Assessment of risks related to increasing heavy metal limits for fertilizers in Finland

2 2018

Publications of the Ministry of Agriculture and Forestry 2/2018

Assessment of risks related to increasing heavy metal limits for fertilizers in Finland

Tapio Salo, Kari Ylivainio, Riikka Keskinen, Minna Sarvi, Merja Eurola,
Marketta Rinne, Elise Ketoja, Jaakko Mannio, Johanna Suomi, Hannu Kivirinta

Ministry of Agriculture and Forestry, Helsinki 2018

Ministry of Agriculture and Forestry

ISBN: 978-952-453-976-0 (PDF)
Layout: Government Administration Unit, Publications / Erja Kankala

Helsinki 2018

Description sheet

Published by	Ministry of Agriculture and Forestry		2018
Authors	Tapio Salo, Kari Ylivainio, Riikka Keskinen, Minna Sarvi, Merja Eurola, Marketta Rinne, Elise Ketoja, Jaakko Mannio, Johanna Suomi, Hannu Kivirinta		
Title of publication	Assessment of risks related to increasing heavy metal limits for fertilizers in Finland		
Series and publication number	Publications of the Ministry of Agriculture and Forestry 2018:2		
ISBN PDF	978-952-453-976-0	**ISSN (PDF)**	1797-397X
Website address (URN)	http://urn.fi/URN:ISBN:978-952-453-976-0		
Pages	80	**Language**	English
Keywords	fertilisers,heavy metal limits, assessment of risks		

Abstract

Higher limits of metals than currently allowed in Finland are suggested in the proposal for EU regulations. In this report, the effects of increased load of Cd, Hg, Ni, Pb, Cr and As into agricultural soils of Finland are assessed.

Mass balance calculations for 100-year scenarios of metal inputs were performed to spring wheat rotation. Cd balances were also calculated for grassland, potato and carrot. Concentration in soil water, annual leaching and erosion, concentration and annual uptake in yield, soil concentration and annual balance are reported. In addition, the effect of increased cereal metal concentrations on the total dietary exposure of Finnish children was calculated.

In 100-year time scale, the current metal inputs would lead to a negative (As, Cr and Ni) or at most slightly positive balance (Cd, Pb, Hg), whereas the current maximum level and that of the EU proposal generate positive balances. The inputs allowed in the EU proposal would lead to the following increases in environmental loading and metal concentrations in crops from the level of current realization: As over 13 %, Cr 2 %, Pb 30 %, Hg 64 %, Ni 5.5% and Cd 17–44 % depending on the crop rotation. The increase in total dietary exposure of 3-year-old Finnish children at the age group median level would be 2–5 % for As, 12–13 % for Cd, 9 % for Pb and at least 2 % for Hg.

The Finnish environment is vulnerable to metal pollution and any increase in the environmental loading would be negative. Particularly for Cd there is no margin of safety. For the Finnish population, the dietary increases would be harmful as for As, Cd, Ni and Pb even the current exposure levels should be reduced.

Publisher	Ministry of Agriculture and Forestry
Distributed by/ publication sales	Distribution by: julkaisut.valtioneuvosto.fi Publication sales: julkaisutilaukset.valtioneuvosto.fi

Presentationsblad

Utgivare	Jord- och skogsbruksministeriet		2018
Författare	Tapio Salo, Kari Ylivainio, Riikka Keskinen, Minna Sarvi, Merja Eurola, Marketta Rinne, Elise Ketoja, Jaakko Mannio, Johanna Suomi, Hannu Kivirinta		
Publikationens titel	Riskbedömning av förhöjda gränsvärden för tungmetaller i gödselmedel i Finland		
Publikationsseriens namn och nummer	Jord- och skogsbruksministeriets publikationer 2018:2		
ISBN PDF	978-952-453-976-0	**ISSN PDF**	1797-397X
URN-adress	http://urn.fi/URN:ISBN:978-952-453-976-0		
Sidantal	80	**Språk**	engelska
Nyckelord	gödselmedel, gränsvärden för tungmetaller, riskbedömning		

Referat

I förslaget till EU-förordning om gödselmedel är gränsvärdena för tungmetaller större än vad våra gällande författningar tillåter. I denna rapport analyseras effekterna av halten av Cd, Hg, Ni, Pb, Cr och As i finsk odlingsmark.

Beräkningen av massbalans för ökande belastning hos vårvete i växtföljd togs fram för en period på hundra år. Kadmiumbalansen beräknades också för vall, potatis och morot i växtföljd. Som resultat föreslås: halten i jordvatten, mängden som årligen försvinner med avrinningsvatten och genom erosion, halten och totalmängden i skörd, halten i mark samt en årlig balans. Vidare undersöktes hur den ökande halten metaller i spannmål inverkar på finska barns exponering.

Om belastningen av metaller i åkermark hålls på dagens nivå leder detta på 100 års sikt till negativa (As, Cr och Ni) eller en aning positiva (Cd, Pb, Hg) balanser. En belastning enligt de gränsvärden som i dag är tillåtna i Finland och de gränsvärden som föreslås i EU:s förordning får metallbalanserna att gå uppåt. Jämfört med nuläget skulle de gränsvärden som föreslås i EU-förordningen öka odlingsmarkens belastning på miljön och halten i skörden enligt följande: As 13 procent, Cr 2 procent, Pb 30 procent, Hg 64 procent, Ni 5,5 procent och Cd 17–44 procent beroende på växtföljden. Den totala exponeringen hos treåriga barn via maten skulle öka på mediannivån för åldersgruppen: As 2–5 procent, Cd 12–13 procent, Pb 9 procent och Hg minst 2 procent.

Vår miljö är känslig för metallbelastningen. Det finns ingen säkerhetsmarginal, i synnerhet när det gäller Cd. En större exponering särskilt för As, Cd och Pb skadar folkhälsan eftersom exponeringen borde redan nu minskas..

Förläggare	Jord- och skogsbruksministeriet
Distribution/ Beställningar	Elektronisk version: julkaisut.valtioneuvosto.fi Beställningar: julkaisutilaukset.valtioneuvosto.fi

Kuvailulehti

Julkaisija	Maa- ja metsätalousministeriö		2018
Tekijät	Tapio Salo, Kari Ylivainio, Riikka Keskinen, Minna Sarvi, Merja Eurola, Marketta Rinne, Elise Ketoja, Jaakko Mannio, Johanna Suomi, Hannu Kivirinta		
Julkaisun nimi	Riskinarvio lannoitteiden kasvavista raskasmetalliraja-arvoista Suomessa		
Julkaisusarjan nimi ja numero	Maa- ja metsätalousministeriön julkaisuja 2018:2		
ISBN PDF	978-952-453-976-0	**ISSN PDF**	1797-397X
URN-osoite	http://urn.fi/URN:ISBN:978-952-453-976-0		
Sivumäärä	80	**Kieli**	englanti
Asiasanat	lannoitteet, raskasmetalliraja-arvot, riskinarvio		

Tiivistelmä

EU:n lannoiteasetusehdotuksessa metalleille esitetään suurempia raja-arvoja kuin Suomessa sallitaan. Tässä raportissa arvioidaan kasvavan Cd-, Hg-, Ni-, Pb-, Cr- ja As-pitoisuuden vaikutusta suomalaisessa viljelymaassa.

Massataselaskelmat kasvavilla kuormitustasoilla laadittiin sadan vuoden ajalle viljelykiertona kevätvehnä. Kadmiumtaseet laskettiin myös nurmi-, peruna- ja porkkanakierrolle. Tuloksena esitetään: pitoisuus maavedessä, vuotuinen poistuma valumavesissä ja eroosioaineksessa, pitoisuus ja kokonaismäärä sadossa sekä pitoisuus maassa ja vuosittainen tase. Lisäksi määritettiin viljojen metallipitoisuuden kasvun vaikutus suomalaisten lasten altistukseen.

Peltomaan metallikuormituksen pysyminen nykytasolla johtaisi sadassa vuodessa negatiivisiin (As, Cr ja Ni) tai hieman positiivisiin (Cd, Pb, Hg) taseisiin. Suomessa sallittujen raja-arvojen ja EU:n esityksen raja-arvojen mukainen kuormitus kääntäisi metallitaseet nousuun. EU:n lannoiteasetusesityksen mukaisilla raja-arvoilla viljelymaan kuormitus ympäristöön ja sadon pitoisuudet kasvaisivat nykytason mukaiseen tilanteeseen verrattuna seuraavasti: As 13 %, Cr 2 %, Pb 30 %, Hg 64 %, Ni 5,5 % ja Cd viljelykierrosta riippuen 17– 44 %. Kolmevuotiaiden lasten ravinnon kautta saatava kokonaisaltistus ikäryhmän mediaanitasolla kasvaisi: As 2–5 %, Cd 12–13 %, Pb 9 % ja Hg vähintään 2 %.

Suomen ympäristö on herkkä metallikuormitukselle. Erityisesti Cd osalta turvavaraa ei ole. Väestön terveydelle altistuksen kasvusta olisi haittaa etenkin As, Cd, Ni ja Pb osalta, sillä jo nykytasolla altistusta tulisi vähentää.

Kustantaja	Maa- ja metsätalousministeriö
Julkaisun jakaja/myynti	Sähköinen versio: julkaisut.valtioneuvosto.fi Julkaisumyynti: julkaisutilaukset.valtioneuvosto.fi

Table of contents

Foreword

New regulations for fertilizers, liming materials, soil improvers, growing media and plant biostimulants are currently in preparation at the European Commission. The risks related to hygiene and contaminants in these substances are being discussed in an ad hoc working group. Proposal for a regulation of the European Parliament and of the Council laying down rules on the making available on the market of CE marked fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 was announced in March 2016. In the proposal, limits of acceptable heavy metal concentrations in inorganic fertilizers are included.

In this report, the effects of increased load of cadmium (Cd), mercury (Hg), nickel (Ni), lead (Pb), chromium (Cr) and arsenic (As) from fertilizers into agricultural soils of Finland are assessed. The report contains 1) short introductions into the behavior and occurrence of the above-mentioned elements in the Finnish environment, 2) sources of the elements into agricultural soil and mass balance calculations for 100-year scenarios of heavy metal inputs to cereal cropping systems at different levels and 3) assessment of the risks to the environment and human health by the increased exposure to heavy metals. In addition, mass balance calculations for copper (Cu) and zinc (Zn) are given as an appendix. The chapter on Cd builds on the previous report: Cadmium in fertilizers, Risks to human health and the environment (Study report for the Finnish Ministry of Agriculture and Forestry, October 2000).

The work has been commissioned by the Finnish Ministry of Agriculture and Forestry. The working group consisted of the following members:

Natural Resources Institute Finland (Luke)

Principal Research Scientist Tapio Salo: Mass balance calculations
Senior Scientist Kari Ylivainio: Soil chemistry, plant heavy metal uptake
Senior Scientist Riikka Keskinen: Soil chemistry, soil heavy metal content
Researcher Minna Sarvi: Soil chemistry, behavior of heavy metals in soil
Researcher Merja Eurola: Heavy metals in plants and food supplies
Professor Marketta Rinne: Heavy metals in animal production
Biometrician Elise Ketoja: Heavy metal trends in soil

Finnish Environment Institute

Leading Researcher Jaakko Mannio: Assessment of environmental effects

Finnish Food Safety Authority Evira

Senior Researcher Johanna Suomi: Assessment of effects on human health and dietary exposure calculations

National Institute for Health and Welfare

Chief Researcher Hannu Kiviranta: Assessment of effects on human health

1 Introduction

The bedrock of Finland is at least 1,000 million years old but the current soils are young (less than 150,000 years old, mostly an order of magnitude less than that) due to glacial erosion (Koljonen 1992). Consequently, the time of weathering has been short and the soils are rather undeveloped (Lilja et al. 2006). Mineral soils predominate, till being the most common, though clay soils occur in the most important agricultural areas of south and west. Due to the cool climate of Finland, organic matter tends to accumulate more rapidly than decompose, if not disturbed by soil turning. Organic soils (mull and peat) are thus rather common and also mineral soils contain typically around 4% organic carbon. However, recent studies on agricultural soils show a decreasing trend in the soil carbon concentration (Heikkinen et al. 2013). In addition to the richness of organic matter, the slight acidity of Finnish soils affects the behavior and consequently the hazardous effect of heavy metals. The pH of agricultural (limed) mineral soils is typically around 6 and that of organic soils 5.5 (Keskinen et al. 2016). In European level, the agricultural soils of Finland are found to be high in total C, and low in pH, As, Cd, Ni and Pb (Reimann et al. 2014a,b).

The mean annual precipitation in Finland (550 – 750 mm) exceeds evaporation, wherefore elements are leached from soil to waterways. Surface waters are abundant, covering almost 10% of Finland's land area, but typically shallow, which makes them particularly vulnerable to pollution.

The risk of heavy metal accumulation in agricultural soils has been related to the use of mineral fertilizers, municipal wastes and deposition close to industrial activities (Yläranta 1996). Regulation of field applications has been implemented in Fertilizer act (232/1993) followed by Fertilizer product act (539/2006) and in Government decision on the use of sewage sludge in agriculture (Vnp 282/1994) followed by the Decree of the Ministry of Agriculture and Forestry on Fertiliser Products (24/11, 11/12, 12/12). Environmental regulation (86/2000 followed by 527/2014) has set guidelines for air emissions to keep deposition of heavy metals as low as possible.

2 Arsenic (As)

2.1 Occurrence and behavior in the environment

Arsenic is a toxic and carsinogenic element (Koljonen et al. 1992, Reimann et al. 2014a). It has one naturally occurring isotope (^{75}As) and many different oxidation states: -3, 0, +3 and +5 of which As^0 and As^{3+} appear in reducing environments (Kabata-Pendias 2010, Reimann et al. 2014a). In soil and bedrock, As forms many compounds like arsenides, sulphides, oxides, arsenates and arsenites; arsenopyrite (FeAsS) and other sulphides being the most common forms (Koljonen et al. 1992, Reimann et al. 2014a). In soil, As is originated largely from soil parent material but there are also many anthropogenic sources, e.g. industrial activities, wood preservation, pesticides, fertilizers and feed preparations (Matschullat 2000, Hakala and Hallikainen 2004, Mäkelä-Kurtto et al. 2007a, Nziguheba and Smolders 2008, Kabata-Pendias 2010). In Finland, As emissions to the air have decreased significantly (Kyllönen et al. 2009, Finnish Environment institute 2014). In 1990 emission was 33 t, whereas in 2012 it was 2.9 t (Finnish Environment Institute 2014). In 2012, the main As sources were energy production and industrial processes (Finnish Environment Institute 2014).

Globally, the mean As concentration in soils is estimated to be 6.83 mg/kg, background values ranging in different soil groups from <0.1 to 67 mg/kg (Kabata-Pendias 2010). In Finland, As concentrations (aqua regia extraction) in cultivated soils (plough layer) lie between 0.32 and 18 mg/kg dry matter (DM), the average concentration and median being 4.13 and 2.76 mg/kg DM (n=338), respectively (Mäkelä-Kurtto et al. 2007a). In the study of Mäkelä-Kurtto et al. (2007a), the majority (>95 %) of the sampled soils had an As concentration below 10 mg/kg DM. According to Reimann et al. (2014a) the As concentrations in Finnish agricultural and grazing land are the lowest in Europe, although the variation is largest in Finland. At the continental level, As concentrations (aqua regia extraction) in European agricultural (0 – 20 cm) and grazing land (0 – 10 cm) vary between <0.1 – 666 mg/kg (n=2212) and <0.1 – 292 mg/kg (n=2119) medians being 5.7 and 5.8

mg/kg, respectively (Tarvainen et al. 2013). Concentrations in agricultural soils were 3 times higher in the southern Europe (median 8 mg/kg) than in the northern Europe (median 2.5 mg/kg).

In general, As concentrations are higher in fine-textured than in coarse-textured soils (Tarvainen and Kuusisto 1999, Tarvainen 2004, Mäkelä-Kurtto et al. 2007a). According to Mäkelä-Kurtto et al. (2007a) the mean As concentration in coarse-textured mineral soils of Finland was 3.61 mg/kg DM (n=219), whereas in clay soils it was 7.51 mg/kg DM (n=51). In organic soils the corresponding value was 3.30 mg/kg DM (n=68). The concentrations of As from natural origin tend to increase with depth (Backman et al. 2006). Mäkelä-Kurtto et al. (2007a) found that the As concentrations in soils of Finland were slightly higher in topsoil than deeper in the soil profile, which indicates As inputs to the soil. Due to regional variation in parent material, soil types and anthropogenic sources, there is regional variation in As concentrations. In Finland, higher As concentrations in glacial till are found in Pirkanmaa, Häme and Ilomantsi region and also in Kittilä (Koljonen et al. 1992, Backman et al. 2006, Hatakka et al. 2010). However, As concentrations in the cultivated soils in Pirkanmaa region don’t differ from those in other parts of Finland (Mäkelä-Kurtto et al. 2007a).In the southern part of Finland, As concentrations in the plough layer of cultivated soils are on average higher than in eastern and northern Finland due to the abundance of clay soils in southern part of Finland and coarse-textured mineral soils in other parts of Finland (Mäkelä-Kurtto et al. 2007a).

In soil solution, the distribution of different As species is mainly dependent on pH and oxidation/reduction state (Sadiq 1997). In oxidizing environments, soluble As occurs as arsenates ($H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}) and in slightly reducing environments as H_3AsO_3 or dissociated as arsenites ($H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-}) (e.g. Sadiq 1997, Heikkinen 2000). According to Kabata-Pendias (2010) also cations As^{3+} and As^{5+} can occur. In addition to the inorganic forms of As, organic As compounds of both natural and anthropogenic origin can be found in the soil environment (Huang et al. 2011). However, the concentrations of organic As are usually low in uncontaminated soils (Huang et al. 2011).

