 1988. Phosphate sorption by calcium carbonate in some soils of the Mediterranean part of Spain. *Geoderma* **42**, 264–269.

Borsos, E., Makra, L., Béczi, R., Vitányi, B. & Szentpeteri, M. 2003. Anthropogenic air pollution in the ancient times. *Acta Climatologica et Chorologica* **36-37**, 5–15.

Bradl, H.B. 2004. Adsorption of heavy metal ions on soils and soils constituents. *Journal of Colloid and Interface Science* **277**, 1–18.

Breeuwsma, A. & Schoumans, O.F. 1986. Fosfaatophoping en -uitspoeling in de bodem van mestoverschotgebieden. *Stichting voor Bodemkartering, Rapport* **1866**, Stiboka, Wageningen, Netherlands. 66 p.

Cao, X., Ma, L.Q., Chen, M., Hardison, D.W. & Harris, W.G. 2003. Lead transformation and distribution in the soils of shooting ranges in Florida, USA. *Science of the Total Environment* **307**, 179–189.

Cao, X., Ma, L.Q., Rhue, D.R. & Appel, C.S. 2004. Mechanisms of lead, copper, and zinc retention by phosphate rock. *Environmental Pollution* **131**, 435–444.

Cao, X., Ma, L., Singh, S.P. & Zhou, Q. 2008. Phosphate-induced lead immobilization from different lead minerals in soils under varying pH conditions. *Environmental Pollution* **152**, 184–192.

Cao, X., Wahbi, A., Ma, L., Li, B. & Yang, Y. 2009. Immobilization of Zn, Cu, and Pb in contaminated soils using phosphate rock and phosphoric acid. *Journal of Hazardous Materials* **164**, 555–564.

Cerezine, P.C., Nahas, E. & Banzatto, D.A. 1988. Soluble phosphate accumulation by *Aspergillus niger* from fluorapatite. *Applied Microbiology and Biotechnology* **29**, 501–505.

Chang, S.C. & Jackson, M.L. 1957. Fractionation of soil phosphorus. *Soil Science* **84**, 133–144.

Chardon, W.J. & van Faassen, H.G. 1999. Soil indicators for critical source areas of phosphorus leaching, *Rapporten Programma Geïntegreerd Bodemonderzoek* Deel **22**, Grafisch Service Centrum van Gils B.V., Wageningen, Netherlands. 38 p.

Chatli, A.S., Beri, V., Sidhu, B.S. 2008. Isolation and characterisation of the phosphate solubilising microorganisms from the cold desert habitat of Salix Alab Linn in trans Himalayan region of Himachal Pradesh. *Indian Journal of Microbiology* **48**, 267–273.

Chen, X.B., Wright, J.V., Conca, J.L. & Peurrung, L.M. 1997. Effects of pH on heavy metal sorption on mineral apatite. *Environmental Science & Technology* **31**, 624–631.

Chen, C., Coleman, M.L. & Katz, L.E. 2006. Bridging the gap between macroscopic and spectroscopic studies of metal ion sorption at the oxide/water interface: Sr(II), Co(II), and Pb(II) sorption to quartz. *Environmental Science & Technology* **40**, 142–148

Chou, L., Garrels, R.M. & Wollast, R. 1989. Comparative study of the kinetics and mechanisms of dissolution of carbonate minerals. *Chemical Geology* **78**, 269–282.

Christl, I. & Kretzschmar, R. 2001. Relating ion binding by fulvic and humic acids to chemical composition and molecular size. 1. Proton binding. *Environmental Science & Technology* **35**, 2505–2511.

Cole, C.V., Olsen, S.R. & Scott, C.O. 1953. The nature of phosphate sorption by calcium carbonate. *Soil Science Society of America Proceedings* **17**, 352–356.

Cordell, D., Drangert, J.-O. & White, S. 2009. The Story of phosphorus: global food security and food for thought. *Global Environmental Change* **19**, 292–305.

Davies, N.A., Hodson, M.E. & Black, S. 2002. Changes in toxicity and bioavailability of lead in contaminated soils to the earthworm *Eisenia Fetida* (Savigny 1826) after bone meal amendments to the soil. *Environmental Toxicology and Chemistry* **21**, 2685–2691.

Deiss, J., Byers, C., Clover, D., D'amore, D., Love, A., Menzies, M.A., Powell, J. & Walter M.T. 2004. Transport of lead and diesel fuel through a peat soil near Juneau, AK: a pilot study. *Journal of Contaminant Hydrology* **74**, 1–18.

Dong, D., Nelson, Y.M., Lion, L.W., Shuler, M.L. & Ghiorse, W.C. 2000. Adsorption of Pb and Cd onto metal oxides and organic material in natural surface coatings as determined by selective extractions: new evidence for the importance of Mn and Fe oxides. *Water Research* **34**, 427–436.

Dybowska, A., Manning, D.A.C., Collins, M.J., Wess, T., Woodgate, S. & Valsami-Jones, E. 2009. An evaluation of the reactivity of synthetic and natural apatites in the presence of aqueous metals. *Science of The Total Environment* **407**, 2953–296.

Elouear, Z., Bouzid, J., Boujelben, N., Feki, M., Jamoussi, F. & Montiel, A. 2008. Heavy metal removal from aqueous solutions by activated phosphate rock. *Journal of Hazardous Materials* **156**, 412–420.

Elzinga, E.J. & Sparks, D.L. 2002. X-ray absorption spectroscopy study of the effects of pH and ionic strength on Pb(II) sorption to amorphous silica. *Environmental Science & Technology* **36**, 4352–4357.

Environmental Protection Act 86/2000. Databank of Finnish legistlation. Unofficial translation of the original Act available from: http://www.finlex.fi/fi/laki/kaannokset/2000/en20000086.pdf. Last accessed 7/11/2012.

Environmental Protection Agency (EPA), 1994. Method 3051. Microwave-assisted acid digestion of sediments, sludges, soils and oils, Washington DC, United States of America. 30 p.

Eurostat, 2012a. Phosphorus balance in agriculture - Statistics Explained (2012/10/2). Available from: http://epp.eurostat.ec.europa.eu/statistics_explained/index.php/Phosphorus_balance_in_agriculture#Gross_phosphorus_balance_trends. Last accessed 09/10/2012.

Eurostat, 2012b.Water statistics - Statistics Explained (2012/10/4). Available from: http://epp.eurostat.ec.europa.eu/statistics_explained/index.php/Water_statistics#Public_water_supply. Last accessed 11/10/2012.