In general, As concentrations in soil solution are dependent on different sorption and microbiological reactions that are controlled by the chemical circumstances in the soil (pH, oxidation/reduction state, amount of oxides, hydroxides, clay and organic matter) (e.g. Sadiq 1997, Kabata-Pendias 2010, Huang et al. 2011). Furthermore, As speciation has an influence on its reactions and mobility in the soil environment (e.g. Dixit and Hering 2003). The chemical behavior of arsenate resembles that of phosphate and thus it chemisorbs to Fe and Al oxides, noncrystalline aluminosilicates and layer silicate clays (McBride 1994, Kabata-Pendias 2010). According to Dixit and Hering (2003) sorption of arsenate onto amorphous iron oxide and goethite is more favorable than sorption of arsenite when pH is below 5 – 6. When pH is over 7 – 8, sorption of arsenite is more favorable and arsenate sorption decreases. In general it can be said that As is more mobile in neutral and alkaline than in acidic environments (McBride 1994). In addition, presence of competing ions (e.g. phosphate) can affect the sorption and mobility of As (e.g. Manning and Goldberg 1996, Jain and Loeppert 2000, Dixit and Hering 2003).

In reduced conditions, As combined with Fe and Mn oxides can be liberated back to soil solution by dissolution of oxides, after which desorbed arsenate is reduced to arsenite (e.g. McBride 1994). Arsenites can then precipitate as sulfides (Sadiq 1997). Inorganic arsenic can also be methylated by microorganisms (Huang et al. 2011). Under anaerobic conditions highly toxic, volatile organo-arsine compounds such as mono-, di- and trimethylarsine and inorganic gaseous arsine (AsH_3) can be formed.

Arsenic concentrations in bedrock and soil reflect to the concentrations in surface waters and groundwaters. Typical As concentrations in Finnish stream waters have been reported to be 0.06 – 1.6 µg/l (1157 streams), concentrations being higher in the southern part of Finland than in north (Lahermo et al. 1996). Concentrations in lake waters have been reported to be at the same order of magnitude (Tarvainen and Mannio 2004). In general, As concentrations are low also in drinking water, median concentrations varying between 0.1 – 1.7 µg/l, but in some cases the safe concentration limit (10 µg/l) set by the Ministry of Social Affairs and Health (STM 2000, 2001) is exceeded (Ahonen et al. 2008). According to Lahermo et al. (2002) As concentrations in groundwaters in Finland vary between <0.05 and 23.6 µg/l medians for dug and drilled wells being almost the same and mean values 0.35 µg/l and 1.00 µg/l, respectively. Thus, in general, the concentrations are low but higher values are found more often in drilled wells. In drilled bedrock wells (n=263), 3% of the concentrations exceeded the safe concentration limit (10 µg/l). Higher concentrations are found in the region of Pirkanmaa and Kittilä (Juntunen et al. 2004, Tanskanen et al. 2004).

Soluble and bioavailable forms of As are more relevant for plant uptake than the total concentrations in soil. Thus the same factors (e.g. pH, oxidation/reduction state, oxides) that affect the sorption of As also influence plant uptake. Therefore, the bioavailability of arsenate is usually low because of its strong tendency to be sorbed by oxides in soil (Zhao et al. 2010). In general, the As concentrations in plants grown in uncontaminated soils are low and plants avoid the uptake of As (Reimann et al. 2009). According to the review by Mahimairaja et al. (2005) accumulation of As in the edible parts of plants is in most cases low due to low bioavailability of As in soils, restricted uptake by plant roots, limited translocation of As from roots to shoots, and phytotoxicity at relatively low As levels of plant tissues. Plants grown nearby an anthropogenic As source react differently to the increased levels of airborne As (Reimann et al. 2009). According to the review by Zhao et al. (2010) plants can be divided into three classes depending on their ability to accumulate As. Plants with low As transfer factor (TF) from soil to plant are called as excluders due to their restricted uptake and translocation of As from roots to shoots. On the other hand, some plants are so called hyperaccumulators (12 species identified so far) that have the ability to accumulate As up to ca. 2% content in the above-ground parts. Between these two classes are plants with intermediate ability to take up As. In addition to plant species and cultivars, other factors like climate and cultivation practices have an effect on the As uptake (reviewed by Mäkelä-Kurtto et al. 2007a).

Arsenic is taken up by plants passively with water flow from soil (Kabata-Pendias and Mukherjee 2007, Kabata-Pendias 2010). According to Zhao et al. (2010) plant roots take up arsenate as dissociated oxyanions ($H_2AsO_4^-$, $HAsO_4^{2-}$) via phosphate transporters, and arsenite mainly as the neutral molecule ($As(OH)_3$). According to the review of Kabata-Pendias (2010), high As concentrations can be found from old leaves and roots. In terrestrial plants As occurs mainly in inorganic form, predominantly as arsenite (Zhao et al. 2010). Symptoms of As toxicity are growth reduction, leaf wilting, violet coloration, root discoloration and cell plasmolysis (Kabata-Pendias 2010).

2.2 Environmental exposure to As

Mass balance for As in Finnish agricultural fields has been calculated by Mäkelä-Kurtto et al. (2007c). In their study, data was collected from different sources and As concentrations were measured from soil, crop plants and manure. They calculated mass balances for five crop farms in southwestern Finland and for five dairy farms in Ostrobothnia. Calculation was done by RAKAS-model developed by the authors and by an European ARAMIS-model.

In this assessment, mass balance calculations were done by the methodology used with cadmium (see 3.2 Environmental exposure to Cd). Parameters used in the calculations are listed in Table 1. Soil total concentration was based on aqua regia extractions by Mäkelä-Kurtto et al. (2007b). As input was summed from fertilization, deposition and liming. Annual liming demand was set to 400 kg/ha (http://www.farmit.net/kasvinviljely/kalkitus-ja-maanparannus/kalkitussanastoa) and As concentration in liming materials was taken from Mäkelä-Kurtto et al. (2007c). Deposition was set to 0.96 g As/ha (Mäkelä-Kurtto et al. 2007c). Fertilizer rate was based on the current recommended P rate for spring wheat, 10 P kg/ha. According to the average fertilizer P concentrations reported in Mäkelä-Kurtto et al. (2007c), a fertilizer rate of 310 kg/ha leads to an input of 10 P kg/ha.

1. The current dose of As from the commonly used mineral fertilizers in Finland was calculated according to their As concentrations (0.7 mg/kg DM) reported in Mäkelä-Kurtto et al. (2007c). Arsenic concentration against NP content of fertilizers averaged 18.5 mg/kg P and 3.4 mg/kg N.

2. The current maximum dose of As was calculated according to the maximum allowed As concentration in fertilizers based on Finnish law for fertilizer products (25 mg /kg DM).
3. Third possible dose of As was calculated according to the EU legislation proposal, where maximum 60 mg/kg DM is accepted for mineral fertilizers.
4. Fourth As concentration used in the calculations was 40 mg/kg DM that was suggested in the modified EU proposal on 6.9.2016.

The output of As was summed from uptake in harvested yield and losses via leaching and eroded soil material. Calculation was done for 100 years, using spring wheat as the crop. Plant uptake in harvested part was based on soil-plant transfer coefficient (SPTC):

$$SPTC = \frac{Cplant}{Csoil}$$

$$Plant\ uptake = Yield \times Cplant$$

Where Cplant is the total As concentration in harvested plant part per dry matter and Csoil is the aqua regia extractable As concentration per dry matter in 0 – 20 cm top layer of the soil. Yield level was set to the average yield during 2010 – 2014. Transfer coefficient from soil to plant was calculated from the results reported by Mäkelä-Kurtto et al. (2007a).

Leaching was based on distribution coefficient (Kd), which shows the relationship between the total (Csoil, aqua regia extractable) concentration in soil against that in the soil pore water (Cwater). Soil properties did not affect the calculation directly, but Kd-value was selected considering the soil to be clay. Kd-values from sandy soils had usually considerably lower values.

$$Kd = \frac{Csoil}{Cwater}$$

$$Leaching = Cwater \times annual\ runoff$$

Annual runoff was set to 200 mm that was used in the previous Cd mass balance calculations (Finnish Environment Institute 2000) and annual erosion based on the same source to 500 kg/ha. The amount of eroded element was calculated:

$$Erosion = Csoil \times annual\ soil\ erosion$$

Table 1. Parameters used in the mass balance calculations of As.

Model parameters		Source
Soil concentration, mg As/kg	4.1	Mäkelä-Kurtto et al. 2007b, Table 1
Deposition, g As/ha/a	0.96	Mäkelä-Kurtto et al. 2007c, Table 40
Liming kg/ha/a	400	Recommended liming rate
Concentration in liming materials, mg As/kg	2.8	Mäkelä-Kurtto et al. 2007c, Table 17
Fertilizer rate, kg/ha	310	10 kg P/ha and 3.2% P concentration
Transfer function, plant/soil	0.001	Median from Mäkelä-Kurtto et al. 2007a, Tables 39 and 58
Yield kg/ha, 14% moisture	3750	Finnish agricultural statistics 2010-2014
Kd	1200	Sheppard et al. 2011, Table 3-3.
Annual runoff, m^3/ha	2000	Finnish Environment Institute 2000
Annual erosion, kg/ha	500	Finnish Environment Institute 2000

After running the model calculations for 100 years using a code programmed by SAS statistical package, following output values were reported: As concentration in soil water, annual As leaching and erosion, As concentration in yield and annual As content in yield, soil As concentration and annual As balance (Table 2).

Table 2. The effect of different As concentrations in mineral fertilizer on As concentrations in soil water, grain yield and soil, and on leaching, erosion, yield uptake and annual balance of As for 100-years mass balance calculations.

As mg/ kg fert. DM	Year	Soil water µg/l	Leached g/ha/a	Eroded g/ha/a	Yield µg/kg DM	Yield uptake g/ha/a	Soil mg/kg	Annual balance g/ha
0.7	1	3.42	6.83	2.05	32.80	0.11	4.10	-6.72
	100	3.15	6.31	1.89	30.28	0.10	3.78	-6.03
25	1	3.42	6.84	2.05	32.83	0.11	4.10	0.81
	100	3.45	6.90	2.07	33.14	0.11	4.14	0.73
40	1	3.42	6.84	2.05	32.85	0.11	4.10	5.45
	100	3.63	7.27	2.18	34.89	0.11	4.36	4.89
60	1	3.42	6.85	2.05	32.87	0.11	4.11	11.63
	100	3.88	7.76	2.33	37.24	0.12	4.65	10.43

In the 100-year time scale, the current realization of As inputs would lead to a negative As balance and consequently to a decreasing trend in the amounts of As leached, eroded and taken up by the crop (Table 2). All the other scenarios with higher As inputs generate a positive As balance. Using the current maximum level of As input (25 mg/kg fertilizer) the environmental loading (As leached and eroded) and As concentrations in crop yields would increase 1% from the level of the current realization (year 1). With the As inputs allowed in the modified EU proposal, the corresponding increases would be 6% and if applying the inputs of the EU proposal, over 13%.

2.3 Risk assessment on As at increased levels of exposure

The toxicity of arsenic depends on its chemical form. Organic As compounds are generally less toxic than inorganic ones. Of the organic As compounds, arsenobetaine is considered fairly nontoxic, but monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) are toxic to humans. Inorganic As(III) and As(V) species are generally toxic, and the As(III) species are more toxic than the As(V) ones. IARC has classified inorganic arsenic as Group I carcinogen, i.e., it is carcinogenic to humans, and MMA as well as DMA have also been found to cause DNA damage making them Group II carcinogens (IARC 2012). As compounds are not mutagenic nor do they react directly with DNA; instead their damaging effect is based on oxidative damages to the DNA. They may also increase the mutagenicity of other stressors such as UV light, and MMA and DMA are worse than inorganic As species in this regard (IARC 2012).

There is no tolerable daily intake limit set for As, but benchmark dose lower confidence limits (BMDL) have been presented by EFSA and by the JECFA for inorganic As. In 2009, EFSA presented a $BMDL_{01}$ value range of 0.3 to 8 µg/kg body weight/day on the basis of lung, skin and bladder cancer risk as well as skin lesions; lowest values were estimated for lung cancer risk (EFSA 2009a). In 2011, JECFA estimated a $BMDL_{0.5}$ value of 3.0 µg/kg body weight/day on the basis of lung cancer risk (JECFA 2011).

Ecotoxicity of As has been well reviewed in the risk assessment by Sorvari et al. (2007). They summarize that plants in general are more sensitive to As than animals, and phytotoxic effects can be expected at soil concentrations of 5 – 20 mg As/kg. As is known to be toxic to most microorganisms and earthworms, whereas chronic toxicity to birds and mammals varies from harmful to very toxic. In water ecosystems, susceptibility to As varies greatly among species, the most sensitive ones suffering already at As concentrations below 10 µg/l. The guideline values based on ecological risks for As in Finnish soils are 5 mg/kg DM (benchmark/background concentration), 50 mg/kg DM (lower guideline value) and 100 mg/kg DM (upper guideline value). In aquatic ecosystems, no national guideline values for As exist.

2.3.1 Estimates of dietary intake and its sources

In 2014, EFSA estimated the dietary As intake of consumers in European countries based on national consumption data and concentration data collected from all EU countries, mainly from Central Europe. Most of the concentration data was given as total As, and the portion of inorganic As was calculated by EFSA using fixed percentages of total As. The concentration data contained results below the limit of detection (LOD), and the following results are middle bound estimates, where values below the LOD were calculated as 50% of LOD. The mean dietary exposure in Finland was estimated by EFSA to be 0.66 µg/kg body weight (bw)/day for toddlers, 0.54 µg/kg bw/day for older children and 0.20 µg/kg bw/day for adults. High dietary exposure, i.e., 95th percentile, was estimated to be 1.42, 0.83 and 0.32 µg/kg bw/day for toddlers, other children and adults, respectively. These estimates were mainly at the European median or less. The exposure of Finnish children at age group mean level and adults with high exposure exceeded the lowest BMDL determined for increased cancer incidence linked to inorganic arsenic, 0.3 µg/kg bw/day.

A national risk assessment (Suomi et al. 2015) determined the dietary exposure of Finnish children of 1, 3 and 6 years, based on national concentration data and individual consumption data of children. High exposure (95th percentile, middle bound estimate) was estimated to be 0.96 µg/kg bw/day for 1-year-olds, mostly corresponding with "toddlers" of EFSA estimate, and 0.50 and 0.41 µg/kg bw/day for 3-year-olds and 6-year-olds, respectively. The lowest BMDL of inorganic arsenic was exceeded by 79 % of the 1-year-olds, 43 % of 3-year-olds and 29 % of the 6-year-olds. The exposure to total arsenic at 95th percentile was 2.76, 1.92 and 1.83 µg/kg bw/day for children aged 1, 3 and 6 years, respectively. The main sources for total arsenic were fish-based foods (where the As was mainly as nontoxic arsenobetaine) and rice.

According to national concentration data, rice and other grain-based products contributed two thirds of the total exposure to inorganic As. In contrast to the EFSA results, where milk and drinking water were also significant sources of dietary exposure, in the national study the contribution of drinking water was minimal (2 %) and the contribution of milk and dairy products was 6% or less of the total exposure.

Effect of change in the As concentrations during 100 years

The effect on the total dietary exposure of Finnish children was estimated on the assumption that only the concentration in cereals would change whereas all other sources of exposure, as well as consumption habits of the children, would remain unchanged. Comparison was made with the total dietary exposure (including exposure from drinking water) of 3-year-old Finnish children (calculated in Suomi et al. 2015).

The current realization of As inputs over 100 years (leading to an 8 % decrease in the As concentration of cereal grains) would lead to a decrease of total exposure by 3% at the age group median level and by 2% at the 95th percentile of exposure, corresponding to the high intake group. In comparison, the concentration increases of 6% (EU proposal modified) and 14 % (EU proposal) would lead to an increase of total As exposure by 2–5 % at age group median level and by 2–4 % for the 95th percentile, corresponding to the high intake group.

An increase in the As content of grass would also increase the levels in meat and milk to a lesser degree, so the true increase, assuming unchanged food consumption behavior, would be higher. If exposure exceeds the BMDL daily throughout the life, the risk to get cancer during lifetime increases by 1% compared with those with lower/no exposure.

Even though the increased loading of As would increase the soil As content, the concentrations remain far from the guideline values indicating no significant ecological risks. Similarly, the surface water As concentrations in Finland are currently very low and a slight increase would probably not lead to significant deterioration of the aquatic life. However, it must be kept in mind that some species are very sensitive to As and a thorough risk assessment on different environments would be in order.

2.3.2 Estimated maximum acceptable annual load of As to a field hectare in Finland

In estimating the maximum acceptable load of a harmful element, degradation of the soil by accumulation of the element, degradation of the environment by increased loading of the element via leaching and erosion, and impacts on human health via increased dietary exposure to the element need to be considered. Overall, any increases in these values can be regarded negative. For As, the model calculations showed that the current maximum limit of As in fertilizers in Finland (25 As mg/kg) is rather well set. With the annual As input of 9 g per ha from mineral fertilizers, liming and deposition, the increases (1 %) in the output values from the level of current realization are marginal.

3 Cadmium (Cd)

3.1 Occurrence and behavior in the environment

3.1.1 The forms and amounts of Cd in soil

Cd is thought to be one of the most ecotoxic metals that accumulates in some plants and aquatic biota (Kabata-Pendias 2010, Reimann et al. 2014b). In the environment, it occurs in the oxidation state of +2 and it has eight naturally occurring isotopes of which ^{114}Cd, ^{112}Cd, ^{111}Cd, ^{110}Cd and ^{113}Cd are the most common ones (Reimann et al. 2014b). In soils, Cd is originated either from soil parent material or anthropogenic sources such as coal combustion, metal smelting (especially Zn smelters), iron and steel milling, electroplating, battery, paint, ink and plastic manufacture, waste incinerators, fertilizers, sewage sludge and car traffic (Kabata-Pendias 2010, Reimann et al. 2014b). In Finland, Cd emissions to the air have decreased significantly. In 1990, emission was 6.3 t, whereas in 2012 it was 1.3 t, the main sources being energy production and industrial processes (Finnish Environment Institute 2014). Cd containing minerals are e.g. greenockite (CdS), octavite ($CdCO_3$) and monteponite (CdO) (Kabata-Pendias 2010, Reimann et al. 2014b). It can also occur in trace amounts in mica and amphibole and it can be incorporated into the sphlerite (ZnS) replacing 0.5–1.5 % of the Zn (Reimann et al. 2014b). According to Reimann et al. (2014b), the highest values are in shale and schist (0.25 mg/kg), especially black shale and coal (1 mg/kg).