Essington, M.E. 2004. Soil and water chemistry: an integrative approach. CRC PressINC, United States of America. 534p.

Feng, M., Ngwenya, B.T., Wang, L., Li, W., Olive, V. & Ellam, R.M. 2011. Bacterial dissolution of fluorapatite as a possible source of elevated dissolved phosphate in the environment. *Geochimica et Cosmochimica Acta* **75**, 5785–5795.

Fife, C.V. 1959. An evaluation of ammonium fluoride as a selective extractant for aluminum bound soil phosphate. II. Preliminary studies on soils. *Soil Science* **87**, 83–88.

The Finnish Environment Institute, 2012. Air pollutant emissions in Finland. Available from:http://www.ymparisto.fi/default.asp?contentid=381942&lan=fi&clan=en. Last accessed 13/11/2012.

Fonseca, B., Pazos, M., Figueiredo, H., Tavares, T. & Sanromán, M.A. 2011. Desorption kinetics of phenanthrene and lead from historically contaminated soil. *Chemical Engineering Journal* **167**, 84–90.

Food, Agriculture Organization of the United Nations (FAO). 2006. World reference base for soil resources 2006. A framework for classification, correlation and communication. Food and Agriculture Organization of the United Nations, Rome. *World Soil Resources Report* **103**. 128p.

Forsling, W. & Wu, L. 1993. Surface complexation at hydrous fluorapatite. *Aquatic Science* **55**, 336–346.

Freeman, J.S. & Rowell, D.L. 1981. The adsorption and precipitation of phosphate onto calcite. *Journal of Soil Science* **32**, 75–84.

Frossard, E., Brossard, M., Hedley, M.J. & Metherell, A. 1995. Reactions controlling the cycling of P in soils. In: Tiessen, H. (ed.) Phosphorus cycling in terrestrial and aquatic ecosystems: a global perspective. SCOPE/Wiley, New York, United States of America. pp. 107–137.

Galarneau, E. & Gehr, R. 1997. Phosphorus removal from wastewaters: Experimental and theoretical support for alternative mechanisms. *Water Research* **31**, 328–338.

Giles, C.H., McEwan, T.H., Nakhawa, S.N. & Smith, D. 1960. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *Journal of Chemical Society*, 3973–3993.

Girouard, E. & Zagury, G.J. 2009. Arsenic bioaccessibility in CCA-contaminated soils: Influence of soil properties, arsenic fractionation, and particle-size fraction. *Science of the Total Environment* **407**, 2576–2585.

Godelitsas, A., Astilleros, J.M., Hallam, K., Harissopoulos, S. & Putnis, A. 2003. Interaction of calcium carbonates with lead in aqueous solutions. *Environmental Science & Technology* **37**, 3351–3360.

Government Decree on Treating Domestic Wastewater in Areas Outside Sewer Networks 542/2003. Databank of Finnish legistlation. Unofficial translation of the original Decree available from: http://www.finlex.fi/fi/laki/kaannokset/2003/en20030542.pdf. Last accessed 19/12/2012.

Grandjean, P. 1978. Widening perspectives of lead toxicity: A review of health effects of lead exposure in adults. *Environmental Research* **17**, 303–321.

Granstedt, A. 2000. Increasing the efficiency of plant nutrient recycling within the agricultural system as a way of reducing the load to the environment-experience from Sweden and Finland. *Agriculture, Ecosystems & Environment* **80**, 169–185.

Gustafsson, J.P. 2000. Visual Minteq. KTH Royal Institute of Technology, Department of Land and Water Resources Engineering, Stockholm. Available from: http://www2.lwr.kth.se/English/OurSoftware/Vminteq/index.html. Last accessed 21/11/2012.

Hallanaro, E-L. & Kujala-Räty, K. 2011. Haja-asutuksen jätevedet. Lainsäädäntö ja käytännöt. Ympäristöopas **2011**, Ympäristöministeriö. ISBN 978-952-11-3945-1 (PDF). In Finnish. Available from: http://www.ymparisto.fi/download.asp?contentid=132989&lan=fi. Last accessed 21/11/2012.

Hardison, D.W., Ma, L., Luongo, T. & Harris, W.G. 2004. Lead contamination in shooting range soils from abrasion of lead bullets and subsequent weathering. *Science of the Total Environment* **328**, 175–183.

Harris, N.J., New, P.B. & Martin P.M. 2006. Laboratory tests can predict beneficial effects of phosphate-solubilising bacteria on plants. *Soil Biology and Biochemistry* **38**, 1521–1526.

Hartikainen, H. 1979. Phosphorus and its reactions in terrestrial soils and lake sediments. Journal of Scientific *Agricultural Society of Finland* **51**, 537–624.

Hartikainen, H. 1982. Relationship between phosphorus intensity and capacity parameters in Finnish mineral soils. I interpretation and application of phosphorus sorption-desorption isotherms. *Journal of Scientific Agricultural Society of Finland* **54**, 245–250.

Hartikainen, S.H. & Hartikainen, H.H. 2008. Phosphorus retention by phlogopite-rich mine tailings. *Applied Geochemistry* **23**, 2716–2723.

Hartikainen, H. & Kerko, E. 2009. Lead in various chemical pools in soil depth profiles on two shooting ranges of different age. *Boreal Environ Research* **14 (Suppl. A)**, 61–69.

Hashimoto,Y. & Sato, T. 2007. Removal of aqueous lead by poorly-crystalline hydroxyapatites. *Chemosphere* **69**, 1775–1782.

Heier, L.S., Lien, I.B., Strømseng, A.E., Ljønes, A.E., Rosselan, B.O., Tollefsen, K.-E. & Salbu, B. 2009. Speciation of lead, copper, zinc and antimony in water draining a shooting range - Time dependant metal accumulation and biomarker responses in brown trout (*Salmo trutta* L.). *Science of the Total Environment* **407**, 4047–4055.

Heier, L.S., Meland, S., Ljønes, M., Salbu, B. & Strømseng, A.E. 2010. Short-term temporal variations in speciation of Pb, Cu, Zn and Sb in a shooting range runoff stream. *Science of the Total Environment* **408**, 2409–2417.

Helal, M.I.D. 2006. Sorption/desorption characteristics of heavy metal on amorphous Al and Fe hydroxides formed in the presence of oxalate, citrate and tannate, ligands. *Journal of Agronomy* **5**, 440–450.

Henze, M., Harremoës, P., Jansen, J.I.C. & Arvin, E. 2002. Wastewater treatment. Biological and chemical processes. 3rd ed. Springer, Berlin. 430 p.

Hernberg, S. 2000. Lead poisoning in historical perspective. *American Journal of Industrial Medicine* **38**, 244–254.

Herring, J.R. & Fantel, R.J. 1993. Phosphate rock demand into the next century: impact on world food supply. *Natural Resources Research* **2**, 226–246.

Hingston, F.J., Atkinson, R.J., Posner, A.M. & Quirk, J.P. 1967. Specific adsorption of anions. *Nature* **215**, 1459–1461.

Hong, S., Candelone, J-P., Patterson, C.C. & Boutron, C.F. 1994. Greenland ice evidence of hemispheric lead pollution two millenia ago by Greek and Roman civilizations. *Science* **265**, 1841–1843.

Hunting Act 615/93. Databank of Finnish legistlation. Unofficial translation of the original Act available from: http://www.finlex.fi/en/laki/kaannokset/1993/en19930615.pdf. Last accessed 26/11/2012.

International Food Policy Research Institute (IFPRI) 2002. Reaching sustainable food security for all by 2020: Getting the priorities and responsibilities right. International Food Policy Research Institute, Washington. Available from: http://www.ifpri.org/sites/default/files/pubs/2020/books/actionlong.pdf. Last accessed 21/11/2012.

Ioannidis, T.A, & Zouboulis, A.I. 2003. Detoxification of a highly toxic lead-loaded industrial solid waste by stabilization using apatites. *Journal of Hazardous Materials* **97**, 173–191.

Issaq, H.J. & Zielinski Jr., W.L. 1974. Loss of Lead from aqueous Solutions during Storage. *Analytical chemistry* **46**, 1328–1329.

Isoyama, M. & Wada, S. 2007. Remediation of Pb-contaminated soils by washing with hydrochloric acid and subsequent immobilization with calcite and allophanic soil. *Journal of Hazardous Materials* **143**, 636–642.

Jaakkonen, S. 2008. Treatment of Contaminated Soil in Finland. Reports of the Finnish Environment Institute 36/2008, pp. 45 Finnish Environment Institute, Helsinki (2008) In Finnish with an English abstract. Available from: http://www.ymparisto.fi/download.asp?contentid=97280&lan=fi. Last accessed 21/11/2012.

Jenssen, P.D., Mæhlum, T., Krogstad, T. & Vråle, L. 2005. High performance constructed wetlands for cold climates. Journal of environmental science and health. Part A, T*oxic/hazardous substances & environmental engineerin*g **40**, 1343–1353.

Jenssen, P.D., Krogstad, T., Paruch, A.M., Mæhlum, T., Adam, K., Arias, C.A., Heistad, A., Jonsson, L., Hellström, D., Brix, H., Yli-Halla, M., Vråle, L. & Valve, M. 2010. Filter bed systems treating domestic wastewater in the Nordic countries – Performance and reuse of filter media. *Ecological Engineering* **36**, 1651–1659.

Jin, Z. & Heo, J. 1998. Soil remediation effects of a Na2O–P2O5 binary phosphate glass on Pb-contaminated soils. *Journal of Materials Science Letters* **17**, 633–635.

Johansson, L. 1997. The use of Leca (light expanded clay aggregrates) for the removal of phosphorus from wastewater. *Water Science and Technology* **35**, 87–93.

Jørgensen, S.S. & Willems, M. 1987. The fate of lead in soils: the transformation of lead pellets in shooting range soils. *Ambio* **16**, 11–5.

Kaludjerovic-Radoicic, T. & Raicevic, S. 2010. Aqueous Pb sorption by synthetic and natural apatite: Kinetics, equilibrium and thermodynamic studies. *Chemical Engineering Journal* **160**, 503–510.

Kang, S.M., Joo, G.J., Hamayun, H., Na, C.I., Shin, D.H., Kim, H.Y., Hong, K. & Lee, I.J. 2009. Gibberellin production and phosphate solubilisation by newly isolated strain of *Acinetobacter calcoaceticus* and its effects on plat growth. *Biotechnology Letters* **31**, 277–281.

Kerndorff, H. & Schnizer, M. 1979. Humic and fulvic acids as indicators of soil and water pollution. *Water, Air & Soil Pollution* **12**, 319–329.

Khan, F.I., Husain, T. & Hejazi, R. 2004. An overview and analysis of site remediation technologies. *Journal of Environmental Management* **71**, 95–122.

Klucakova, M. & Pekar, M. 2008. Behaviour of partially soluble humic acids in aqueous suspension. *Colloids and Surfaces A* **318**, 106–110.

Koljonen, T. 1992. Results of the mapping. In: Koljonen T, editor. Suomen geokemian atlas, osa 2: moreeni – The Geochemical Atlas of Finland, Part 2: Till. Geological Survey of Finland: Espoo, 1992. p. 106–125.

Koski-Vähälä, J., Hartikainen, H. & Tallberg, P. 2001. Phosphorus mobilization from various sediment pools in response to increased pH and silicate concentration. *Journal of Environmental Quality* **30**, 546–552.

Kuperman, R.G. & Carreiro, M.M. 1997. Soil heavy metal concentrations, microbial biomass and ezyme activities in a contaminated grassland ecosystem. *Soil Biology & Biochemistry* **29**, 179–190.

Levonmäki, M. & Hartikainen, H. 2007. Efficiency of liming in controlling the mobility of lead in shooting range soils as assessed by different experimental approaches. *Science of the Total Environment* **388**, 1–7.

Lin, C-W., Lian, J. & Fang, H-H. 2005. Soil lead immobilization using phosphate rock. *Water, Air, & Soil Pollution* **161**, 113–123.

Lindsay, W.L. 1979. Chemical equilibria in soils. John Wiley & Sons, Inc, USA. 449p.

Lockitch, G. 1993. Perspectives on lead toxicity. *Clinical Biochemistry* **26**, 371–381.

Loeppert, R.H. & Inskeep, W.P. 1996. Iron. In: Bigham, J.M. (ed.). Methods of soil analysis. Soil Science Society of America, Inc., American Society of Agronomy, Inc., Madison, WI, USA, pp. 639–664.