Globally, the average soil Cd concentration is estimated to be 0.41 mg/kg, mean background values ranging between 0.2 and 1.1 mg/kg (Kabata-Pendias 2010). However, Cd contents in soils depend on various factors and according to Kabata-Pendias (2010), the main factors controlling the distribution of Cd in soils are in the descending order Fe and Mn content, base saturation, clay fraction (<0.002 mm), soil organic matter content, cation exchange capacity and soil pH. In uncontaminated sandy and loamy soils, Cd content can vary from 0.01 to 0.3 mg/kg and from 0.2 to 0.8 mg/kg, respectively (Kabata-Pendias 2010). According to Mäkelä-Kurtto et al. (2007b) Cd concentrations (aqua regia extraction) in Finnish cultivated soils (plough layer, n=338) are in average 0.183 mg/kg DM. The concentrations varied between 0.016 and 0.748 mg/kg DM while the median was 0.153 mg/kg DM. The concentrations differed between soil types and regions. Organic soils (n=68) contained more Cd than clay soils (n=51) and coarse textured mineral soils (n=219), mean concentrations being 0.298, 0.222 and 0.138 mg/kg DM, respectively. Also many other Finnish studies have shown corresponding variation in Cd contents between different soil types (e.g. Hatakka et al. 2007, Mäntylahti and Laakso 2002). Cd concentrations also vary regionally (e.g. Hatakka et al. 2007, Mäkelä-Kurtto et al. 2007b). According to Mäkelä-Kurtto et al. (2007b) Cd concentrations were descending towards the northern part of Finland due to the abundance of industry and traffic in southern Finland and differences in dominant soil types between southern and northern Finland. The same trend in Cd concentrations in Finnish arable soils between different soil types and regions were observed by Tarvainen and Kuusisto (1999). They also observed that concentrations were higher in topsoils (0 – 25 cm) than in subsoils (50 – 75 cm) due to the use of Cd containing P-fertilizers. According to Reimann et al. (2014b) Cd concentrations (aqua regia extraction) in Finnish agricultural soils are at the same level with other Nordic countries. In general, Cd concentrations are significantly higher in the southern Europe (0.061 mg/kg) than in northern Europe (0.043 mg/kg) (Reimann et al. 2014b). At the continental level, Cd concentrations vary between <0.01 and 7.5 mg/kg (Reimann et al. 2014b). The concentrations are slightly higher in grazing land (0 – 10 cm, median 0.20 mg/kg, n=2024) than in arable soils (0 – 20 cm, median 0.18 mg/kg, n=2108), perhaps due to higher organic matter content in grazing land (Reimann et al. 2014b).

From an environmental and health risk point of view, soluble and bioavailable forms of Cd are more relevant than the total concentrations. In soil solution, Cd can occur as various species and its concentrations vary depending on soil properties and reactions as well as the method used for obtaining the solution. Kabata-Pendias (2010) reviewed, that Cd can occur in soil solution as inorganic cationic (Cd^{2+}, $CdCl^{+}$, $CdOH^{+}$, $CdHCO_3^{+}$, $CdHS^{+}$) and anionic ($CdCl_3^{-}$, $Cd(OH)_3^{-}$, $Cd(OH)_4^{2-}$, $Cd(HS)_4^{2-}$) species, as $CdSO_4$ and in organic complexes. In Finland, Mäkelä-Kurtto et al. (2003) estimated mean soil water Cd concentrations in cultivated soils to be 0.093 µg/l (n=338), the concentrations being highest in organic soils (0.183 µg/l, n=68). In clay (n=51) and coarse-textured (n=219) mineral soils, the concentrations were 0.090 and 0.066 µg/l, respectively. In comparison, corresponding values in Norway used in their risk characterization range between 0.021–2.087 µg/l (Amundsen et al. 2000).

Bioavailability and ecotoxicity of Cd is dependent on its reactions (e.g. adsorption, precipitation) in soils. Distribution of Cd between soil and soil solution depends on many factors like soil characteristics (e.g. organic matter, clay and oxide contents, pH), total soil Cd concentration and concentrations of other ions and organic ligands in soil solution (Bradl 2004). Thus sorbed Cd can easily be released when conditions in soil solution change. The fact that soil pH strongly influences the solubility of soil Cd has been documented in many studies (Christensen 1984, Christensen 1989, Bradl 2004, Kabata-Pendias 2010). At pH less than 6 Cd can be adsorbed electrostatically by negatively charged soil constituents (e.g. clay and hydroxides) meaning that it can be replaced by competing cations and thus returned to soil solution (e.g. McBride 1994). From a review of the literature, Kabata-Pendias (2010) concluded that Cd is most mobile in the pH range 4.5–5.5, although soil organic matter and sesquioxides also control the labile pool of Cd. At pH higher than 7.5 adsorbed Cd is not easily mobile and in alkaline soils precipitation of Cd compounds becomes more likely (McBride 1994, Kabata-Pendias 2010). In general, precipitation is favored by high Cd^{2+} concentrations (Bradl 2004). Under anaerobic conditions Cd precipitates as low-soluble CdS (McBride 1994).

In Finland, agricultural soils are rich in organic matter, which makes Finnish cultivated soils vulnerable for Cd accumulation but on the other hand the slight acidity of the soils enhances the mobility of Cd and may increase its uptake by crops and loss by leaching. At low concentrations, adsorption of Cd is the main reaction type (Bradl 2004). However, the presence of other ions affects the Cd adsorption due to the competitive sorption and complexation (Christensen 1984, Bradl 2004). The presence of competing cations, such as Ca^{2+} and Zn^{2+}, can compete with Cd for sorption sites and displace Cd from cation exchange sites to soil solution (Christensen 1984, Bradl 2004). According to Bradl (2004) Cl^- in soil solution can form complexes with Cd that are less strongly adsorbed than Cd^{2+}. Furthermore, dissolved organic C or chelates can decrease Cd adsorption and thus increase its mobility (Bradl 2004). In agroecosystems e.g. fertilization can affect the mobility and availability of Cd in soils (Kabata-Pendias 2010).

The easily soluble, acid ammonium acetate – ethylenediaminetetra-acetic acid (AAAc-EDTA) extractable concentrations of Cd in the 20-cm surface layer of cultivated soils in Finland have been followed in the national soil survey since 1987 (Mäkelä-Kurtto and Sippola 2002). The monitoring network, which covers all agricultural area of Finland, was established in 1974 (n = 2042) and resampled in 1987 (n = 1362), 1998 (n = 720) and 2009 (n = 611). The follow-up data shows a declining trend in the AAAc-EDTA extractable Cd in all soil types between 1998 and 2009 except in clay and mull soils, in which the Cd concentrations have remained at a constant level (Fig 1a and b).

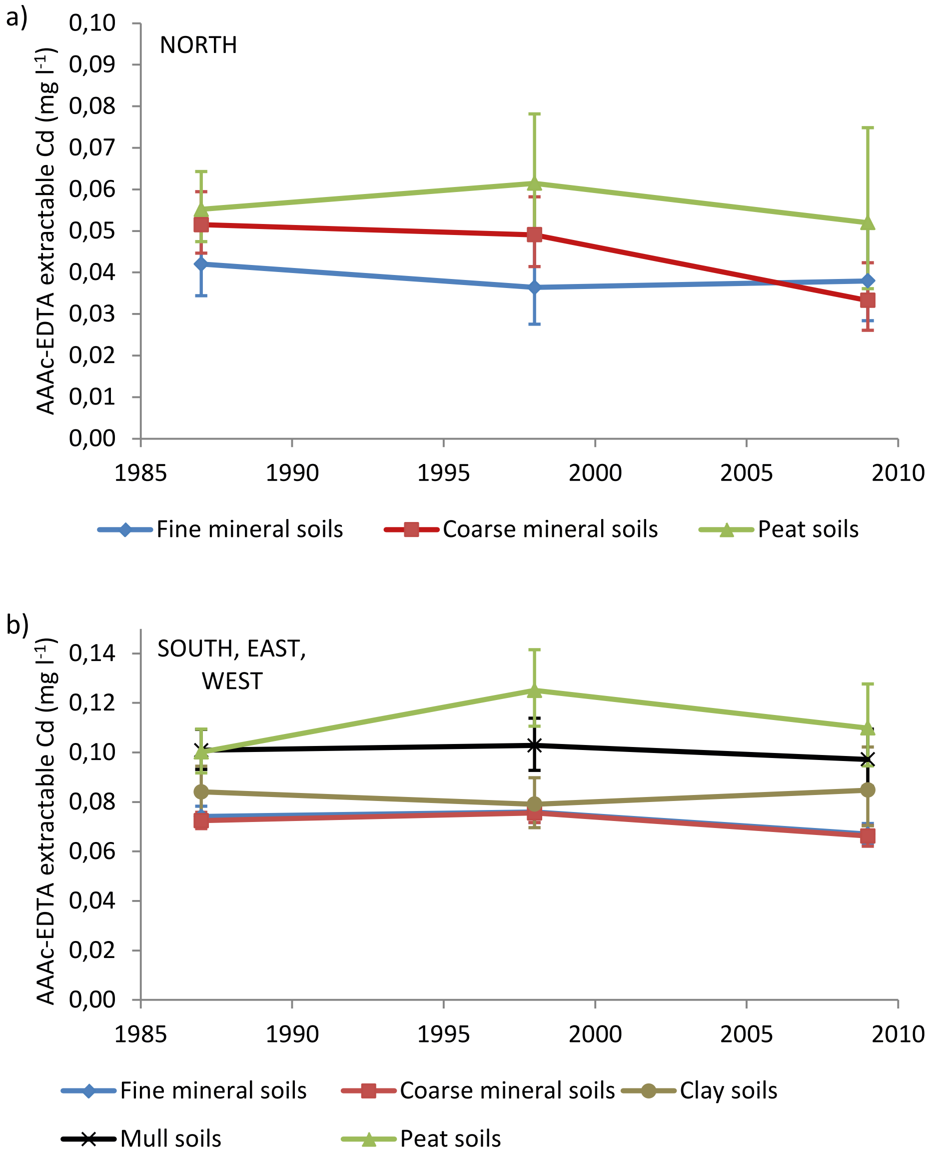


Figure1. AAAc-EDTA extractable Cd in the 20-cm surface layer of cultivated fine and coarse mineral soils, clay, mull, and peat soils in north (a), and in other parts (b) of Finland. The graphs show estimated mean concentrations with 95% confidence intervals.

Regional examination of the AAAc-EDTA extractable concentrations of Cd in the most recent sampling of the Finnish national survey of cultivated soils shows lowest estimated means in the northern and highest in the southern part of the country in all soil types (Table 3). Organic soils tend to have higher concentrations of easily soluble Cd than mineral soils.

Table 3. Easily soluble (AAAc-EDTA extractable) cadmium concentrations (mg l^{-1} soil) in five soil types and four geographical regions of Finland. The data is from the latest sampling campaign of the Finnish national soil survey conducted in 2009. The figures are mean estimates ± standard error. The number of samples (n) is shown in italics.

	South	East	West	North
Fine mineral soils	0.08 ± 0.00 n = 67	0.06 ± 0.00 n = 41	0.06 ± 0.00 n = 46	0.03 ± 0.00 n = 16
Coarse mineral soils	0.08 ± 0.01 n = 34	0.06 ± 0.00 n = 66	0.04 ± 0.00 n = 49	0.03 ± 0.00 n = 24
Clay soils	0.11 ± 0.01 n = 81	0.06 ± 0.01 n = 22	0.09 ± 0.02 n = 3	n = 0
Mull soils	0.15 ± 0.03 n = 7	0.11 ± 0.01 n = 15	0.09 ± 0.01 n = 15	0.10 ± 0.04 n = 2
Peat soils	0.12 ± 0.03 n = 5	0.09 ± 0.02 n = 7	0.08 ± 0.01 n = 17	0.05 ± 0.01 n = 9

3.1.2 The content and uptake of Cd by plants

Cd is thought to be non-essential to plants, but despite of this, Cd is relatively easily available to plants thus causing risks to human health (Clemens 2006, Kabata-Pendias and Mukherjee 2007, Kabata-Pendias 2010). Plants can take up Cd both by roots (passively and metabolically) from soil and by leaves from the air (Kabata-Pendias 2010). In general, soluble Cd species in soil are easily plant available (Kabata-Pendias 2010) and therefore the composition of soil solution indicates well the plant uptake and Cd concentrations in plants (Kabata-Pendias and Mukherjee 2007). The same main factors that govern the solubility of Cd in soil also affect the plant uptake: total Cd concentration in soil, content of clay, organic matter and oxides, soil salinity, presence of other ions in soil solution and redox state (Kabata-Pendias 2010). Also e.g. fertilization and the plant species have been reported to have an effect on the plant Cd uptake (Kabata-Pendias and Mukherjee 2007, Kabata-Pendias 2010). However, total content of Cd and soil pH are suggested to be the main factors influencing the content of Cd in plants (Eriksson et al. 1996).

Once absorbed by plant, Cd is mobile within the plant. According to Kabata-Pendias (2010) Cd distribution within plant varies indicating its fast transport between plant organs (roots, tops, leaves). Clemens (2006) reviewed that for Cd it is probable to accumulate also to other parts of the plant than roots, although Cd concentrations are often higher in roots than in leaves, fruits or seeds. The main reason for Cd toxicity is that it disturbs enzyme activity (Kabata-Pendias 2010). In general, symptoms for Cd toxicity in plants are growth retardation and root damage, red-brown coloration of leaf margins, veins and petioles and reduction of stem conductivity, chlorophyll and carotenoids (Clemens 2006, Kabata-Pendias 2010). Due to the similarities with Zn^{2+}, Cd^{2+} can replace Zn^{2+} and thus interfere in the Zn-dependent processes in plant (Clemens 2006). Cd also inhibits photosynthesis and decreases water stress tolerance (Kabata-Pendias and Mukherjee 2007, Kabata-Pendias 2010).

EU legislation (EC No 1881/2006 and its updates, latest consolidated version available at http://data.europa.eu/eli/reg/2006/1881/2016-04-01) sets maximum levels for cadmium in vegetables and fruit, root and tuber vegetables, leaf vegetables, fungi, cereal grains, meat and offal, fish and seafood, and children's foods.

3.1.4 Cd in domestic animal production

Cd has a tendency to accumulate both in animals and humans. While the main part of Cd in domestic animals is found in the offal, a part is also found in the meat. EU legislation has set maximum limits to Cd levels in the meat, liver and kidney of most domestic animals.

3.1.5 Cd in waterways

Natural background concentrations of Cd in Finnish surface waters are generally low, usually under the limit value (0.08 µg/l) set by the Directive 2008/105/EC (Verta et al. 2010). According to Verta et al. (2010) the median Cd concentration in Finnish lakes is 0.015 µg/l. In stream waters, however, the limit value can be exceeded especially in the areas of acid sulfate soils. In the Baltic Sea, Cd concentrations vary between 0.01 and 0.02 µg/l, being also under the limit value (Verta et al. 2010). However, due to geological reasons, in some areas natural background Cd concentrations can be higher (Verta et al. 2010). Also in Finnish drinking waters Cd concentrations are low. According to Ahonen et al. (2008), Cd concentrations are under the limit value (5.0 µg/l) set by the Ministry of Social Affairs and Health (STM 2000, 2001). In their study, median Cd concentrations varied between 0.02–1 µg/l. Cd concentrations in Finnish dug wells and drilled bedrock wells are also low, the median values being below 0.02 µg/l (Lahermo et al. 2002). In dug wells, the mean Cd concentration was 0.04 µg/l. The maximum values were 0.56 µg/l and 1.27 µg/l for drilled bedrock wells and dug wells, respectively. Higher concentrations in dug wells may originate from technical appliances of wells (Lahermo et al. 2002). However, concentrations were well below the safe concentration limit (5 µg/l) set by the Ministry of Social Affairs and Health (STM 2001).

3.2 Environmental exposure to Cd

3.2.1 Cd flows in Finland

Cadmium flows in Finland were estimated, and values for the flows in different conditions were given in the studies by Finnish Environment Institute (2000) and Mäkelä-Kurtto et al.

(2003, 2007b,c). Input to soil originates from fertilizers, manure, soil improvers, liming agents and deposition. Fertilizer input is usually related to Cd concentration of phosphate rock used by fertilizer industry. Phosphate rock of igneous origin available in Finland and north-east Russia is low in Cd, generally below 5 mg/kg. Sedimentary phosphate rocks contain 3–120 mg Cd/kg (Ghoshesh et al. 1996). When producing single superphosphate (SSP) or triple superphosphate (TSP), all the Cd in the phosphate rock is transferred to the final product (SSP or TSP). Thus SSP can contain 2–40 mg Cd /kg and TSP 10–100 mg Cd /kg (Roberts 2013). Average concentration of Cd in phosphate fertilizers marketed in Europe is 7.4 mg/kg fertilizer and on a P basis 83 mg/kg P (Nziguheba and Smolders 2008). In fertilizers from Finnish origin, Cd concentration has varied from 2.5 mg/kg P (Mäkelä-Kurtto et al. 2003) to 5.5. mg/kg P (calculated from Mäkelä-Kurtto et al. 2007c). Annual input of Cd from P fertilizers into Finnish soils has been estimated to be 0.1 g/ha (Nziguheba and Smolders 2008), 0.1–0.2 g/ha (Mäkelä-Kurtto et al. 2007c), or 0.4–0.7 g/ha (Mäkelä-Kurtto et al. 2003).

Cd concentrations in Finnish manure samples have varied between 0.10 and 0.30 mg/kg DM (Mäkelä-Kurtto and Kemppainen 1993, Mäkelä-Kurtto et al. 2007c). If manure would be distributed evenly into Finnish croplands (644 kg DM/ha), the annual Cd input would be 0.32 g/ha.