Lookman, R., Vandeweert, N., Merckx, R. & Vlassak, K. 1995. Geostatistical assessment of the regional distribution of phosphate sorption capacity parameters (Fe_{ox} and Al_{ox}) in northern Belgium. *Geoderma* **66**, 285–296.

Louekari, K., Mäkelä-Kurtto, R., Pasanen, J., Virtanen, V., Sippola, J. & Malm, J. 2000. Cadmium in fertilizers - Risks to human health and environment. Ministry of Agriculture and Forestry in Finland. Publications 4/2000. 120 p.

Ma, Q.Y., Traina, S.J., Logan, T. & Ryan, J.A. 1993. In situ lead immobilization by apatite. *Environmental Science & Technology* **27**, 1803–1810.

Ma, Q.Y., Logan, T.J. & Traina, S.J. 1995. Lead immobilization from aqueous solutions using phosphate rocks. *Environmental Science & Technology* **29**, 1118–1126.

Mager, E.M., Brix, K.V., Gerdes, R.M., Ryan, A.C. & Grosell, M. 2011. Effects of water chemistry on the chronic toxicity of lead to the cladoceran, Ceriodaphnia dubia. *Ecotoxicology and Environmental Safety* **74**, 238–43.

Mariussen, E., Ljønes, M. & Strømseng, A.E. 2012. Use of sorbents for purification of lead, copper and antimony in runoff water from small arms shooting ranges. *Journal of Hazardous Materials* **243**, 95–104.

Mavropoulos, E., Rossi, A.M., Costa, A.M., Perez, C.A.C. & Moreira, J.C. 2002. Studies on the mechanism of lead immobilization by hydroxyapatite. *Environmental Science & Technology* **36**, 162–1629.

Mavropoulos, E., Rocha, N.C.C., Moreira, J.C., Rossi, A.M. & Soares, G.A. 2004. Characterization of phase evolution during lead immobilization by synthetic hydroxyapatite.*Materials Characterization* 53, 71–78.

Mavropoulos, E., da Rocha, N.C.C., Moreira, J.C., Beryolino, L.C. & Rossi, A.M. 2005. Pb^{2+}, Cu^{2+} and Cd^{2+} ions uptake by Brazilian phosphate rocks. *Journal of Brazilian Chemical Society* **16**, 62–68.

MacKenzie, A.B., Farmer, J.G. & Sugden, C.L. 1997. Isotopic evidence of the relative retention and mobility of lead and radiocaesium in Scottish ombrotrophic peats. *Science of the Total Environment* **203**, 115–127.

McBride, M.B. 1989. Reactions controlling heavy metal solubility in soils. *Advances in Soil Sciences* **10**, 1–56.

McKeague, J.A. & Day, J.H. 1966. Dithionite- and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Canadian Journal of Soil Science* **46**, 13–22.

Mokma, D.L., Yli-Halla, M. & Lindqvist, K. 2004. Podsol formation in sandy soils of Finland. *Geoderma* **120**, 259–272.

Mortula, M.M. & Gagnon, G.A. 2007. Alum residuals as a low technology for phosphorus removal from aquaculture processing water. *Aquacultural Engineering* **36**, 233-238.

Muljadi, D., Posner, A.M. & Quirk, J.P. 1966. The mechanism of phosphate adsorption by kaolinite, gibbsite and pseudoboehmite I. the isotherms and the effect of pH on adsorption. *Journal of Soil Science* 17, 212-229.

Mulligan C.N, Yong, R.N. & Gibbs, B.F. 2001. Remediation technologies for metal-contaminated soils and groundwater: an evaluation. *Engineering Geology* **60**, 193–207.

Munsell Color (ed.) 1994. Munsell soil color chart. New Windsor, New York.

Needleman, H. 2009. Low level lead exposure: History and discovery. *Annals of Epidemiology* **19**, 235–238.

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 Scientific Agricultural Society of Finland* 61, 73–78.

Nodvin, S.C., Driscoll, C.T. & Likens, G.E. 1986. Simple partitioning of anions and dissolved organic carbon in a forest soil. *Soil Science* **142,** 27–35.

Nriagu, J.O. 1996. A history of global metal pollution. *Science* **272**, 223–224.

Official Statistics of Finland (OSF): Buildings and free-time residences (e-publication). ISSN=1798-6796. 2011, Free-time Residences 2011. Helsinki: Statistics Finland. Available from: http://www.stat.fi/til/rakke/2011/rakke_2011_2012-05-25_kat_001_en.html. Last accessed 21/11/2012.

Omoike, A.I. & vanLoon, G.W. 1999. Removal of phosphorus and organic matter removal by alum during wastewater treatment. *Water Research* **33**, 3617–3627.

Onsite Wastewater System Decree 209/2011. Databank of Finnish legistlation. In Finnish. Available from: http://www.finlex.fi/fi/laki/alkup/2011/20110209. Last accessed 19/12/2012.

Parfitt, R.L., Atkinson, R.J. & Smart, R. St.C. 1975. The mechanism of phosphate fixation by iron oxides. *Soil Science Society of America Proceedings* **39**, 837–841.

Pautler, M.C. & Sims, J.T. 2000. Relationships between soil test phosphorus, soluble phosphorus, and phosphorus saturation in delaware soils. *Soil Science Society of America Journal* **64**, 765–773.

Peltovuori, T., Uusitalo, R. & Kauppila, T. 2002. Phosphorus reserves and apparent phosphorus saturation in four weakly developed cultivated pedons. *Geoderma* **110**, 35–47.

Peltovuori, T., 2006. Phosphorus in agricultural soils of Finland – characterization of reserves and retention in mineral profiles. Pro Terra **26**. University of Helsinki, Helsinki. Doctoral dissertation. 69 p.

Perelomov L.V., Pinskiy, D.L. & Violante, A. 2011. Effect of organic acids on the adsorption of copper, lead, and zinc by goethite. *Eurasian Soil Science* **44**, 22–28.

Persson, I., Lykzco, K., Lundberg, D., Eriksson, L. & Placzek, A. 2011. Coordination chemistry study of hydrated and solvated lead(II) ions in solution and solid state. *Inorganic Chemistry* **50**, 1058–1072.

Plummer, L.N., Wigley, T.M.L. & Parkhurst, D.L. 1978. The kinetics of calcite dissolution in CO_2-water systems at 5° to 60ºC and 0.0 to 1.0 atm CO_2. *American Journal of Science* **278**, 179–216.

Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Leuz, A.-K., Sjöberg, S. & Wanner, H. 2007. Chemical speciation of environmentally significant metals with inorganic ligands. Part 2: The Cu^{2+}-OH^-, Cl^-, CO_3^{2-}, SO_4^{2-} and PO_4^{3-} systems. (IUPAC Technical Report). *Pure and Applied Chemistry* **79**, 895–950.

Powell, K.J., Brown, P.L., Byrne, R.H., Gajda, T., Hefter, G., Leuz, A.-K., Sjöberg, S. & Wanner, H. 2009. Chemical speciation of environmentally significant metals with inorganic ligands. Part 3: The Pb^{2+} + $OH^–$, $Cl^–$, $CO_3^{2–}$, $SO_4^{2–}$, and $PO_4^{3–}$ systems (IUPAC Technical Report). *Pure and Applied Chemistry* **81**, 2425–2476.

Puustinen, K. 1971. Geology of the Siilinjärvi carbonatite complex, Eastern Finland. Bulletin of the Geological Society of Finland **249**. 43 p.

Pietarila, H., Salmi, T., Saari, H. & Pesonen, R. 2001. The preliminary assessment under the EC air quality directives in Finland. SO_2, NO_2/NO_X, PM_{10}, lead. Finnish Meteorological Institute. 51 p.

Rantalainen, M.L., Torkkeli, M., Strömmer, R. & Setälä, H. 2006. Lead contamination of an old shooting range affecting the local ecosystem – a case study with a holistic approach. *Science of the Total Environment* **369**, 99–108.

Rashed, M.N. 2010. Monitoring of contaminated toxic and heavy metals, from mine tailings through age accumulation, in soil and some wild plants at Southeast Egypt. *Journal of Hazardous Materials* **178**, 739–746.

Renberg, I., Persson, M.W. & Emteryd, O. 1994. Pre-industrial atmospheric lead contamination detected in Swedish lake sediments. *Nature* **368**, 323–326.

Rouff, A.A., Reeder, R.J. & Fisher, N.S. 2002. Pb (II) sorption with calcite: A radiotracer study. *Aquatic Geochemistry* **8**, 203–228.

Rouff, A.A., Elzinga, E.J., Reeder, R.J. & Fisher, N.S. 2005. The influence of pH on the kinetics, reversibility and mechanisms of Pb(II) sorption at the calcite-water interface. *Geochimica et Cosmochimica Acta* **69**, 5173–5186.

Ryden, J.C., McLaughlin, J.R. & Syers, J.K. 1977. Mechanisms of phosphate sorption by soils and hydrous ferric oxide gel. *Journal of Soil Science* **28**, 72–92.

Ryden, J.C., Syers, J.K. & Tillman, R.W. 1987. Inorganic anion sorption and interactions with phosphate sorption by hydrous ferric oxide gel. *Journal of Soil Science* **38**, 211–217.

Sandrine, B., Ange, N., Didier, B., Eric, C. & Patrick, S. 2007. Removal of aqueous lead ions by hydroxyapatites: Equilibria and kinetic processes. *Journal of Hazardous Materials* **139**, 443–446.

Sauvé, S., McBride, M. & Hendershot, W. 1997. Speciation of lead in contaminated soils. *Environmental Pollution* **98**, 149–155.

Schindler, P.W., Fürst, B., Dick, R. & Wolf, P.U. 1976. Ligand properties of surface silanol groups. I. Surface complex formation with Fe^{3+}, Cu^{2+}, Cd^{2+}, and Pb^{2+}. *Journal of Colloid and Interface Science* **55**, 469–475.

Schwertmann, U. 1964. The diffrentiation of iron oxide in soils by a photochemical extraction with acid ammonium oxalate. *Zeitschrift für Pflanzeneraehrung und Bodenkunde* **105**, 194–201.

Sewage Sludge Directive 86/278/EEC. European Council. Available from: http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31986L0278:EN:NOT. Last accessed 13/11/2012.

SFS-EN ISO 3696. Analyyttiseen laboratoriokäyttöön tarkoitettu vesi. Määritelmä ja testimenetelmät. (Water for analytical laboratory use. Specification and test methods). 1995. Suomen standardoimisliitto, Helsinki. In Finnish. 8 p.

Shanmukhappa, H. & Neelakantan, K. 1990. Influence of humic acid on the toxicity of copper, cadmium and lead to the unicellular alga, *Synechosystis aquatilis*. *Bulletin of Environmental Contamination and Toxicology* **44**, 840–843.

Sharpley, A.N. & Rekolainen, S. 1997. Phosphorus in agriculture and its environmental implications. In: Tunney, H., Carton, O.T., Brookes, P.C. & Johnston, A.E. (Eds.). Phosphorus loss from soil to water. CAB International Press, Cambridge, UK. pp. 1–54.

Simojoki, A. 2000. Responses of soil respiration and barley growth to modified supply of oxygen in the soil. *Agricultural and Food Science in Finland* **9**, 303–318.

Singh, R.P., Tripathi, R.D., Sinha, S.K., Maheshwari, R.K. & Srivastava, H.S., 1997. Response of higher plants to lead contaminated environment. *Chemosphere* **34**, 2467–2493.

Smil, V. 2000. Phosphorus in the environment: natural flows and human interferences. *Annual Review of Energy and the Environment* **25**, 53–88.

Smit, A.L., Bindraban, P.S., Schröder, J.J., Conijn, J.G. & van der Meer, H.G. 2009. Phosphorus in agriculture: global resources, trends and developments: report to the Steering Committee Technology Assessment of the Ministry of Agriculture, Nature and Food Quality, The Netherlands. Report 282. Plant Research International B.V., Wageningen. 36 p.

Sorvari, J., Antikainen, R. & Pyy, O. 2006. Environmental contamination at Finnish shooting ranges—the scope of the problem and management options. *Science of the Total Environment* **366**, 21–31.

Steen, I. 1998. Phosphorus availability in the 21st Century: management of a nonrenewable resource. *Phosphorus and Potassium* **217**, 25–31.

Stén, P., Parvinen, P., Miettinen, M., Luukkanen, S., Kaskiniemi, V. & Aaltonen, J. 2003. On-line analysis of flotation process waters at Siilinjärvi (Finland) apatite concentrating plant. *Minerals Engineering* **16**, 229–236.

Stevenson, F.J. 1982. Humus chemistry. John Wiley & Sons, Inc. Canada. 443 p.