Annual liming in Finland has decreased from 400 kg/ha in 1990's to 190 kg/ha after 2010. Annual demand of liming is evaluated to be 400 kg/ha (http://www.farmit.net/kasvinviljely/kalkitus-ja-maanparannus/kalkitussanastoa). Part of this decrease can probably be explained by increased use of slags and ashes. Cd concentrations in conventional liming materials have been low in Finland, 0.06 – 0.15 mg/kg (Mäkelä-Kurtto et al. 2007c). Although slags contain often considerable amounts of heavy metals, they tend to be low in Cd, values less than 0.1 mg/kg were reported by Mäkelä-Kurtto et al. (2007c). Cd concentration of ashes can be high depending on the source materials and combustions techniques, and the Cd concentration of ashes used in agriculture must be less than 2.5 mg/kg.

Deposition of Cd has been reported to vary from 0.17 to 0.29 g/ha/a (Mäkelä-Kurtto et al. 2007c) and from 0.09 to 0.53 g/ha/a (Kyllönen et al. 2009) at different sites.

Cadmium outputs from the soil consist of uptake in harvested yield and losses via leaching and eroded soil material. The magnitude of plant uptake can be estimated using soil to plant transfer functions.

$$SPTC = \frac{Cfresh\ yield}{Csoil}$$

Where C*plant* is the total concentration per fresh matter in harvested fresh plant organ and C*soil* is *aqua regia* extractable Cd concentration in 0 – 20 cm top layer of the soil. SPTC is a crop specific coefficient. This equation increases plant Cd concentration when soil Cd concentration increases. Transfer coefficients have varied e.g. for wheat 0.05–0.16 (Smolders 2013, Sternbäck et al. 2011), for potato 0.04 – 0.13 (Smolders 2013) and for carrot 0.03–0.33 (Smolders 2001). Transfer coefficients can also be related to soil characteristics like pH and organic matter.

Flow of leached Cd is usually based on distribution coefficient (Kd), that shows the relationship between the total (Csoil, aqua regia extractable) concentration in soil and that in the soil pore water (Cwater).

$$Kd = \frac{Csoil}{Cwater}$$

$$Leaching = Cwater \times annual\ runoff$$

Distribution coefficient is usually described as a function of soil pH and organic matter. Different equations for Finnish conditions were discussed in Finnish Environment Institute (2000) in pages 30–31. Later Mäkelä-Kurtto et al. (2003) reported an equation based on measurements from 16 Finnish agricultural soils. Annual water runoff can be averaged to 200 mm that was used in previous Cd mass balance calculations (Finnish Environment Institute 2000).

$$Log\ Kd = -2.26 + 0.92 * pH(water) + 0.62 * \log(\ \%\ Organic\ C)$$

The newest suggestion to estimate Kd values came from Smolders (2013) who combined existing European data in one comparison.

$$Log\ Kd = -0.94 + 0.51 * pH\ (CaCl2) + 0.79 * \log(\ \%\ Organic\ C)$$

This equation results to much lower Kd-values and higher Cd-leaching than the equation by Mäkelä-Kurtto et al. (2003) (Fig. 2).

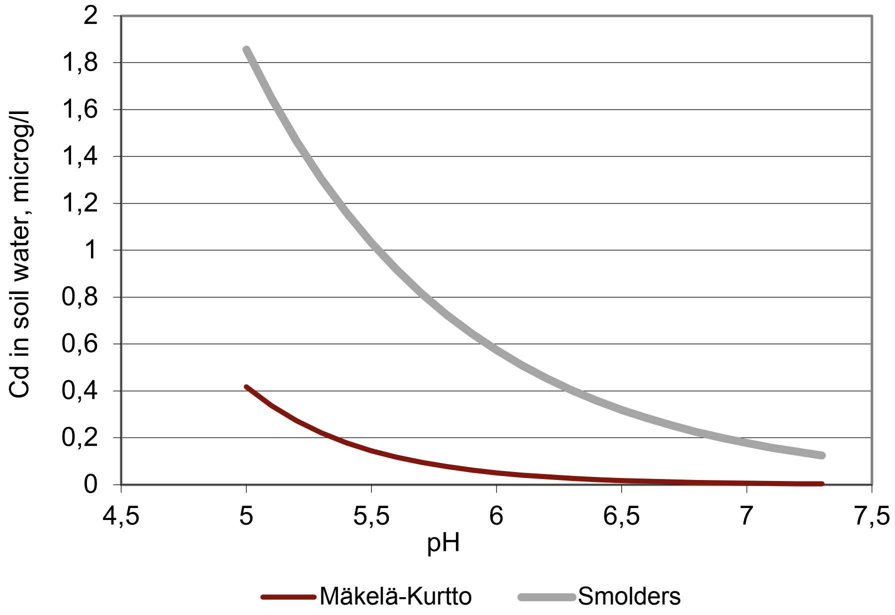


Figure 2. Soil pore water Cd concentrations calculated by Kd-equations of Mäkelä-Kurtto et al. (2003) and Smolders (2013). Organic carbon content used in calculation was 3% and pH measured with $CaCl_2$ was estimated to be 0.5 pH-units lower than pH measured with water.

Annual erosion was set to 500 kg/ha (Finnish Environment Institute 2000). The amount of eroded element can be calculated:

$$Erosion = Csoil \times annual\ soil\ erosion$$

3.2.2 Mass balance calculations

Mass balance calculations for Cd were based on the Cd flow estimations above (chapter 3.2.1) and conducted for four different crop rotations: continuous spring wheat, two years of potato followed by two years of wheat, one year of carrot followed by three years of wheat, and three year grassland followed by cereal to establish a new grass crop for the next three years. Model calculation was run for 100 years using code programmed by SAS statistical package, and following output values were reported: Cd concentration in soil water, annual Cd leaching and erosion, Cd concentration in yield and annual Cd uptake in yield, soil Cd concentration and annual Cd balance.

Cd input was related to the recommended P rates for the studied crops in satisfactory soil P levels (Table 4). The dose of Cd was calculated according to the three different Cd concentrations in P fertilizers:

1. 2.5 mg/kg P, reported e.g. in Mäkelä-Kurtto et al. (2007c) as typical Cd concentration in phosphorus produced from apatite in Siilinjärvi
2. the maximum allowed Cd concentration in fertilizers based on Finnish law of fertilizer products, 50 mg/kg P
3. Cd concentration according to the EU legislation proposal, where allowed maximum Cd concentration of 137.5 mg/kg P is decreased after three years to 91.7 mg/kg P and to 45.8 mg/kg P after twelve years.

Mineral fertilizers were decided to be the only source of nutrients in the crop rotations except for grassland, where one annual application of cow slurry, providing 11 kg P/ha was included. Manure dry matter concentration was set to 5.5% and Cd concentration to 0.28 mg/kg DM (Finnish Environment Institute 2000).

Annual liming demand was set to 400 kg/ha http://www.farmit.net/kasvinviljely/kalkitus-ja-maanparannus/kalkitussanastoa. Cd concentration in liming materials was taken from Mäkelä-Kurtto et al. (2007c). Deposition was set to 0.35 g Cd/ha (Smolders 2013), which is consistent with the values reported in other sources (Finnish Environment Institute 2000, Mäkelä-Kurtto et al. 2007c).

Yield level was set to the average yield during 2010 – 2014 in Finnish agricultural statistics. Transfer coefficient from soil to plant was calculated from the results reported by Mäkelä-Kurtto et al. (2003).

Distribution coefficient was calculated using the average soil pH and organic carbon content reported by Eurofins with the equation suggested by Mäkelä-Kurtto et al. 2003. For comparison, crop rotations of spring wheat were calculated with the equation of Smolders (2013), which leads to considerably higher Cd leaching. In order to test the effect of soil properties on the leaching of Cd, two additional pH and organic C combinations typical for Finnish soils according to the national soil monitoring programme were selected to represent highest and lowest Kd values based on the equation of Mäkelä-Kurtto et al. (2003). Annual runoff was set to 200 mm that was used in the previous cadmium mass balance calculations (Finnish Environment Institute 2000) and annual erosion based on the same source was set to 500 kg/ha. All modelling parameters are listed in Table 4.

After running the model calculation for 100 years using code programmed by SAS statistical package, following output values were reported: Cd concentration in soil water, annual Cd leaching and erosion, Cd concentration in yield and annual Cd uptake in yield, soil Cd concentration and annual Cd balance.

Spring wheat rotations

Annual Cd input for spring wheat in mineral fertilizers (P 10 kg/ha/a) is 0.025 g/ha when using Finnish apatite with 2.5 mg/kg P, and 0.500 g/ha if P fertilizer has the maximum Cd concentration of 50 mg/kg P allowed by the current Finnish law of fertilizer products. Cd doses according to the proposed new EU legislation would be 0.458 g/ha when using P fertilizer with 45.8 mg/kg P, 0.917 g/ha with P fertilizer containing 91.7 mg/kg P and 1.375 g/ha with P fertilizer containing 137.5 mg/kg P.

In spring wheat rotation with the same distribution coefficient as used by Mäkelä-Kurtto et al. (2003), annual balance is 0.17 – 0.18 g/ha positive (Table 5). This leads to 5% increase in soil total Cd concentration. If cadmium concentration in P fertilizer would be 50 mg/kg P, then annual Cd balance would be over 0.6 g/ha, and soil total Cd concentration would increase 18%. Although annual Cd balances would be 1.0 – 1.5 g/ha during the transition period of the proposed EU legislation, the overall effect after 100 years would be negligible in soil total Cd concentration.

Table 4. Parameters used in the mass balance calculations of Cd for four crop rotations.

Model parameters	Cd	Source
Soil concentration, mg Cd/kg	0.18	Mäkelä-Kurtto et al. 2003
Deposition, g Cd/ha/a	0.35	Mäkelä-Kurtto et al. 2007c, Table 40
Mineral phosphorus rate kg/ha/a	10	Spring wheat, Smolders 2013
	55	Potato
	55	Carrot
	14	Grassland
Manure phosphorus kg/ha/a	11	Grassland
Liming kg/ha/a	400	Recommended liming rate
Concentration in liming materials, mg/kg	0.15	Mäkelä-Kurtto et al. 2007c, Table 17
Transfer function, plant/soil	0.1296	Spring wheat (Smolders 2013)
	0.0601	Potato (Smolders 2013)
	0.0800	Carrot (Smolders 2001)
	0.0333	Grassland (Mäkelä-Kurtto et al. 2007c)
Yield kg/ha	3750	wheat, 14% moisture
	26000	potato, 22 % DM
	41860	carrot, 20% DM
	15600	grass, 32 % DM
Kd	4775	Mäkelä-Kurtto et al. 2003, pH 6.0, C 4.75%
	2572	Mäkelä-Kurtto et al. 2003, pH 5.8, C 3.30%
	12801	Mäkelä-Kurtto et al. 2003, pH 6.46, C 4.80%
	251	Smolders 2013, pH 6, C 4.75%
Annual runoff, m3/ha	2000	Finnish Environment Institute 2000
Annual erosion, kg/ha	500	Finnish Environment Institute 2000

Table 5. The effect of P fertilizers with different Cd concentrations on Cd leaching and erosion and consequent impact on Cd uptake by crop and soil Cd concentrations when spring wheat is grown in a soil having a pH of 6.0 and organic C concentration of 4.75% on a time scale up to 100 years.

Cd in P_2O_5	Cd in P	Time period	Kd	Year	Soil water mikrog/l	Leached g/ha/a	Eroded g/ha/a	Yield mikrog/ kg DM	Cd uptake g/ha/a	Soil mg/kg	Annual balance g/ha
1.1	2.5	1	4775	1	0.038	0.075	0.090	23.321	0.087	0.180	0.182
1.1	2.5	100	4775	100	0.040	0.079	0.094	24.450	0.092	0.189	0.170
21.8	50.0	1	4775	1	0.038	0.076	0.090	23.352	0.088	0.180	0.657
21.8	50.0	100	4775	100	0.044	0.089	0.106	27.422	0.103	0.212	0.613
60	137.5	1	4775	1	0.038	0.076	0.090	23.409	0.088	0.181	1.530
40	91.7	4	4775	4	0.038	0.077	0.091	23.676	0.089	0.183	1.069
20	45.8	12	4775	12	0.039	0.078	0.094	24.229	0.091	0.187	1.063
20	45.8	100	4775	100	0.045	0.089	0.106	27.576	0.103	0.213	0.569

Table 6. The effect of P fertilizers with different Cd concentrations on Cd leaching and erosion and consequent impact on Cd uptake by crop and soil Cd concentrations when spring wheat is grown in a soil with a pH of 5.8 and organic C concentration of 3.31% on a time scale up to 100 years.

Cd in P_2O_5	Cd in P	Time period	Kd	Year	Soil water mikrog/l	Leached g/ha/a	Eroded g/ha/a	Yield mikrog/ kg DM	Yield uptake g/ha/a	Soil mg/kg	Annual balance g/ha
1.1	2.5	1	2572	1	0.070	0.140	0.090	23.3	0.087	0.180	0.118
1.1	2.5	100	2572	100	0.072	0.144	0.093	24.0	0.090	0.186	0.108
21.8	50	1	2572	1	0.070	0.140	0.090	23.4	0.088	0.180	0.592
21.8	50	100	2572	100	0.081	0.162	0.104	27.0	0.101	0.208	0.543
60	137.5	1	2572	1	0.070	0.140	0.090	23.4	0.088	0.181	1.465
40	91.7	4	2572	4	0.071	0.142	0.091	23.7	0.089	0.183	1.004
20	45.8	12	2572	12	0.073	0.145	0.093	24.2	0.091	0.187	0.997
20	45.8	100	2572	100	0.081	0.163	0.105	27.1	0.102	0.210	0.499

When using the soil pH and organic carbon concentrations that estimate the smallest distribution coefficient and the highest Cd leaching, water Cd concentration and Cd leaching are almost doubled (Table 6). Increases in soil total Cd concentrations are still close to the values acquired with modelling by using the average soil properties.

Table 7. The effect of P fertilizers with different Cd concentrations (mg Cd/kg P) on Cd leaching and erosion and consequent impact on Cd uptake by crop and soil Cd concentrations when spring wheat is grown in a soil with a pH of 6.5 and organic C concentration of 4.80% on a time scale up to 100 years.

Cd in P_2O_5	Cd in P	Time period	Kd	Year	Soil water mikrog/l	Leached g/ha/a	Eroded g/ha/a	Yield µg/kg DM	Yield uptake g/ha/a	Soil mg/kg	Annual balance g/ha
1.1	2.5	1	12801	1	0.014	0.028	0.090	23.3	0.087	0.180	0.229
1.1	2.5	100	12801	100	0.015	0.030	0.096	24.8	0.093	0.191	0.217
21.8	50	1	12801	1	0.014	0.028	0.090	23.4	0.088	0.180	0.704
21.8	50	100	12801	100	0.017	0.033	0.107	27.7	0.104	0.214	0.665
60	137.5	1	12801	1	0.014	0.028	0.090	23.4	0.088	0.181	1.578
40	91.7	4	12801	4	0.014	0.029	0.091	23.7	0.089	0.183	1.117
20	45.8	12	12801	12	0.015	0.029	0.094	24.3	0.091	0.187	1.112
20	45.8	100	12801	100	0.017	0.034	0.108	27.9	0.105	0.215	0.622

When the evaluation of leaching is based on soil properties showing the lowest Cd leaching, annual balances and soil total Cd concentration increase (Table 7), but the differences are not big.

The equation for distribution coefficient according to Smolders (2013) accelerates Cd leaching considerably (Table 8). Water Cd concentrations increase to 0.6–0.8 µg/l, and annual Cd leaching is as high as 1.6 g/ha. Annual Cd balances become negative in all Cd levels, and soil total Cd concentrations would decrease 17% and end up below 0.15 mg/kg.

Table 8. The effect of P fertilizers with different Cd concentrations (mg Cd/kg P) on Cd leaching and erosion and consequent impact on Cd uptake by crop and soil Cd concentrations when spring wheat is grown in a soil with a pH of 6.0 and organic C concentration of 4.75% on a time scale up to 100 years. Distribution coefficient and the resulting leaching are calculated according to the equation of Smolders (2013).

Cd in P_2O_5	Cd in P	Time period	Kd	Year	Soil water mikrog/l	Leached g/ha/a	Eroded g/ha/a	Yield mikrog/ kg DM	Yield uptake g/ha/a	Soil mg/kg	Annual balance g/ha
1.1	2.5	1	251	1	0.813	1.625	0.090	23.3	0.087	0.179	-1.368
1.1	2.5	100	251	100	0.571	1.142	0.063	16.4	0.061	0.126	-0.832
21.8	50	1	251	1	0.814	1.627	0.090	23.4	0.088	0.180	-0.895
21.8	50	100	251	100	0.656	1.311	0.073	18.8	0.071	0.145	-0.544
60	137.5	1	251	1	0.816	1.631	0.090	23.4	0.088	0.180	-0.025
40	91.7	4	251	4	0.814	1.629	0.090	23.4	0.088	0.180	-0.481
20	45.8	12	251	12	0.806	1.612	0.089	23.1	0.087	0.178	-0.462
20	45.8	100	251	100	0.658	1.316	0.073	18.9	0.071	0.145	-0.591

Potato rotation

Annual Cd input in mineral fertilizers (P application 55 kg/ha/a) for cultivation of potato is 0.138 g/ha when using Finnish apatite with 2.5 mg/kg P, and 2.75 g/ha if P fertilizer has the maximum Cd concentration of 50 mg/kg P allowed by the current Finnish law of fertilizer products. Cd doses according to the proposed new EU legislation would be 2.52 g/ha when using P fertilizer with 45.8 mg/kg P, 5.04 g/ha with P fertilizer containing 91.7 mg Cd/kg P and 7.56 g Cd/ha with P fertilizer containing 137.5 mg Cd/kg P.

Table 9. The effect of P fertilizers with different Cd concentrations on Cd concentration in soil pore water, yield and soil, the amount of Cd leached, eroded and taken off from the field in yield and annual Cd balance, when crop rotation is two years potato followed by two years spring wheat, soil pH is 6.0 and organic C 4.75%. First year crop is potato, while crop in 4th, 12th and 100th year is spring wheat.