Strømseng, A.E., Ljønes, M., Bakka, L. & Longva, K.S. 2008. Filter medias for purification of heavy metals in runoff water from shooting ranges. Field tests at Steinsjoen shooting range Norwegian Defence Research Establishment, Norway. Report No., FFI/RAPPORT-2007/0132. Available from: http://rapporter.ffi.no/rapporter/2007/01321.pdf In Norwegian. Last accessed 21/11/2012.

Suzuki, T., Hatsushika, T. & Miyake, M. 1982. Synthetic hydroxyapatites as inorganic cation exchangers Part 2. *Journal of the Chemical Society, Faraday Transactions 1* **78**, 3605–3611.

Syers, J.K., & Curtin, D. 1989. Inorganic reactions controlling phosphorus cycling. In: Tiessen, H. (ed.). Phosphorus cycles in terrestrial and aquatic ecosystems. Regional workshop I: Europe. SCOPE/UNEP Proceedings. University of Saskatchewan, Saskatoon, Canada. pp. 17–29.

Taylor. P. & Lopata, V.J. 1984. Stability and solubility relationships between some solids in the system lead oxide-carbon dioxide-water. *Canadian Journal of Chemistry* **62**, 395–402.

Tunney, H., Csathó, P. & Ehlert, P. 2003. Approaches to calculating P balance at the field-scale in Europe. *Journal of Plant Nutrition and Soil Science* **166**, 438–446.

Tuomela, M., Steffen, K., Kerko, E., Hartikainen, H., Hofrichter, M. & Hatakka, A. 2005. Influence of Pb contamination in boreal forest soil on the growth and ligninolytic activity of litter-decomposing fungi. *FEMS Microbiology Ecology* **53**, 179–186.

Uusitalo, R., Turtola, E., Grönroos, J., Kivistö, J., Mäntylahti, V., Turtola, A., Lemola, R. & Salo, T. 2007. Finnish trends in phosphorus balances and soil test phosphorus. *Agricultural and Food Science* **16**, 301–316.

Valsami-Jones, E., Ragnarsdottir, K.V., Putnis, A., Bosbach, D., Kemp, A.J. & Cressey, G. 1998. The dissolution of apatite in the presence of aqueous metal cations at pH 2–7. *Chemical Geology* **151**, 215–233.

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.

Venäläinen, S.H. 2009. Utilization of phlogopite-rich mine tailings in abatement of phosphorus loading to watercourses. In: Willis, T.P. (ed.). Sorbents: Properties, Materials and Applications. Nova Science Publishers, Inc. Hauppauge, NY, USA, pp. 201–216.

Venäläinen, S.H. 2011. Apatite ore mine tailings as an amendment for remediation of a lead-contaminated shooting range soil. *Science of the Total Environment* **409**, 4628–4634.

Venäläinen, S.H. 2012. Sorption of lead by phlogopite-rich mine tailings. *Applied Geochemistry* **27,** 1593–1599.

Vilpas, R., Kujala-Räty, K., Laaksonen, T. & Santala, E. 2005. Enhancing nutrient removal efficiency of onsite wastewater treatment systems – Ravinnesampo. Part 1: treatment of domestic wastewater, The Finnish Environment, vol. 762. Vammala Printers, Finland. In Finnish. Available from: http://www.ymparisto.fi/download.asp?contentid=37356&lan=fi. Last accessed 21/11/2012.

Vinnerås, B. 2007. Comparison of composting, storage and urea treatment for sanitising of faecal matter and manure. *Biosource Technology* **98**, 3317–3321.

Violante, A., Pigma, M., Ricciardella, M. & Gianfreda, L. 2002. Adsorption of phosphate on variable charge minerals and soils as affected by organic and inorganic ligands. *Developments in Soil Science* **28**, Part A, 279–295.

Vreysen, S. & Maes, A. 2006. Adsorption mechanism of fulvic acid onto freeze dried poly(hydroxo aluminum) intercalated bentonites. *Applied Clay Science* **32**, 190–196.

Wang, M.K. & Tzou, Y.M. 1995. Phosphate sorption by calcite, and iron-rich calcareous soils. *Geoderma* **65**, 249–261.

Wang, C.-L., Chuang, H.-Y., Ho, C.-K., Yang, C.-Y., Tsai, J.-L., Wu, T.-S. & Wu, T.-N. 2002. Relationship between blood lead concentrations and learning achievement among primary school children in Taiwan. *Environmental Research Section A* **89,** 12–18.

Welch, S.A., Taunton, A.E. & Banfield, J.F. 2002. Effect of microorganisms and microbial metabolites on apatite dissolution. *Geomicrobiology Journal* **19**, 343–367.

Wellmer, F.-W. & Kürsten, M. 1992. International perspective of mineral resources. *Episodes* **15**, 182–194.

Weng, L.P., Koopal, L.K., Hiemstra, Meeussen, J., & van Riemsdijk, W.H. 2005. Interactions of calcium and fulvicacid at the goethite-water interface. *Geochimica et Cosmochimica Acta* **69**, 325–339.

Xu, Y., Boonfueng, T., Axe, L., Maeng, S. & Tyson, T. 2006. Surface complexation of Pb(II) on amorphous iron oxide and manganese oxide: Spectroscopic and time studies. *Journal of Colloid and Interface Science* **299**, 28–40.

Yamada, H., Tamura, K., Watanabe, Y., Iyi, N. & Morimoto, K. 2011. Geomaterials: their application to environmental remediation. *Science and Technology of Advanced Materials* **12**, 064705.

Yang, Y., Zhao, Y.Q., Babatunde, A.O., Wang, L., Ren, Y.X. & Han,Y. 2006. Characteristics and mechanisms of phosphate adsorption on dewatered alum sludge. *Separation and Purification Technology* **51**, 193–200.

Zhu, K., Qiu, J., Ji, H., Yanagisawa, K., Shimanouchi, R., Onda, A. & Kajiyoshi, K. 2010. Crystallographic study of lead-substituted hydroxyapatite synthesized by high-temperature mixing method under hydrothermal conditions. *Inorganica Chimica Acta* **363**, 1785–1790.