Cd in P_2O_5	Cd in P	Time period	Kd	Year	Soil water mikrog/l	Leached g/ha/a	Eroded g/ha/a	Yield mikrog/ kg DM	Yield uptake g/ha/a	Soil mg/kg	Annual balance g/ha
1.1	2.5	1	4775	1	0.038	0.075	0.090	49.2	0.281	0.180	0.101
1.1	2.5	100	4775	100	0.039	0.078	0.093	28.1	0.091	0.187	0.173
21.8	50	1	4775	1	0.038	0.076	0.091	49.5	0.283	0.181	2.710
21.8	50	100	4775	100	0.054	0.109	0.130	39.2	0.126	0.260	0.544
60	137.5	1	4775	1	0.038	0.077	0.092	50.2	0.287	0.184	7.511
40	91.7	4	4775	4	0.040	0.079	0.094	28.4	0.092	0.189	1.061
20	45.8	12	4775	12	0.042	0.084	0.100	30.2	0.098	0.201	1.044
20	45.8	100	4775	100	0.055	0.111	0.132	39.8	0.128	0.264	0.497

In rotation with 50% of potato with a considerable P fertilizer rate, soil total Cd concentrations increase clearly when Cd level of more than 45 mg/kg P is used (Table 9). Annual balances with P rates of potato can be as high as 2.7 g/ha with 50 mg/kg P and 7.5 g Cd/ha with 137.5 g Cd/kg P. Soil total Cd concentration increases towards 0.25 mg/kg when Cd level of about 50 mg Cd/kg P is used.

Carrot rotation

Annual Cd input in mineral fertilizers (P application 55 kg/ha/a) for carrot is 0.138 g/ha when using Finnish apatite with 2.5 mg/kg P, and 2.75 g/ha if P fertilizer has the maximum Cd concentration of 50 mg/kg P allowed by the current Finnish law of fertilizer products. Cd doses according to the proposed new EU legislation would be 2.52 g/ha when using P fertilizer with 45.8 mg/kg P, 5.0 g/ha with P fertilizer containing 91.7 mg Cd/kg P and 7.563 g Cd/ha with P fertilizer containing 137.5 mg Cd/kg P.

Table 10. The effect of P fertilizers with different Cd concentrations on Cd concentration in soil pore water, yield and soil, the amount of Cd leached, eroded and taken off from the field in yield and annual Cd balance, when crop rotation is carrot followed by three years of spring wheat, soil pH is 6.0 and organic C 4.75%. First year crop is carrot, while crop in 4th, 12th and 100th year is spring wheat.

Cd in P_2O_5	Cd in P	Time period	Kd	Year	Soil water mikrog/l	Leached g/ha/a	Eroded g/ha/a	Yield mikrog/ kg DM	Yield uptake g/ha/a	Soil mg/kg	Annual balance g/ha
1.1	2.5	1	4775	1	0.038	0.075	0.090	72.0	0.603	0.180	-0.221
1.1	2.5	100	4775	100	0.038	0.077	0.092	27.7	0.089	0.184	0.177
21.8	50	1	4775	1	0.038	0.076	0.091	72.6	0.607	0.181	2.386
21.8	50	100	4775	100	0.049	0.097	0.116	34.9	0.113	0.232	0.585
60	137.5	1	4775	1	0.038	0.077	0.092	73.5	0.615	0.184	7.183
40	91.7	4	4775	4	0.039	0.078	0.093	28.0	0.090	0.186	1.065
20	45.8	12	4775	12	0.041	0.081	0.097	29.1	0.094	0.193	1.054
20	45.8	100	4775	100	0.049	0.098	0.117	35.3	0.114	0.234	0.539

Carrot is well-known of its high affinity to absorb Cd, and thus yield uptakes are over 0.6 g Cd/ha (Table 10). With low Cd level in P fertilizer, annual balance can be negative, but due to high P fertilizer rates turns it positive with higher Cd concentrations in fertilizers. With Cd levels higher than 45 g/kg P, soil total Cd concentrations increase up to 0.23 mg/kg soil.

Grassland rotation

Annual Cd input for silage grass in mineral fertilizers (P application 14 kg/ha/a) is 0.035 g/ha when using Finnish apatite with 2.5 mg Cd/kg P, and 0.70 g Cd/ha if P fertilizer has the maximum Cd concentration 50 mg/kg P allowed by the current Finnish law of fertilizer products. Cd doses according to the proposed new EU legislation would be 0.641 g/ha when using P fertilizer with 45.8 mg Cd/kg P, 1.28 g Cd/ha with P fertilizer containing 91.7 mg Cd/kg P and 1.93 g Cd/ha with P fertilizer containing 137.5 mg Cd/kg P. Cd dose from annual application of cow slurry would be an additional 0.339 g/ha.

In grassland rotation, Cd input in cow slurry is the main source when P fertilizers with low Cd content is used and 50% of Cd input comes from cow slurry if the used mineral fertilizer contains 50 mg Cd/kg P fertilizer. Annual balances are 0.5 g Cd/ha even with low Cd content fertilizer and tend to increase soil Cd concentration 14% up to 0.20 mg Cd/kg soil (Table 11). With higher Cd concentration in fertilizers, annual balances are slightly above 1 g Cd/ha and soil total Cd concentration increases to 0.23 mg/kg, which is still in the range found in Finnish agricultural soils (Mäkelä-Kurtto et al. 2007b).

Table 11. The effect of P fertilizers with different Cd concentrations on Cd concentration in soil pore water, yield and soil, the amount of Cd leached, eroded and taken off from the field in yield and annual Cd balance, when crop is silage grass, soil pH is 6.0 and organic C 4.75%.

Cd in P_2O_5	Cd in P	Time period	Kd	Year	Soil water mikrog/l	Leached g/ha/a	Eroded g/ha/a	Yield mikrog/ kg DM	Yield uptake g/ha/a	Soil mg/kg	Annual balance g/ha
1.1	2.5	1	4775	1	0.038	0.075	0.090	18.8	0.094	0.180	0.525
1.1	2.5	100	4775	100	0.043	0.086	0.103	21.4	0.107	0.205	0.489
21.8	50	1	4775	1	0.038	0.076	0.090	18.8	0.094	0.181	1.189
21.8	50	100	4775	100	0.050	0.099	0.119	24.7	0.123	0.237	1.107
60	137.5	1	4775	1	0.038	0.076	0.091	18.8	0.094	0.181	2.412
40	91.7	4	4775	4	0.039	0.077	0.092	19.2	0.096	0.184	1.766
20	45.8	12	4775	12	0.040	0.080	0.096	19.9	0.099	0.192	1.756
20	45.8	100	4775	100	0.050	0.100	0.120	24.9	0.124	0.239	1.046

3.3 Risk assessment on Cd at increased levels of exposure

3.3.1 Toxicity to organisms

Ecotoxicity of Cd has been well reviewed in the previous risk assessment for Cd in Finland (Finnish Environment Institute 2000). Overall, most plants are rather insensitive to Cd, the yields decreasing typically at soil Cd concentrations of 2 – 250 mg/kg, but in sensitive plants adverse effects can be seen already at a level of 0.1 mg Cd/kg soil. Microorganisms and terrestrial invertebrates show moderate or high sensitivity to Cd, microbial processes being inhibited already at concentrations exceeding 4 mg/kg soil. For aquatic life, Cd is moderately to highly toxic. According to the risk assessment (Finnish Environment Institute 2000) predicted no-effect concentration (PEC) for Cd in soil is 0.06 mg/kg and for the aquatic environment 0.0085 µg/l. Due to acidity, high organic carbon content and softness of water, the Finnish environment is in general particularly vulnerable to Cd. In conclusion, the current concentrations of Cd in agricultural soils and surface waters of Finland already present a risk for the environments in question.

3.3.2 Effects on human health

Cadmium is absorbed from dietary exposure in relatively low (3 to 5%) amounts, although its bioavailability depends on several factors including the nutritional status of the consumer, body iron stores and pre-existing health conditions (EFSA 2009b). Once cadmium is absorbed into the body, it mainly accumulates both in the kidney and in the liver and is excreted very slowly. Literature estimates of the biological half-life of Cd vary between 7 and 30 years.

Cd is toxic to many parts and processes of the human body. At cell level, many of the toxic effects stem from either oxidative stress or prevention of the functioning of important enzymes. Enzymes can be incapacitated due to Cd replacing other metals, such as calcium or zinc, in the enzyme structure, or due to Cd binding to functional groups of an enzyme. At organ level, Cd exposure has been found in animal tests to be toxic to kidneys, liver, the reproductive system, as well as the nervous system (Flora et al. 2011).

IARC has classified Cd as Group I carcinogen, i.e., carcinogenic to humans. In addition to lung cancer, Cd has a positive correlation to kidney cancer and testicular cancer as well as possibly hormone-dependent cancers (Byrne et al. 2009, EFSA 2009b). While Cd is only slightly mutagenic, it shows indirect genotoxicity, possibly through oxidative stress and disruption of DNA repair mechanisms (IARC 2012).

As Cd tends to accumulate in the kidney, even low level exposure over a prolonged period of time can lead to weakening of kidney tubular function and proteinuria, and finally to kidney failure (EFSA 2012a). Diabetics are especially sensitive to this toxic effect (ATSDR 2012). Other Cd-related harmful health effects are bone demineralization.

Considering the accumulation tendency of Cd, the health-based guidance values for intake of Cd have been set as tolerable weekly intake (2.5 µg Cd/kg body weight/week, nominated by EFSA) or provisional tolerable monthly intake (25 µg Cd/kg bw /month, established by the Joint FAO/WHO Expert Committee on Food Additives, JECFA). The stricter guidance value of EFSA is geared at protecting the whole of the population, including the more sensitive individuals. The value is based on the kidney damaging effects of Cd: the benchmark dose corresponded to exposure causing a 5% increase in urine levels of kidney damage marker protein β-2-microglobulin.

3.3.3 Estimates of dietary intake and its sources

For the non-smoking population, food and water are the main sources of Cd exposure. Smoking increases the Cd burden, and cigarettes also contain other heavy metals.

The dietary Cd intake of Finnish consumers has been estimated by the EFSA (2012) from mainly Central European concentrations and national consumption data. The average intake of Finnish adults is below the EFSA TWI level (tolerable weekly intake), but high intake group may exceed the TWI (2.5 µg/kg bw/week). Finnish children are more vulnerable and exceed the TWI even at age group mean level. EFSA's middle bound estimates of exposure for Finnish toddlers, older children and adults were 5.08, 4.02 and

1.52 µg/kg bw/week at age group mean level, respectively, and 10.1, 6.21 and 2.62 µg/kg bw/week at 95th percentile of exposure. The high intake group among Finnish toddlers had the highest Cd intake of all EU countries and they exceeded the TWI 4-fold and the other Finnish children more than 2-fold. The EFSA Panel of experts concluded that at an individual level the risk of adverse effects on kidney function is still very low, but exposure to Cd at the population level should be reduced (EFSA 2012a). In addition to children, also vegetarians may have high exposure to cadmium according to EFSA's previous estimate (EFSA 2009b).

A national risk assessment (Suomi et al. 2015) determined the dietary exposure to Cd of Finnish children at age 1 to 6 years, based on nationally collected concentration data. The middle bound estimates at 95th percentile of exposure were 4.9, 4.2 and 3.6 µg/kg bw/week for children of 1, 3 and 6 years of age, respectively. Even though the estimates were much lower than those calculated by EFSA in 2012, due to lower levels of Cd in several much consumed food products, the TWI of Cd was exceeded by 88–90% of children between ages of 1 and 3 years and by 64% of the 6-year-olds (Suomi et al. 2015). Cereals contributed roughly one third of the total dietary exposure, while the relative contributions of other food groups were lower: vegetables contributed 5 to 8% of the total exposure, starchy roots 10 to 14% and dairy 10 to 13% of the total exposure.

Effect of change in the Cd concentrations during 100 years

The effect on the total dietary exposure of Finnish children was estimated on the assumption that only the concentration in cereals (or cereals, root vegetables and potatoes) would change and all other sources of exposure, as well as consumption habits of the children, would remain unchanged. Comparison was made with the total dietary exposure (including exposure from drinking water) of 3-year-old Finnish children (calculated in Suomi et al. 2015).

The current realization in the changes in Cd content of cereals (+3 – +6%), root vegetables (+2%) and potatoes (+4%) would lead to an increase of the total Cd exposure at age group median level by 2% (or 1 – 2% if the effect on roots and potatoes was not considered). The total dietary exposure at the 95th percentile of exposure, corresponding to the high intake group, would increase by 1%.

The Cd input level allowed by the EU proposal was calculated to increase the levels of Cd in cereals by 16–20%, root vegetables by 30% and potatoes by 47%. The total exposure of 3-year-old Finns would thus increase by 12–13% at age group median level and by 10–11% at the 95th percentile.

In comparison with the tolerable weekly intake of Cd, the current realization corresponds to 125% of the TWI at age group median, and the EU proposal corresponds to 138–139% of the TWI at age group median.

3.3.4 Estimated maximum acceptable annual load of Cd to a field hectare in Finland

Regarding soil total Cd concentrations, the Cd concentration in P fertilizers produced from local sources keeps the soil total Cd concentration at the existing level. Still with these low-Cd fertilizers we could expect a slight, 3 – 6% increase, if we assume that the Cd leaching is at a level estimated by Mäkelä-Kurtto et al. (2003). If Cd concentration of mineral P fertilizers would increase from the 2.5 mg/ kg P towards 50 mg/kg P, an increase of 17–44% in the soil total Cd concentrations is expected, depending on crop rotations. After 100 years, the soil total Cd concentrations would be approximately 0.23 mg/kg. This is still in the current average range for clay soils and lower than average for peat soils (Mäkelä-Kurtto et al. 2007b).

Considering the recommendations of reducing the Cd exposure of the Finnish population, the current realization of Cd inputs should not be exceeded. From environmental perspective, according to the previous risk assessment for Cd in Finland (Finnish Environment Institute 2000), there is no margin of safety for Cd exposure but any increase from the current level presents an elevated risk for both soil and aquatic environments. The maximum level of Cd allowed currently and that in the EU proposal can thus be considered excessive. A maximum annual input level of 0.5 g Cd/ha from mineral fertilizers, liming and deposition can be recommended. Deposition of Cd with 0.35 g/ha is already a large proportion of the acceptable input.

4 Chromium (Cr)

4.1 Occurrence and behavior in the environment

Cr has earlier thought to be non-essential but nowadays it is considered as an essential element for humans, because it takes part in metabolism of glucose, proteins and carbohydrates (Koljonen et al. 1992, Reimann et al. 2014c). In soil, Cr occurs in the oxidation states of +3 (Cr^{3+}) and +6 (CrO_4^{2-}) (McBride 1994, Reimann et al. 2014c). CrO_4^{2-} is highly toxic whereas Cr^{3+} is considered to be relatively harmless (Reimann et al. 2014c). Cr has four naturally occurring isotopes: ^{50}Cr, ^{52}Cr, ^{53}Cr and ^{54}Cr, of which ^{52}Cr is the most common (Reimann et al. 2014c). Cr in soils originates either from the parent material or from anthropogenic sources. The most important Cr mineral is chromite ($FeCr_2O_4$) (Koljonen et al. 1992, Reimann et al. 2014c), but also crocoite ($PbCrO_4$) is relatively common (Kabata-Pendias 2010). In addition Cr can occur e.g. in pyroxene, amphibole, garnet and mica (Reimann et al. 2014c). The anthropogenic sources for Cr are e.g. dyestuffs, leather tanning and sewage treatment plants that treat industrial and residential sources (Kabata-Pendias 2010). In Finland, the main sources for Cr emissions to the air in 2012 were energy production (72 %), industrial processes (27 %), transport (0.4 %) and waste (0.1 %) (Finnish Environment Institute 2014). During the time-period of 1990 – 2012 Cr emissions to the air have varied quite much in different years, although the emissions have decreased from 29 t to 18 t (Finnish Environment Institute 2014).

Globally, mean Cr concentration in soils is estimated to be 60 mg/kg, although higher concentrations can be found in soils that are derived from mafic rocks, argillaceous sediments and serpentines (Kabata-Pendias 2010). According to Mäkelä-Kurtto et al. (2007b) Cr concentrations (*aqua regia* extraction) in Finnish cultivated soils (plough layer) are in average 29.4 mg/kg DM (*n=338*), concentrations varying between 1.6 and 93.2 mg/kg DM. Median was 22.5 mg/kg DM. Concentrations varied between different soil types and regionally. Clay soils contained significantly more Cr than coarse-textured mineral soils or organic soils, mean concentrations being 57.2, 25.7 and 20.3 mg/kg DM, respectively. Due to this difference between clay soils and other soil types, high Cr concentrations were found in southwestern Finland (Mäkelä-Kurtto et al. 2007b). In addition, high Cr concentrations were found in northern Finland, reflecting regional variation in the Cr concentrations in glacial till (Koljonen et al. 1992). According to Koljonen et al. (1992) the higher Cr concentrations in the glacial till of northern Finland result from mafic and ultramafic rocks prevailing in that area. The same trend between different soil types in Cr concentrations in Finnish arable soils was also observed by Tarvainen and Kuusisto (1999). They observed a slight difference between the Cr concentrations in topsoil (0–25 cm) and subsoil (50–75 cm). In topsoil, the median Cr concentration was 19.0 mg/kg, whereas in subsoil the corresponding value was 22.3 mg/kg. According to Reimann et al. (2014c) the Cr concentrations (*aqua regia*) in Finland are higher than in other Nordic countries studied (Norway and Sweden). In general, Cr concentrations differ substantially between different European countries, the main reason being geology (Reimann et al. 2014c). Cr concentrations are also higher in southern Europe than in northern Europe. The median value for northern Europe is 13 mg/kg and for southern Europe 25 mg/kg (Reimann et al. 2014c). At the continental level, concentrations vary between 0.4 and 696 mg/kg, median being 20 mg/kg for both grazing land and agricultural land soils (Reimann et al. 2014c). In the national soil survey of Finland (1974–2009), the easily soluble, AAAc-EDTA extractable concentrations of Cr in the 20-cm top layer of cultivated soils have ranged between 0 and 5.35 mg/l, the median in 2009 being 0.25 mg/l.