Appendix 1

Measured *Q/I* data of the P desorption-sorption isotherms of the untreated tailings (UtT)

Tailings	**Mesh**	**Equilibration time**	**P concentration of the enrichment solution**	***Q***	***I***
	Ø mm		**mg L^{-1}**	**mg kg^{-1} ± SD**	**mg L^{-1} ± SD**
Untreated tailings (UtT)	> 0.2	24 h	0	-1.0 ± 0.1	0.02 ± 0.00
			0.05	-0.2 ± 0.0	0.05 ± 0.00
			0.1	-0.3 ± 0.1	0.1 ± 0.0
			0.3	0.6 ± 0.0	0.3 ± 0.0
			0.5	1.1 ± 0.0	0.5 ± 0.0
			1.0	5.7 ± 0.3	0.9 ± 0.0
			2.0	2.7 ± 0.2	1.9 ± 0.0
			4.0	4.4 ± 0.9	3.8 ± 0.1
	< 0.2		0	-0.7 ± 0.1	0.01 ± 0.00
			0.05	0.2 ± 0.0	0.04 ± 0.00
			0.1	0.2 ± 0.0	0.1 ± 0.0
			0.3	1.7 ± 0.1	0.2 ± 0.0
			0.5	2.4 ± 0.4	0.4 ± 0.0
			1.0	7.6 ± 0.0	0.8 ± 0.0
			2.0	3.8 ± 0.6	1.8 ± 0.1
			4.0	3.3 ± 0.3	3.8 ± 0.1
Untreated tailings (UtT)	> 0.2	7 d	0	-1.2 ± 0.2	0.02 ± 0.00
			0.1	0.6 ± 0.1	0.1 ± 0.0
			0.3	1.2 ± 0.1	0.3 ± 0.0
			0.5	1.4 ± 0.3	0.5 ± 0.0
			1.0	4.5 ± 0.1	0.9 ± 0.0
			2.0	1.6 ± 0.0	2.0 ± 0.0
			4.0	-1.3 ± 0.2	4.0 ± 0.1
			5.0	-3.3 ± 1.4	5.1 ± 0.0
	< 0.2		0	-1.4 ± 0.1	0.03 ± 0.01
			0.1	1.2 ± 0.1	0.1 ± 0.0
			0.3	2.4 ± 0.1	0.3 ± 0.0
			0.5	2.8 ± 0.2	0.5 ± 0.0
			1.0	7.2 ± 0.6	0.9 ± 0.0
			2.0	4.2 ± 1.3	1.9 ± 0.0
			4.0	6.5 ± 2.4	4.0 ± 0.2
			5.0	-1.9 ± 1.8	5.0 ± 0.1

Appendix 2

Measured *Q/I* data of the P desorption-sorption isotherms of the acid-treated tailings (AtT)

Tailings	**Mesh**	**Equilibration time**	**P concentration of the enrichment solution**	***Q***	***I***
	Ø mm		**mg L^{-1}**	**mg kg^{-1} ± SD**	**mg L^{-1} ± SD**
Acid-treated tailings (AtT)	> 0.2	24 h	0	0.1 ± 0.2	0.01 ± 0.00
			25	2305 ± 7	0.6 ± 0.4
			50	3870 ± 104	9 ± 1
			100	4590 ± 139	50 ± 1
			200	6910 ± 313	136 ± 3
			300	6953 ± 495	242 ± 5
			400	7311 ± 808	348 ± 8
			500	8887 ± 537	449 ± 5
	< 0.2		0	-0.1 ± 0.1	0.0 ± 0.0
			25	2329 ± 9	0.4 ± 0.1
			50	2461 ± 38	2 ± 0
			100	7311 ± 159	22 ± 2
			200	10879 ± 303	97 ± 3
			300	11678 ± 579	195 ± 6
			400	13070 ± 487	291 ± 5
			500	14421 ± 227	388 ± 13
Acid-treated tailings (AtT)	> 0.2	7 d	0	0.2 ± 0.1	0.00 ± 0.00
			25	2329 ± 1	0.01 ± 0.00
			50	4666 ± 34	0.6 ± 0.4
			100	8117 ± 251	21 ± 3
			200	9589 ± 313	109 ± 4
			300	9702 ± 722	203 ± 7
			400	10895 ± 754	307 ± 8
			500	9508 ± 892	410 ± 9
	< 0.2		0	0.0 ± 0.0	0.01 ± 0.00
			25	2328 ± 1	0.01 ± 0.00
			50	4721 ± 3	0.01 ± 0.00
			100	10227 ± 18	0.3 ± 0.1
			200	15211 ± 189	54 ± 2
			300	15465 ± 573	146 ± 6
			400	17110 ± 342	245 ± 3
			500	16854 ± 641	336 ± 6

Appendix 3

Measured *Q/I* data of the P desorption-sorption isotherms of the acid-base-treated tailings (ABtT)

Tailings	**Mesh**	**Equilibration time**	**P concentration of the enrichment solution**	***Q***	***I***
	ø mm		**mg L^{-1}**	**mg kg^{-1} ± SD**	**mg L^{-1} ± SD**
Acid-base-treated tailings (ABtT)	> 0.2	24 h	0	-0.5 ± 0.4	0.01 ± 0.00
			25	2320 ± 7	0.1 ± 0.0
			50	3913 ± 104	8 ± 1
			100	5572 ± 125	47 ± 1
			200	7018 ± 137	136 ± 1
			300	6650 ± 232	234 ± 2
			400	8369 ± 123	332 ± 2
			500	6964 ± 481	435 ± 5
	< 0.2		0	-1.7 ± 0.4	0.02 ± 0.00
			25	2325 ± 1	0.04 ± 0.00
			50	4712 ± 5	0.1 ± 0.0
			100	7463 ± 223	28 ± 2
			200	9643 ± 327	110 ± 3
			300	9708 ± 566	203 ± 6
			400	11417 ± 755	301 ± 8
			500	9739 ± 641	407 ± 6
Acid-base-treated tailings (ABtT)	> 0.2	7 d	0	-2.8 ± 0.6	0.03 ± 0.01
			50	4854 ± 32	2.9 ± 0.3
			100	6931 ± 67	33 ± 1
			200	8271 ± 159	121 ± 2
			300	9717 ± 289	215 ± 3
			400	10696 ± 537	307 ± 5
			500	15404 ± 501	357 ± 5
			600	-7755 ± 6527	667 ± 65
	< 0.2		0	-5.2 ± 0.2	0.05 ± 0.00
			50	5138 ± 5	0.07 ± 0.01
			100	*8183 ± n.a.	*20 ± n.a.
			200	11102 ± 194	92 ± 2
			300	13005 ± 24	184 ± 3
			400	10278 ± 2843	311 ± 28
			500	3439 ± 1797	477 ± 18
			600	-154 ± 2422	591 ± 24

*Calculation is based on two replicate samples
n.a. = SD not available

Appendix 4

Measured *Q/I* data of the Pb sorption isotherms of the untreated tailings (UtT)

Tailings	**Mesh**	**Pb concentration of the enrichment solution**	***Q***	***I***
	Ø mm	**mg L^{-1}**	**mg kg^{-1} ± SD**	**mg L^{-1} ± SD**
Untreated tailings (UtT)	> 0.2	0	0.1 ± 0.1	0.00 ± 0.00
		2.5	102 ± 7	0.03 ± 0.01
		5.0	193 ± 30	0.11 ± 0.03
		7.5	298 ± 53	0.20 ± 0.04
		10	479 ± 4	0.40 ± 0.05
		12.5	593 ± 2	0.48 ± 0.06
		15	724 ± 4	0.42 ± 0.08
		20	950 ± 7	0.53 ± 0.10
		25	1180 ± 2	0.55 ± 0.11
		30	1410 ± 3	0.41 ± 0.14
		35	1664 ± 6	0.29 ± 0.03
	< 0.2	0	0.1 ± 0.1	0.00 ± 0.00
		2.5	101 ± 8	0.00 ± 0.00
		5.0	197 ± 29	0.01 ± 0.00
		7.5	338 ± 53	0.01 ± 0.01
		10	497 ± 4	0.02 ± 0.01
		12.5	614 ± 3	0.06 ± 0.03
		15	743 ± 2	0.09 ± 0.01
		20	971 ± 5	0.03 ± 0.03
		25	1199 ± 4	0.07 ± 0.02
		30	1422 ± 7	0.12 ± 0.04
		35	1676 ± 5	0.17 ± 0.07

Appendix 5

Measured *Q/I* data of the Pb sorption isotherms for the control soil and the soil amended with the different dosages of the untreated tailings (UtT) and the acid-treated tailings (AtT).

Amendment	Mesh	Tailings dosage (g)	Pb concentration of the enrichment solution	*Q*	*I*
	Ø mm		mg L^{-1}	mg kg^{-1} ± SD	mg L^{-1} ± SD
Control		-	0	0.8 ± 1.6	0.00 ± 0.00
			50	2403 ± 44	0.2 ± 0.2
			75	3911 ± 85	0.7 ± 0.1
			100	5337 ± 122	2.9 ± 1.6
			250	9419 ± 239	113 ± 8
			500	11107 ± 528	409 ± 8
			750	11448 ± 1017	722 ± 18
			1000	10792 ± 1496	1031 ± 19
Untreated tailings (UtT)	> 0.2	5	0	0.7 ±1.5	0.00 ± 0.00
			50	2421 ± 12	0.1 ± 0.1
			75	3948 ± 91	0.3 ± 0.2
			100	5349 ± 100	1.6 ± 2.2
			250	12221 ± 239	58 ± 6
			500	14436 ± 1012	343 ± 24
			750	14383 ± 1376	665 ± 25
			1000	14077 ± 962	964 ± 20
	< 0.2	5	0	0.7 ± 1.5	0.00 ± 0.00
			50	2402 ± 32	0.2 ± 0.2
			75	3929 ± 73	0.4 ± 0.3
			100	5411 ± 129	0.8 ± 0.7
			250	14129 ± 142	16 ± 2.5
			500	18396 ± 458	261 ± 19
			750	19580 ± 938	559 ± 16
			1000	19360 ± 1033	855 ± 10
Untreated tailings (UtT)	> 0.2	10	0	0.7 ± 1.5	0.00 ± 0.00
			50	2375 ± 18	0.3 ± 0.1
			75	3852 ± 32	0.3 ± 0.2
			100	5324 ± 65	1.2 ± 0.5
			250	13001 ± 521	38 ± 6
			500	15912 ± 682	307 ± 12
			750	15983 ± 1176	625 ± 16
			1000	15506 ± 1066	929 ± 20
	< 0.2	10	0	0.7 ± 1.5	0.00 ± 0.00
			50	2358 ± 51	0.3 ± 0.3
			75	3901 ± 41	0.3 ± 0.4
			100	5336 ±140	0.5 ± 0.3
			250	14351 ±131	11 ± 2
			500	19536 ± 966	237 ± 20
			750	21069 ±1406	520 ± 26
			1000	20822 ±1316	824 ± 19

Amendment	**Mesh**	**Tailings dosage (g)**	**Pb concentration of the enrichment solution**	***Q***	***I***
	Ø mm		**mg L^{-1}**	**mg kg^{-1} ± SD**	**mg L^{-1} ± SD**
Acid-treated Tailings (AtT)	> 0.2	5	0	0.03 ± 0.04	0.01 ± 0.01
			100	5258 ± 78	2.2 ± 0.6
			250	14266 ± 109	8.2 ± 0.6
			500	28026 ± 1001	34 ± 21
			750	29395 ± 4626	313 ± 83
			1000	31376 ± 5356	598 ± 102
			1500	32280 ± 1146	1210 ± 25
			2000	31967 ± 2136	1841 ± 36
	< 0.2	5	0	0.01 ± 0.03	0.01 ± 0.01
			100	5054 ± 119	6.2 ± 0.5
			250	14434 ± 276	5.1 ± 1.9
			500	29402 ± 598	10 ± 5
			750	34728 ± 6363	209 ± 132
			1000	36969 ± 4064	489 ± 101
			1500	39457 ± 6955	1070 ± 131
			2000	38153 ± 4231	1715 ± 72
Acid-treated tailings (AtT)	> 0.2	10	0	0.05 ± 0.09	0.00 ± 0.00
			100	5156 ± 98	2.9 ± 0.5
			250	14231 ± 166	5.8 ± 0.5
			500	29305 ± 480	8.3 ± 0.6
			750	42327 ± 1736	57 ± 18
			1000	47580 ± 1962	257 ± 56
			1500	49470 ± 1099	836 ± 21
			2000	49566 ± 2382	1458 ± 26
	< 0.2	10	0	0.00 ± 0.00	0.02 ± 0.03
			100	5351 ± 280	2.6 ± 0.6
			250	14870 ± 804	2.0 ± 0.1
			500	30398 ± 1559	3.0 ± 0.2
			750	46047 ± 1747	5.5 ± 1.0
			1000	60726 ± 3311	31 ± 7
			1500	69674 ± 3869	470 ± 19
			2000	70928 ± 2766	1064 ± 25