The speciation of Cr in soil is governed by redox potential, pH, and the contents of organic matter and hydrous metal oxides (Mukherjee 1998, Kimbrough et al. 1999, Pantsar-Kallio et al. 2001). Generally, the trivalent form is most common in soil environments, and it is relatively immobile due to its tendency to adsorb on negative surfaces, complex with organic matter and precipitate as hydroxides (McBride 1994, Mukherjee 1998, Pantsar-Kallio et al. 2001 and references therein). In acidic soil, Cr(III) is more mobile than in neutral/alkaline soil (Pantsar-Kallio et al. 2001). Under aerobic conditions, high pH and presence of MnO_2 or kaolinite, Cr(III) can be oxidized to Cr(VI), which adsorbs poorly onto soils and is thus highly mobile (Mukherjee 1998, Pantsar-Kallio et al. 2001). In contrast to Cr(III), adsorption of Cr(VI) increases in acidic pH due to increase in positive charges on soil surfaces. In the presence of a suitable reducing agent, e.g. organic matter, S^{-2} or Fe^{2+}, Cr(VI) can be reduced to the immobile Cr(III) (McBride 1994, Mukherjee 1998, Kimbrough et al. 1999, Pantsar-Kallio et al. 2001).

In Finnish stream waters the mean Cr concentration in the year 2000 was 0.52 mg/l (Koivuhuhta and Nikkarinen 2006). The Cr concentrations in drinking water from waterworks and single wells are in general low, median concentrations varying between 0.2–5.0 µg/l (Ahonen et al. 2008). According to Lahermo et al. (2002) median and mean values in Finnish dug wells (*n=739*) are 0.2 and 0.33 µg/l, whereas in drilled bedrock wells (*n=263*) the median Cr concentration is less than 0.2 µg/l. Maximum values detected were 3.76 and 2.5 µg/l for dug and drilled bedrock wells, respectively. The Ministry of Social Affairs and Health (STM 2000, 2001) has set 50 µg/l as the safe concentration limit for Cr.

Cr concentrations in drinking water usually originate from the materials in water supply network (Ahonen et al. 2008).

Cr has not been shown essential for plants though some positive effects of Cr application on plant growth and development have been reported (Peralta-Videa et al. 2009). Plants can absorb Cr both in the trivalent and hexavalent forms. Cr (III) is taken up passively by diffusion via non-specific carriers, whereas Cr(VI) enters the plant actively, likely through sulphate carriers (Singh et al. 2013). Within the roots, Cr(VI) is converted into Cr(III), which mainly retains in the roots in insoluble form (Kabata-Pendias and Mukherjee 2007, Peralta-Videa et al. 2009, Singh et al. 2013). Cr complexed with organic ligands is more easily translocated to the aerial parts of the plant (Singh et al. 2013). High Cr concentrations are toxic to plants causing e.g. alterations in metabolic processes, growth inhibition and decrease in chlorophyll synthesis (Peralta-Videa et al. 2009, Singh et al. 2013).

4.2 Environmental exposure to Cr

Mass balance for Cr in Finnish agricultural fields has been calculated by Mäkelä-Kurtto et al. (2007c). In their study, data were collected from different sources and Cr concentrations were measured from soil, crop plants and manure. In this assessment, mass balance calculations were done by the same methodology used with cadmium (see 3.2 Environmental exposure to Cd) and used parameters are listed in Table 12. Soil total concentration was based on *aqua regia* extractions by Mäkelä-Kurtto et al. (2007b). Cr input was summed from fertilization, deposition and liming. Annual liming demand was set to 400 kg/ha (http://www.farmit.net/kasvinviljely/kalkitus-ja-maanparannus/kalkitussanastoa) and Cr concentration in liming materials, 3.3 mg/kg, was taken from Mäkelä-Kurtto et al. (2007c). Deposition was set to 0.74 g Cr/ha (Mäkelä-Kurtto et al. 2007c). Fertilizer rate was based on the current recommended P rate for spring wheat, 10 kg P/ha. With the average P-concentrations in fertilizers (3.2%) reported in Mäkelä-Kurtto et al (2007c) this means that fertilizer rate of 310 kg/ha leads to 10 P kg/ha.

Following calculations were done:

1. The current dose of Cr from the commonly used mineral fertilizers in Finland was calculated according to Cr concentrations, 3.6 mg/kg DM, reported in Mäkelä-Kurtto et al. (2007c). Cr concentration against NP content of fertilizers averaged to 120 mg/kg P and 20 mg/kg N.

2. The current maximum dose of Cr was calculated according to the maximum allowed Cr concentration in fertilizers based on Finnish law of fertilizer products, 300 mg/kg DM.
3. A third possible dose of Cr was calculated according to the EU legislation proposal, where maximum 100 mg/kg DM is accepted for mineral fertilizers.

The output of Cr was summed from uptake in harvested yield and losses via leaching and eroded soil material. Calculation was done for 100 years, using spring wheat as the crop. Plant uptake in harvested part was based on soil-plant transfer coefficient (SPTC):

$$SPTC = \frac{Cplant}{Csoil}$$

$$Plant\ uptake = Yield \times Cplant$$

Where Cplant is the total Cr concentration in harvested plant organ per dry matter and Csoil is the aqua regia extractable Cr concentration per dry matter in 0 – 20 cm top layer of the soil. Yield level was set to the average yield during 2010 – 2014. Transfer coefficient from soil to wheat grains was taken from the results reported by Mäkelä-Kurtto et al. (2007a).

Leaching was based on distribution coefficient (Kd), which shows the relationship between the total concentration in soil (C*soil*, *aqua regia* or HNO_3/HF extraction) and soil pore water (*Cwater*). In case of Kd-values for Cr from the Finnish agricultural soils, values were found only from sandy soils (Lahdenperä 2014) where total Cr was extracted by HNO_3/HF.

$$Kd = \frac{Csoil}{Cwater}$$

$$Leaching = Cwater \times annual\ runoff$$

Annual runoff was set as 200 mm that was used in previous Cd mass balance calculations (Finnish Environment Institute 2000) and annual erosion based on Finnish Environment Institute (2000) was set to 500 kg/ha. The amount of eroded element was calculated:

$$Erosion = Csoil \times annual\ soil\ erosion$$

Table 12. Parameters used in the mass balance calculations of Cr.

Model parameters		Source
Soil concentration, mg Cr/kg	29.4	Mäkelä-Kurtto et al. 2007b, Table 1
Deposition, g Cr/ha/a	0.74	Mäkelä-Kurtto et al. 2007c, Table 40
Liming kg/ha/a	400	Recommended liming rate
Concentration in liming materials, mg Cr/kg	3.3	Mäkelä-Kurtto et al. 2007c, Table 17
Fertilizer rate, kg/ha	310	10 kg P/ha, and 3.2% P concentration
Transfer function, plant/soil	0.001	Median from Mäkelä-Kurtto et al. 2007a, Table 60
Yield kg/ha, 14% moisture	3750	Finnish agricultural statistics 2010 – 2014
Kd	9400	Lahdenperä 2014, Appendix 4c
Annual runoff, m^3/ha	2000	Finnish Environment Institute 2000
Annual erosion, kg/ha	500	Finnish Environment Institute 2000

After running the model calculations for 100 years using a code programmed by SAS statistical package, following output values were reported: Cr concentration in soil water, annual Cr leaching and erosion, Cr concentration in yield and annual Cr uptake in yield, soil Cr concentration and annual Cr balance.

Table 13. The effect of Cr concentrations in mineral fertilizers on Cr concentrations in soil water, yield and soil, and on leaching, erosion and annual balance of Cr in 100-years mass balance calculations.

mg Cr/ kg fert. DM	Year	Soil water µg/l	Leached g/ha/a	Eroded g/ha/a	Yield µg/kg DM	Yield uptake g/ha/a	Soil mg/kg	Annual balance g/ha
3.6	1	3.13	6.26	14.7	29.4	0.09	29.4	-17.8
	100	3.04	6.07	14.3	28.5	0.09	28.5	-17.2
100	1	3.13	6.26	14.7	29.4	0.09	29.4	11.9
	100	3.19	6.38	15.0	30.0	0.10	30.0	11.5
300	1	3.13	6.27	14.7	29.5	0.11	29.4	73.8
	100	3.51	7.03	16.5	33.0	0.12	33.0	71.2

In the 100-year time scale, the current realization of Cr inputs would lead to a negative Cr balance and consequently to a decreasing trend in the amounts of Cr leached, eroded and taken up by the crop (Table 13). All the other scenarios with higher Cr inputs generate a positive Cr balance. Using the current maximum level of Cr input (300 mg/kg fertilizer) the environmental loading (Cr leached and eroded) and Cr concentrations in crop yields would increase around 12 % from the level of the current realization. With the Cr inputs allowed in the EU proposal, the corresponding increases would be smaller, 2 %.

4.3 Risk assessment on Cr at increased levels of exposure

Toxicity of Cr depends on its species, Cr(VI) being highly toxic to bacteria, plants, and animals whereas Cr(III) not being particularly toxic (e.g. Kimbrough et al. 1999). Toxic exposure to Cr causes lung cancer, liver, kidney and gastric damage, and epidermal irritation and sensitization in humans. The estimated safe and adequate daily dietary intake for Cr is 50 to 200 µg but the safety range for Cr(III) is very large and no signs of Cr toxicity have been observed at intake levels up to 1 mg per day (Anderson 1997). More recently, EFSA has set an tolerable daily intake (TDI) for Cr(III) to be 300 µg/kg bw/day based on the lowest NOAEL in chronic oral toxicity studies on rats (EFSA 2014). Inhalation of industrial particles containing Cr is the principal Cr related health risk and Cr toxicity symptoms are usually limited to occupational exposure.

Plants evidence Cr toxicity symptoms at total soil Cr concentrations above 75–100 mg/kg, while an available concentration of only 1–5 mg/kg is critical (Zayed and Terry 2003). Excess Cr hampers different physiological processes via oxidative stress and enzyme inhibition (Shanker et al. 2005). In soil, Cr(VI) inhibits many biological processes, the most sensitive being denitrification (ED_{50} 63–730 nmol Cr /g soil) (Speir et al. 1995). According to Zayed and Terry (2003) the maximum acceptable Cr concentration for agricultural soils is in the range of 50 – 200 mg/kg and the guideline values for freshwaters 1 *µ*g/l for Cr(VI) and 8 *µ*g/l for Cr(III), for marine life 1 *µ*g/l for Cr(VI) and 50 *µ*g/l for Cr(III), for irrigation water 8 *µ*g/l for Cr(VI) and 5 *µ*g/l for Cr(III) and for drinking water 50 *µ*g/l for Cr(VI).

In general, the mobile and toxic Cr(VI) is short-lived in the soil environment as it tends to reduce into Cr(III). However, converting of Cr(III) to Cr(VI) in the environment is possible and thereby Cr(III) may as well pose a risk (Kimbrough et al. 1999).

4.3.1 Estimates of dietary intake and its sources

Cr is an essential nutrient for humans as it is required in sugar and fat metabolism (Anderson 1997). Varo and Koivistoinen (1980) reported an average daily supply of 29 µg Cr from Finnish foods, which is below the recommended level. In most industrialized countries, normal dietary intake of Cr is suboptimal (Anderson 1997). In the Finnish diet, the main sources of Cr are vegetables (23%), dairy products (21%), meat (18%), cereals (13%) and fish (2%) (Varo and Koivistoinen 1980). A notable portion, 23%, of the daily Cr intake comprises of beverages, confectionaries and condiments.

National exposure assessments have not been made in the recent years, but in the EFSA report (EFSA 2014), the dietary intake in EU countries was assessed. The 95th percentile of dietary intake in all age groups was below the TDI (300 µg/kg bw/day) of Cr(III). The highest exposure estimated for any age group in Finland (toddlers, 95th percentile of exposure, upper bound estimate) was 8.4 µg Cr(III)/kg bw/day and 184.2 ng Cr(VI)/kg bw/day (or 0.18 µg Cr(VI)/kg bw/day).

4.3.2 Estimated maximum acceptable annual load of Cr to a field hectare in Finland

In estimating the maximum acceptable load of a harmful element, degradation of the soil by accumulation of the element, degradation of the environment by increased loading of the element via leaching and erosion and impacts on human health via increased dietary exposure to the element need to be considered. Overall, any increases in these values can be regarded negative. As for Cr, the model calculations showed that the Cr input allowed for fertilizers in the EU proposal leads to an annual Cr input of roughly 32 g per ha in mineral fertilizers, liming and deposition. This results to minor increases in the amounts of Cr leached, eroded and taken up by the crop. Annual balance would be close to zero if maximum Cr content in mineral fertilizers would be 60 mg Cr/kg fertilizer.

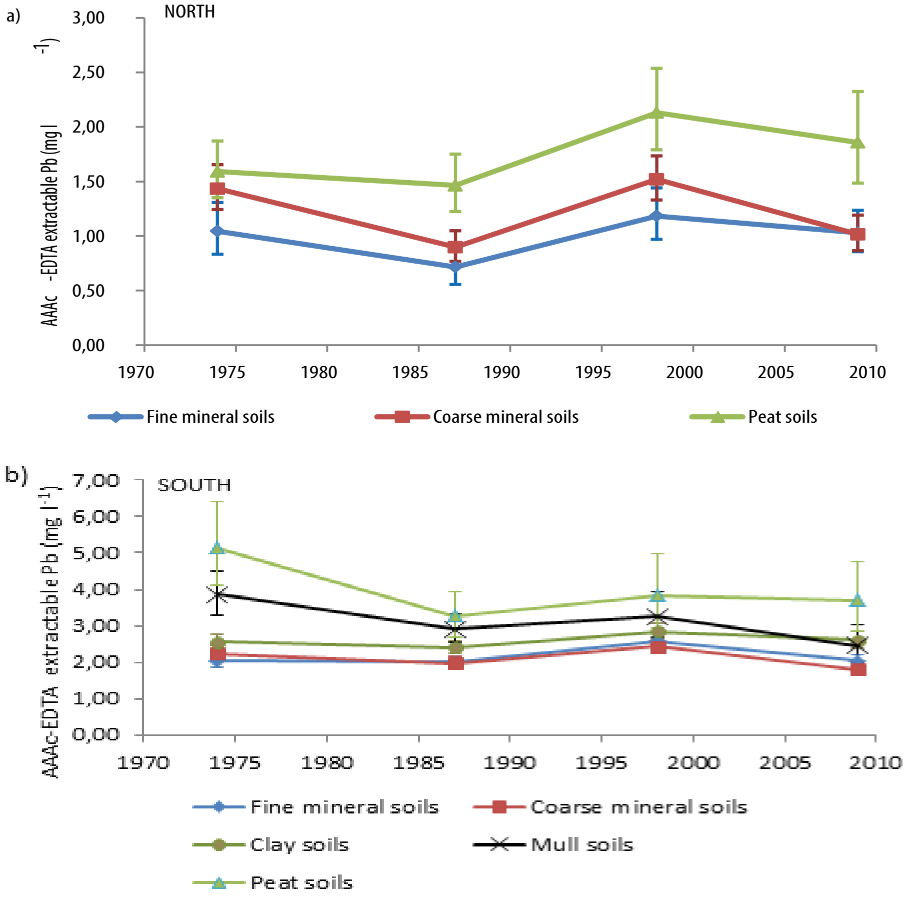
5 Lead (Pb)

5.1 Occurrence and behavior in the environment

Pb is non-essential for all living organisms and it is toxic, teratogenic and carcinogenic (e.g. Koljonen et al. 1992, Kabata-Pendias 2010), although the carcinogenic response is unlikely to occur at dietary intake levels (EFSA 2010). In the environment, lead occurs predominantly as Pb^{2+}, but also oxidation states of 0 and +4 are known (Koljonen et al. 1992, Kabata-Pendias 2010). Pb has four naturally occurring stable isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb), ^{208}Pb being the most common (Reimann et al. 2014d). Natural Pb in soils originates either from the parent material (geogenic origin) or from the decay of uranium (U) and thorium (Th) (radiogenic origin) (Kabata-Pendias 2010). Pb is highly chalcophilic thus it forms sulphur compounds, galena (PbS) being the main Pb mineral in bedrock (Koljonen et al. 1992, McBride 1994, Kabata-Pendias 2010, Reimann et al. 2014d). Other common Pb minerals are anglesite ($PbSO_4$), cerussite ($PbCO_3$), minium (Pb_3O_4), pyromorphite ($Pb_5(PO_4)_3Cl$) and mimetesite ($Pb_5(AsO_4)_3Cl$) (Kabata-Pendias 2010, Reimann et al. 2014d). In addition, Pb is present as an accessory element in many minerals especially K-feldspar and feldspars in general, mica, zircon and magnetite (Reimann et al. 2014d). In feldspars, Pb can replace potassium, strontium and also calcium (Koljonen et al. 1992). The anthropogenic sources for Pb are e.g. mining and smelting, coal combustion, car traffic and shooting activity (Reimann et al. 2014d). Regulations have eliminated the use of leaded petrol in the developed countries (Kabata-Pendias and Mukherjee 2007). In Finland, using leaded petrol was ended in 1993 (Pietarila et al. 2001) thus decreasing the Pb emissions in Finland significantly (Finnish Environment Institute 2014).

Globally, mean Pb concentration in soils is estimated to be 27 mg/kg, background values ranging in different countries from 18 to 32 mg/kg (Kabata-Pendias 2010). According to Mäkelä-Kurtto et al. (2007b) Pb concentrations (*aqua regia* extraction) in Finnish cultivated soils (plough layer) are on average 9.7 mg/kg DM (*n=338*) concentrations varying between 2.1 and 57.9 mg/kg DM. Median was 8.6 mg/kg DM. Concentrations varied between different soil types and regionally. Clay soils (*n=51*) contained significantly more Pb than coarse-textured mineral soils (*n=219*) or organic soils (*n=68*), average concentrations being 15.4, 8.3 and 9.7 respectively. In southern Finland concentrations were higher than in north mainly due to the abundance of clay soils, traffic and industry in southern Finland. Thus soil Pb concentrations reflect the regional variation in concentrations in glacial till (Koljonen et al. 1992). The same trend in Pb concentrations in Finnish arable soils according to soil types and regions was observed by Tarvainen and Kuusisto (1999). They also observed that concentrations were higher in topsoils (0–25 cm) than in subsoils (50 –75 cm). According to Reimann et al. (2012) Pb concentrations in Finnish agricultural soils are at the same level with other Nordic countries. In general, Pb concentrations (*aqua regia* extraction, 0–20 cm) are about two times lower in the Northern Europe (median 9.6 mg/kg) than in the Southern Europe (median 20 mg/kg), mainly due to the differences in geology (Reimann et al. 2012). At the continental level, concentrations (*aqua regia* extraction) vary between 1.6 and 1309 mg/kg, medians for agricultural and grazing land soils being 16 and 18 mg/kg, respectively (Reimann et al 2014d).

The Finnish national monitoring data shows a zig-zag trend in the AAAc-EDTA extractable (easily soluble) Pb concentrations in the top layer of cultivated soils between 1974 and 2009 (Fig. 3). From 1998 towards 2009 the soil soluble Pb has decreased in all regions. In organic soils, the soluble Pb concentrations tend to be higher than in mineral soils, and in clay soils slightly higher than in coarser-grained soils (Table 14). Highest mean concentrations were found in the south and lowest in the north region.



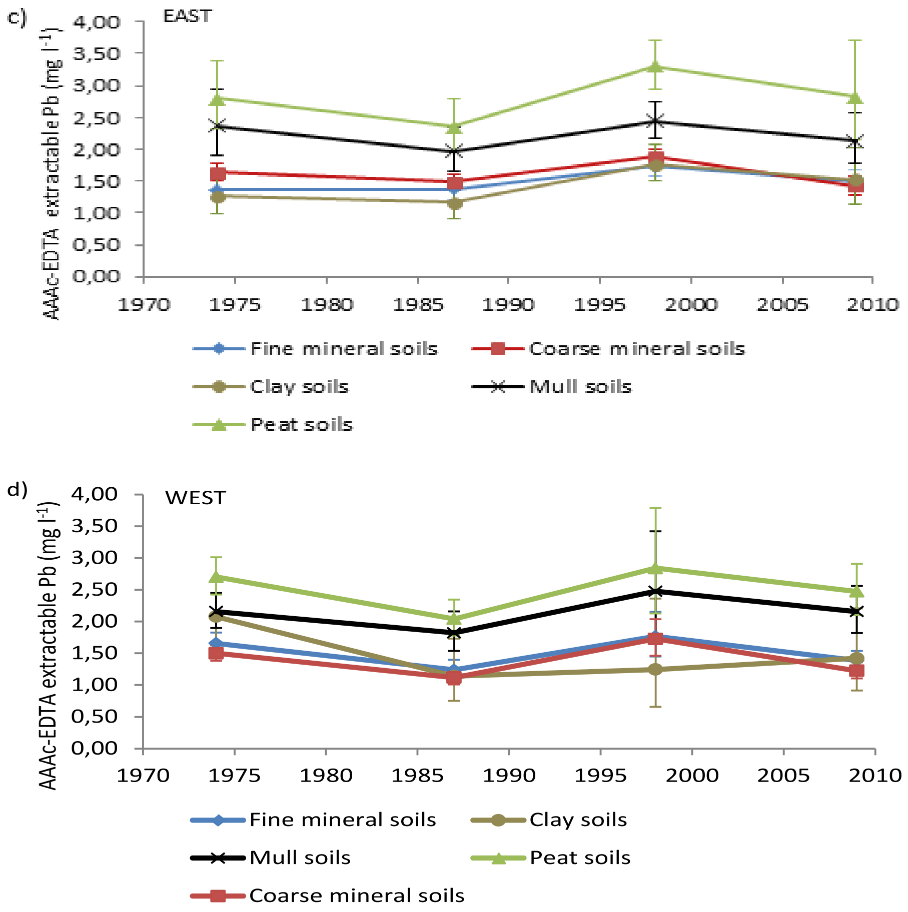


Figure 3. AAAc-EDTA extractable Pb in the 20-cm surface layer of cultivated fine and coarse mineral soils, clay, mull, and peat soils in north (a), south (b), east (c), and west (d) Finland. The graphs show estimated mean concentrations with 95% confidence intervals.

Table 14. Easily soluble (AAAc-EDTA extractable) lead concentrations (mg/l soil) in five soil types and four geographical regions of Finland. The data is from the latest sampling campaign of the Finnish national soil survey conducted in 2009. The figures are mean estimates ± standard error. The number of samples (n) are shown in italics.

	South	East	West	North
Fine mineral soils	1.6 ± 0.1 *n = 67*	1.3 ± 0.1 *n = 41*	1.4 ± 0.1 *n = 46*	1.0 ± 0.1 *n = 16*
Coarse mineral soils	1.6 ± 0.1 *n = 34*	1.3 ± 0.1 n = 66	1.1 ± 0.1 n = 49	1.0 ± 0.1 n = 24
Clay soils	2.6 ± 0.1 n = 81	1.5 ± 0.1 n = 22	1.5 ± 0.3 n = 3	n = 0
Mull soils	2.4 ± 0.4 *n = 7*	2.2 ± 0.2 *n = 15*	2.4 ± 0.2 *n = 15*	2.0 ± 0.5 n = 2
Peat soils	3.8 ± 0.7 *n = 5*	2.9 ± 0.4 *n = 7*	2.5 ± 0.2 *n = 17*	1.8 ± 0.2 *n = 9*

Natural Pb background concentrations in Finnish surface waters are low, the average and median concentrations being 0.30 µg/l and 0.21 µg/l (*n=1812*), respectively (Kohijoki 2013). Concentrations vary between 0-8.78 µg/l and are mainly under the environmental quality standard limit in EU's water framework directive (Kohijoki 2013). According to Kohijoki (2013), Pb concentrations for the most part don't reflect the geological conditions. Also in Finnish drinking waters, Pb concentrations are low, median concentrations varying between 0.05 – 5.0 µg/l (Ahonen et al. 2008). Only single samples exceeded the limit value (10 µg/l) set by the Ministry of Social Affairs and Health (STM 2000, 2001). According to Lahermo et al. (2002) median and mean values in Finnish dug wells (*n*=739) were 0.04 and 0.25 µg/l and in drilled bedrock wells (*n=263*) 0.15 and 0.42 µg/l, respectively. Maximum values were 18.7 µg/l and 6.96 µg/l for dug and drilled bedrock wells, respectively. Only one sample exceeded the safe concentration limit. Thus, the concentrations are usually so low that they don't pose a health risk. Pb concentrations in wells originate mainly from the technical appliances of wells rather than are geological or anthropogenic origin (Lahermo et al. 2002).

Bioavailability and ecotoxicity of Pb depends on its reactions in soil. In general, Pb is evaluated to be the most immobile heavy metal in soils, especially in reducing or non-acidic conditions (e.g. McBride 1994, Kabata-Pendias 2010). The main factors affecting Pb solubility are soil pH, soil constituents/sorption capacity of soil (e.g. clay, organic matter, Fe- and Mn-oxyhydroxides) and reduction/oxidation state. Under pH 6 the Pb^{2+} species becomes more dominant in soil solution, whereas at higher pH hydroxy species ($Pb(OH)^+$, $Pb(OH)_2$ and $Pb(OH)_3^-$) predominate (Bradl 2004). In soil, Pb^{2+} can be adsorbed electrostatically by negatively charged soil constituents (e.g. clay and metal hydroxides) meaning that it can be replaced by competing cations and thus be returned to soil solution which increases its bioavailability and ecotoxicity. In contrast, between the pH range 6 – 10 the predominant species $Pb(OH)^+$ can be sorbed to more strongly forming complexes with Al and Fe (oxy)hydroxides (e.g. Bradl 2004). It has also been reported that Pb^{2+} has a particularly high affinity for Mn oxides (McBride 1994). Thus above pH 6 Pb becomes more immobile. Pb also accumulates into the soil organic matter because Pb^{2+} forms strong complexes with sulfhydryl groups (McBride 1994). Sorption to the soil organic matter becomes more predominant with increasing pH (Kabata-Pendias 2010). However, sorption to the soil organic matter can also, in some cases, increase the solubility of Pb depending on the organic ligand. Complexes with fulvic acids are more soluble than those of humic acids (Kerndorff and Schnizer 1979). In reducing conditions Pb precipitates as PbS (e.g. McBride 1994). In conclusion, mobility of Pb is generally low, but it increases with decreasing pH. Consequently, Pb solubility can be decreased by liming that enhances the precipitation of Pb as hydroxides, phosphates or carbonates (Kabata-Pendias 2010).

Due to the strong sorption tendency in soil, Pb appears to be mostly unavailable to plants. The translocation of Pb within the plant is generally low and most of the Pb concentrates to the root tissues (McBride 1994, Kabata-Pendias 2010). However, certain plants can accumulate Pb (e.g. Kabata-Pendias and Mukherjee 2007). Plants can absorb Pb both from soil and from athmospheric pollution. The take-up is passive and it is restricted by high pH and low temperatures (Kabata-Pendias 2010). According to Kabata-Pendias (2010) the Pb uptake is dependent on several plant (e.g. genotype) and soil factors and on the concentration and Pb species occurring in soil. Low pH and P content in soil, presence of organic ligands and low sorption capacity of soil may enhance plant uptake of Pb (Kabata-Pendias and Mukherjee 2007, Kabata-Pendias 2010). Reviewed by Kabata-Pendias (2010), root vegetables accumulate Pb usually moderately, whereas leafy vegetables are high accumulators. In general, the Pb movement from soils to the edible parts of plants is considered to be low (McBride 1994, Kabata-Pendias 2010). Although several toxic effects of Pb on plant metabolism have been reported (e.g. photosynthesis, mitosis and water adsorption), the toxic symptoms (e.g. dark green leaves, wilting of older leaves, stunted foliage, brown short roots) are very unspecific (Kabata-Pendias 2010).

5.2 Environmental exposure to Pb

Mass balance for Pb in Finnish agricultural fields has been calculated by Mäkelä-Kurtto et al. (2007c). In their study, data were collected from different sources and Pb concentrations were measured from soil, plants and manure.

In this assessment, mass balance calculations were done by applying the same methodology as used with Cd (see 3.2 Environmental exposure to Cd) and used parameters are listed in Table 15. Total concentration of Pb in soil was based on *aqua regia* extractions by Mäkelä-Kurtto et al. (2007b). Pb input was summed from fertilization, deposition and liming. Annual liming demand was set to 400 kg/ha (http://www.farmit.net/kasvinviljely/kalkitus-ja-maanparannus/kalkitussanastoa) and Pb concentration in liming materials, 1.5 mg/kg, was taken from Mäkelä-Kurtto et al. (2007c). Deposition was set to 8.6 g/ha (Mäkelä-Kurtto et al. 2007c). Fertilizer rate was based on the current recommended P rate for spring wheat, 10 kg P/ha. With the average P-content in fertilizers (3.2%) reported in Mäkelä-Kurtto et al (2007c) and thus total fertilizer application would be 310 kg/ha.

Following calculations were done:

1. The current dose of Pb from the commonly used mineral fertilizers in Finland was calculated according to average Pb concentrations, 1 mg/kg DM, reported in Mäkelä-Kurtto et al. (2007c). Pb concentration against NP content of fertilizers averaged to 31 mg/kg P and 6 mg/kg N.

2. The current maximum dose of Pb was calculated according to the maximum allowed Pb concentration in fertilizers based on the Finnish law of fertilizer products, 100 mg/kg DM.
3. Third possible dose of Pb was calculated according to the EU legislation proposal, where maximum 150 mg/kg DM is accepted for mineral fertilizers.

The output of Pb was summed from uptake in harvested yield and losses via leaching and eroded soil material. Calculation was done for 100 years, using spring wheat as the crop. Plant uptake in harvested part was based on soil-plant transfer coefficient (SPTC):

$$SPTC = \frac{Cplant}{Csoil}$$

$$Plant\ uptake = Yield\ \times Cplant$$

Where C*plant* is the total Pb concentration in harvested plant part per dry matter and C*soil* is the aqua regia extractable Pb concentration per dry matter in 0–20 cm top layer of the soil. Yield level was set to the average yield during 2010–2014. Transfer coefficient from soil to wheat grains was taken from the results reported by Mäkelä-Kurtto et al. (2007a).

Leaching was based on distribution coefficient (Kd), which shows the relationship between the total soil concentration (C*soil*, *aqua regia* or HNO_3/HF extractable) and soil pore water (*Cwater*). In case of Kd-values for Pb from the Finnish agricultural soils, values were only found for sandy soils (Lahdenperä 2014) where total Pb was extracted by HNO_3/HF.

$$Kd = \frac{Csoil}{Cwater}$$

$$Leaching = Cwater \times annual\ runoff$$

Annual runoff was set as 200 mm and annual erosion as 500 kg/ha that were used in previous Cd mass balance calculations (Finnish Environment Institute 2000). The amount of eroded element was calculated:

$$Erosion = Csoil \times annual\ soil\ erosion$$

Table 15. Parameters used in the mass balance calculations of Pb.

Model parameters		Source
Soil concentration, mg Pb/kg	8.6	Mäkelä-Kurtto et al. 2007b, Table 1
Deposition, g Pb/ha/a	8.6	Mäkelä-Kurtto et al. 2007c, Table 40
Liming kg/ha/a	400	Recommended liming rate
Concentration in liming materials, mg Pb/kg	1.5	Mäkelä-Kurtto et al. 2007c, Table 17
Fertilizer rate, kg/ha	310	10 P kg/ha, and 3.2% P concentration
Transfer function, plant/soil	0.001	Median from Mäkelä-Kurtto et al. 2007a, Table 60
Yield kg/ha, 14% moisture	3750	Finnish agricultural statistics 2010 – 2014
Kd	15900	Lahdenperä 2014, Appendix 4c
Annual runoff, m^3/ha	2000	Finnish Environment Institute 2000
Annual erosion, kg/ha	500	Finnish Environment Institute 2000

After running the model calculations for 100 years using a code programmed by SAS statistical package, following output values were reported: Pb concentration in soil water, annual Pb leaching and erosion, Pb concentration in yield and annual Pb uptake in yield, soil Pb concentration and annual Pb balance.

Table 16. Output values for 100-years mass balance calculations of Pb.

mg Pb/ kg fert. DM	Year	Soil water µg/l	Leached g/ha/a	Eroded g/ha/a	Yield µg/kg DM	Yield g/ha/a	Soil mg/kg	Annual balance g/ha
0.19	1	0.54	1.08	4.30	8.60	0.03	8.60	4.10
	100	0.55	1.11	4.40	8.80	0.03	8.80	3.97
100	1	0.54	1.08	4.31	8.62	0.03	8.62	34.68
	100	0.65	1.30	5.15	10.31	0.03	10.31	33.62
150	1	0.54	1.08	4.31	8.62	0.03	8.63	50.18
	100	0.70	1.39	5.53	11.07	0.04	11.07	48.64

In the 100-year time scale, the current realization of Pb inputs would lead to small positive Pb balance, and the change in the amounts of Pb leached, eroded and taken up by the crop would be minimal (Table 16). All the other scenarios with higher Pb inputs generate a positive Pb balance. Using the current maximum level of Pb input (100 mg/kg fertilizer), the environmental loading (Pb leached and eroded) and Pb concentrations in crop yields would increase around 20 % from the level of the current realization. With the Pb inputs allowed in the EU proposal, the corresponding increases would be higher, close to 30 %.

5.3 Risk assessment on Pb at increased levels of exposure

Pb accumulates in the human body, mainly in the skeleton where its biological half-time can be as high as two decades. However, changes in the bone metabolism caused by e.g. pregnancy can release the accumulated lead back to the circulation. Thus the foetus or newborn can be exposed to lead taken up by the mother many years previously (Flora et al. 2011).

Lead is a known neurotoxicant and especially toxic to developing nervous system of foetuses and children. Other harmful effects are e.g. nephrotoxicity, anaemia caused by disruption of heme biosynthesis, disruptions of the reproductive system, disruption of bone mineralization, and increasing blood pressure.

Knowledge on the toxicity of lead has increased during the last decade. On the basis of new toxicological information EFSA has recognized that the previous tolerable intake levels have not been low enough to protect all consumers from the harmful effects of lead as there is no evidence of a threshold for a number of critical health effects. EFSA has published a $BMDL_1$ value of 0.5 µg Pb/kg bw/day (or 12 µg Pb/l blood) based on developmental neurotoxicity, and a $BMDL_{10}$ value of 0.63 µg/kg bw/day based on kidney effects (EFSA 2010). These values are lower uncertainty limits to doses which already increase the risk of harmful effect.

IARC has in 1987 classified Pb as a Group 2A carcinogen, i.e., possibly causing cancer to humans. Pb does not react directly with DNA, but it disturbs its repair mechanisms and can cause oxidative stress.

Similarly as for humans, Pb is toxic to other animals, plants and micro-organisms. According to the review by Demayo et al. (1982) toxicity symptoms in plants (inhibition of growth, reduction of photosynthesis, mitosis and water absorption) appear at relatively high soil Pb concentrations. Decreases in yield have been observed at concentrations exceeding 50–125 mg Pb/kg but detrimental effects occur only at total Pb concentrations of several hundred mg/kg of soil. A Health and Environmental Investigation Level of 300 mg/kg soil has been presented for Pb (Markus and McBradney 2001). In aquatic ecosystems, Pb concentrations of 1 to 500 mg/l cause acute lethality in invertebrates and fish but adverse sublethal effects are known to occur already at concentrations of 0.007 to 0.020 mg/l (Demayo et al. 1982). Chronic exposure to Pb concentrations over 0.01–0.02 mg/l likely have detrimental effects on aquatic populations.

5.3.1 Estimates of dietary intake and its sources

The exposure of consumers to lead has decreased significantly in the years after lead-containing fuels were banned.

EFSA estimated in 2012 the Pb dietary exposure in the European population from national consumption data and concentration data collected from the EU Member States. The mean dietary exposures (middle bound estimate) of Finnish toddlers, other children and adults were estimated by EFSA to be 1.35, 1.17 and 0.54 µg/kg bw/day. The 95th percentiles of dietary exposure for these age groups were 2.84, 1.76 and 0.92 µg/kg bw/day. The mean exposure of the toddlers was slightly above the European median, but the high exposure was highest of the surveys. The estimates for other children and adults were slightly above the European median. Important lead sources in the diet according to the EFSA assessment were grains and grain-based products, milk and dairy products, non-alcoholic beverages, and vegetables and vegetable products. The relative contributions of these groups were different for the different age groups, with tap water and potatoes contributing most to the toddlers and the contribution of bread and beverages increasing among the older consumers. (EFSA 2012b)

In a recent national risk assessment (Suomi et al. 2015), based on nationally collected concentration data and individual consumption data of children between 1 and 6 years of age, the mean Pb exposure was 0.58 to 0.77 µg/kg bw/day for 1-year-olds, 0.40 to 0.61 µg/kg bw/day for 3-year-olds and 0.34 to 0.50 µg/kg bw/day for 6-year-olds. The values are lower than those calculated by EFSA, mainly because of lower concentrations in the national data. The Pb levels in Finnish milk has decreased over the years, and the lower exposure values were calculated using milk data only from the last 6 years (when all results were below the limit of detection) while the larger exposure had milk data spanning over 12 years. The 95th percentile of exposure was determined to be 1.25, 0.83 and 0.68 µg/kg bw/day for children aged 1, 3 and 6 years, respectively (Suomi et al. 2015). Due to the high consumption of milk and dairy products, the part of the age group exceeding the BMDL value 0.5 µg/kg bw/day (based on developmental neurotoxicity) was over 80% of 1- and 3-year-olds and over 50 % of 6-year-olds when milk data spanning over 12 years were used in the calculations. With use of the more recent milk data, only 14 % of 3-year-olds and 1 % of 6-year-olds had exposure above the BMDL.

The main lead sources in the national risk assessment were cereals, milk (although as seen above, the contribution of milk products has decreased in the last years due to declining concentrations), meat and beverages. The contribution of drinking water was minimal, thanks to very low levels of lead in Finnish tap water.

Effect of change in the Pb concentrations during 100 years

The effect on the total dietary exposure of Finnish children was estimated on the assumption that only the concentration in cereals would change and all other sources of exposure, as well as consumption habits of the children, would remain unchanged.

Comparison was made with the total dietary exposure (including exposure from drinking water) of 3-year-old Finnish children (calculated in Suomi et al., 2015).

With the current realization of Pb inputs, leading to an increase of 2% in the Pb content of cereals), the total dietary exposure of 3-year-old Finns would increase by 0.6% at age group median and by 0.4% at the 95th percentile, corresponding to the high-intake group. The Pb input level allowed in the EU proposal would increase the cereal Pb content by 29 %. This would lead to an increase of total exposure by 9% at age group median level and by 6 % at the 95th percentile.

5.3.2 Estimated maximum acceptable annual load of Pb to a field hectare in Finland

In estimating the maximum acceptable load of a harmful element, degradation of the soil by accumulation of the element, degradation of the environment by increased loading of the element via leaching and erosion and impacts on human health via increased dietary exposure to the element need to be considered. Overall, any increases in these values can be regarded as negative. As for Pb, annual inputs exceeding ca. 0.5 g Pb/ha from mineral fertilizers, liming and deposition lead to increased amounts of Pb leached, eroded and taken up by the crop. Although Pb emissions have decreased considerably during the last decades, Pb deposition is still main source of Pb into the Finnish soils (Ruoho-Airola et al. 2014). Deposition alone seems to lead to positive Pb balance and increase in soil Pb concentrations.

6 Mercury (Hg)

6.1 Occurrence and behavior in the environment

Hg is non-essential, highly toxic global pollutant, that bioaccumulates in the food chain in methylated form (Reimann et al. 2014e). The oxidation states of Hg are 0, +1, +2 and +3, of which the oxidation state of +2 is the dominant form in nature (Reimann et al. 2014e). According to Reimann et al. (2014e) Hg has seven naturally occurring isotopes, ^{202}Hg, ^{200}Hg, ^{199}Hg and ^{201}Hg being the most abundant forms. Hg is chalcophile and thus it has a tendency to form sulphur compounds, the most common mineral being cinnabar (HgS) (McBride 1994, Kabata-Pendias 2010). According to Reimann et al. (2014e), Hg concentrations are very low in the most common rock types except in black shale. In soil environment Hg is originated both from natural (parent material and volcanic activity) and anthropogenic sources (Kabata-Pendias 2010, Reimann et al. 2014e). The main anthropogenic sources are coal burning, waste incineration, crematoria, chlor-alkali production, paper factories, metal smelters and mining (Kabata-Pendias 2010, Reimann et al. 2014e). Earlier it has also been used as fungicidal seed treatment and some sewage sludges can also contain elevated Hg concentrations. (Reimann et al. 2014e). In Finland, atmospheric emissions have decreased between 1990 and 2012 from 1.2 t to 0.8 t, variation being 0.5–1.2 t (Finnish Environment Institute 2014). The main Hg sources in 2012 were energy production and industrial processes (Finnish Environment Institute 2014). According to Kyllönen et al. (2014), the domestic anthropogenic emissions are a minor Hg source to Finnish people.

Worldwide average Hg concentration in soils is estimated to be 1.1 mg/kg, with a range from 0.58 to 1.8 mg/kg (Kabata-Pendias 2010). According to Mäkelä-Kurtto et al. (2007b) the mean Hg concentration (*aqua regia* extraction) in Finnish agricultural soils (plough layer) is on average 0.047 mg/kg DM (*n=338*), concentrations varying from 0.008 to 0.143 mg/kg DM, and median being 0.039 mg/kg DM. Concentrations varied between different soil types and also regionally. The highest Hg concentrations were in organic soils (0.072 mg/kg DM, *n=68*), almost twice as high as in coarse-textured mineral soils (0.040 mg/kg DM, *n=219*) and clay soils (0.045 mg/kg DM, *n=51*). Therefore, regionally the highest contents were found in the peat-dominated regions. In general, Hg is concentrated in surface soils (Kabata-Pendias 2010). According to Reimann et al. (2014e) Hg concentrations in Finnish agricultural soils are at the same level than in other Scandinavian countries. The median Hg concentration (*aqua regia* extraction, 0–20 cm) in northern Europe is 0.024 mg/kg and in southern Europe 0.036 mg/kg, although there are local Hg anomalies in Scandinavia (Ottesen et al. 2013). The Hg concentrations in Scandinavia are related to organic rich soils to which Hg has a strong tendency to be bound (Ottesen et al. 2013). At the continental level, Hg concentrations in European agricultural soils (0–20 cm, *n*=2108) vary between <0.003 and 1.6 mg/kg, and in grazing land (0–10 cm, *n*=2024) soils between <0.003 and 3.1 mg/kg (Ottesen et al. 2013). The median for agricultural soils is 0.030 mg/kg, and 0.035 mg/kg for grazing land (Ottesen et al. 2013).

The easily soluble (AAAc-EDTA extractable) Hg concentrations tend to be higher in organic than mineral soils and somewhat lower in the north than in other regions in Finland.

Table 17. Easily soluble (AAAc-EDTA extractable) Hg concentrations (mg/l soil) in five soil types and four geographical regions of Finland. The data is from the third sampling campaign of the Finnish national soil survey conducted in 1998. The figures are mean estimates ± standard error. The numbers of samples (*n*) are shown in italics.

	South	East	West	North
Fine mineral soils	0.04 ± 0.00 *n = 37*	0.03 ± 0.00 *n = 20*	0.03 ± 0.00 n = 20	0.03 ± 0.00 n = 5
Coarse mineral soils	0.04 ± 0.00 *n = 22*	0.04 ± 0.00 *n = 47*	0.03 ± 0.00 *n = 30*	0.02 ± 0.00 *n = 21*
Clay soils	0.05 ± 0.00 n = 42	0.04 ± 0.01 n = 3	0.03 ± 0.01 n = 2	n = 0
Mull soils	0.08 ± 0.01 *n = 4*	0.07 ± 0.01 *n = 10*	0.06 ± 0.01 *n = 7*	0.04 ± 0.01 *n = 2*
Peat soils	0.09 ± 0.02 *n = 3*	0.09 ± 0.01 *n = 12*	0.07 ± 0.01 *n = 14*	0.07 ± 0.01 *n = 6*

Hg concentrations in Finnish surface waters are usually low and according to the report by Verta et al. (2010) median concentrations vary between 0.001 and 0.011 µg/l, concentrations being higher in humus rich waters. Verta et al. (2010) also reviewed methylmercury concentrations reported in different studies. Concentrations varied between 0.01–14 ng/l. The Hg concentrations in drinking water from waterworks and single wells are in general low. According to the study by Ahonen et al. (2008) Hg concentrations are under the limit value (1.0 µg/l) set by the Ministry of Social Affairs and Health (STM 2000, 2001). In the study median concentrations varied between 0.1–0.2 µg/l.

The behavior of Hg in soils is highly dependent on its species, which is affected by several factors including soil conditions (e.g. redox potential, pH, organic matter content, soil type) and the concentrations of Hg and other ions (e.g. Gabriel and Williamson 2004, Kabata-Pendias 2010). According to the review by Gabriel and Williamson (2004) dissolved ions, pH and redox potential are the main factors affecting the Hg speciation in solution. In general, Hg has strong tendency to be complexed with Cl^-, OH^- and S^{2-}, as well as S-containing functional groups of organic ligands (Schuster 1991). Gabriel and Williamson (2004) reviewed that the main Hg species under naturally occurring pH- and redox-range and Cl^- concentrations are $Hg(OH)_2$, $HgCl_2$, HgS, Hg^0 and $HgOHCl^0$. According to Schuster (1991), $HgCl_2$ and $Hg(OH)_2$ are the most predominant forms appearing in wide pH range, whereas HgS is precipitated in reducing conditions. Furthermore, Hg can be methylated in soils to methyl-Hg (CH_3Hg^+) and di-methyl-Hg ($(CH_3)_2Hg$), from which di-methyl-Hg is highly volatile and insoluble in water, whereas methyl-Hg is more water soluble (Gabriel and Williamson 2004). Methylated forms occur under intermediate redox conditions (Kabata-Pendias 2010), but usually methyl-Hg concentrations are low (Gabriel and Williamson 2004). According to Gabriel and Williamson (2004), methyl-Hg has a propensity for significant bioaccumulation even at low concentrations.

In soils, Hg can be bound to mineral and organic surfaces, methylated, oxidized/reduced, volatilized or precipitated. In general, Hg is bound strongly to soil constituents, especially to organic matter and oxides (Gabriel and Williamson 2004). The Hg sorption is dependent on pH, sorption being highest in the pH range of 4 to 5 (Kabata-Pendias 2010). According to Schuster (1991) organic material predominates as a sorbent for inorganic Hg in acid soils, whereas in neutral and alkaline soils and soils with low organic matter content, iron oxides and clay minerals are more important. The predominance of organic material as a sorbent for Hg is due to its S-containing functional groups, to which Hg has high affinity for (Schuster 1991). Methyl-Hg is less strongly bound to soil than Hg^{2+} (Gabriel and Williamson 2004). Due to the strong binding to soil constituents, Hg concentrations in soil solution are often low (Schuster 1991, Kabata-Pendias 2010), about 2.5 µg/l (Kabata-Pendias 2010). However, Cl^- ions in soil solution decrease Hg sorption due to formation of highly stable Hg-Cl complexes that are quite poorly sorbed (Schuster 1991, Gabriel and Wiliamson 2004, Kabata-Pendias 2010). Therefore, leaching is possible when Cl^- concentrations are increased and/or pH decreased, although in general Hg leaching from topsoil is generally insignificant (Schuster 1991, Gabriel and Williamson 2004). Leaching becomes more probable in acidic soils with low organic matter content (Schuster 1991).

Transformation of organomercury compounds (especially methylation) is the most important step in Hg cycling in the environment, due to bioavailability of methyl-Hg (Kabata-Pendias 2010). Hg methylation by different bacteria and fungi occurs in both anaerobic and aerobic conditions in soils (Gabriel and Williamson 2004, Kabata-Pendias 2010), but it can also happen abiotically (Kabata-Pendias 2010). According to Kabata-Pendias (2010) organic matter can either enhance or reduce methylation. Labile methyl groups can be released from organic matter and form organomercury molecules, but organic matter has also been reported to convert organic Hg and Hg^{2+} ions to the elemental Hg. However, demethylation (abiotic or biotic) is much slower process than methylation (Kabata-Pendias 2010).

Reduction of Hg^{2+} to Hg^0 is also an environmentally important process due to the Hg^0 volatilization (Gabriel and Williamson 2004). In general, reduction occurs under reducing conditions abiotically (e.g. Fe^{2+} and humic and fulvic compounds as reductants) or biotically (Gabriel and Williamson 2004). According to Gabriel and Williamson (2004) availability of electron donors, low redox potential and sunlight intensity are some of the most important factors affecting the abiotic reduction intensity. Furthermore, Hg adsorption decreases the readiness for biological transformations because bound Hg is less available for reduction (Gabriel and Williamsson 2004). In general, Hg reduction and evaporation decrease with increasing organic matter and Cl^- content (Gabriel and Williamsson 2004). Also decreased moisture content reduces Hg reduction (Gabriel and Williamsson 2004). The volatilization of Hg^0 is influenced mainly by soil structure, sorption and the temperatures of air and soil (Gabriel and Williamson 2004).

In general, Hg availability to plants is low due to the strong binding to the soil constituents (Patra and Sharma 2000). Therefore mainly the same factors (e.g. organic matter and oxide content) that affect Hg sorption in the soil, affect the plant uptake (Patra and Sharma 2000). Often concentrations in plants increase together with increased Hg concentrations in soil, but also specific local soil conditions influence accumulation of Hg in plants (Kabata-Pendias 2010). In addition to the soil factors, plants differ in their ability to take up Hg (Kabata-Pendias and Mukherjee 2007, Kabata-Pendias 2010) and some plant species (e.g. lichens, carrots, lettuce) tend to take up more Hg than others (Kabata-Pendias and Mukherjee 2007). Some plants are also more sensitive to Hg than others (Kabata-Pendias and Mukherhee 2007, Kabata-Pendias 2010), as example sugar beets, corn and roses are the most sensitive plants (Kabata-Pendias and Mukherjee 2007). Within the plant, Hg is translocated between various plant tissues, although it is strongly bound to amino acids in many proteins and enzymes (Kabata-Pendias 2010). Plants can also take up Hg^0 from the atmosphere (Kabata-Pendias and Mukherjee 2007, Kabata-Pendias 2010). In plant, the airborne Hg^0 is converted into Hg^{2+} and translocated within the plant so that most of it is located in leafy parts of plants (Kabata-Pendias and Mukherjee 2007). When taken up from soil, Hg tends to accumulate in roots (Patra and Sharma 2000). As for the organic Hg compounds, those having a relatively small degree of dissociation and adsorbability (e.g. methylated Hg), are taken up readily by plants (Kabata-Pendias 2010). The most toxic Hg species to plants are volatile Hg^0 and methylated Hg forms (Kanata-Pendias 2010). Hg toxicity symptoms are severe stunting of seedlings and roots, leaf chlorosis, browning of leaf points, inhibition of photosynthesis and K uptake, which results to yield reductions (Kabata-Pendias and Mukherjee 2007, Kabata-Pendias 2010). According to Kabata-Pendias (2010) the high affinity to Hg of sulfhydryl groups is the main reason for the metabolic disruptions in plants caused by Hg.

6.2 Environmental exposure to Hg

Mass balance for Hg in Finnish agricultural fields has been calculated by Mäkelä-Kurtto et al. (2007c). In their study, data were collected from different sources and Hg concentrations were measured from soil, plants and manure.

In this assessment, mass balance calculations were done by the methodology used with cadmium (see 3.2 Environmental exposure to Cd) and used parameters are listed in Table 18. Soil total concentration was based on *aqua regia* extractions by Mäkelä-Kurtto et al. (2007b). Hg input was summed from fertilization, deposition and liming. Annual liming demand was set to 400 kg/ha (http://www.farmit.net/kasvinviljely/kalkitus-ja-maanparannus/kalkitussanastoa) and Hg concentration in liming materials, 0.01 mg/kg, was taken from Mäkelä-Kurtto et al. (2007c). Deposition was set to 0.052 g/ha (Kyllönen et al. 2012). Fertilizer rate was based on the current recommended P rate for spring wheat, 10 P kg/ha. With the average fertilizer P-concentrations (3.2%) reported in Mäkelä-Kurtto et al (2007c) this means that fertilizer rate of 310 kg/ha leads to 10 P kg/ha.

Following calculations were done:

1. The current dose of Hg from the commonly used mineral fertilizers in Finland was calculated according to average Hg concentrations, 0.01 mg/kg DM, reported in Mäkelä-Kurtto et al. (2007c). Hg concentration against NP content of fertilizers averaged to 0.40 mg/kg P and 0.07 mg/kg N.
2. The current maximum dose of Hg was calculated according to the maximum allowed Hg concentration in fertilizers based on Finnish law of fertilizer products, 1.0 mg/kg DM.
3. Third possible dose of Hg was calculated according to the EU legislation proposal, where maximum 2.0 mg/kg DM is accepted for mineral fertilizers.

The output of Hg was summed from uptake in harvested yield and losses via leaching and eroded soil material. Calculation was done for 100 years, using spring wheat as the crop. Plant uptake in harvested organ was based on soil-plant transfer coefficient (SPTC):

$$SPTC = \frac{Cplant}{Csoil}$$

$$Plant\ uptake = Yield \times Cplant$$

Where C*plant* is the total Hg concentration in harvested plant organ per dry matter and C*soil* is the *aqua regia* extractable Hg concentration in 0 – 20 cm top layer of the soil. Yield level was set to the average yield during 2010 – 2014. Transfer coefficient from soil to wheat grains was taken from the results reported by Sheppard (2011).

Leaching was based on distribution coefficient (Kd), which shows the relationship between the the total (C*soil*, *aqua regia* or HNO_3/HF extractable) concentration in soil and concentration in soil pore water (*Cwater*). Kd-values for Hg were found from the study of Sheppard et al. 2011 in Sweden, where the Kd value of glacial clay with 10% organic matter content and 35 % clay content was selected. They had extracted total Hg with HNO_3/HCl/HF solution.

$$Kd = \frac{Csoil}{Cwater}$$

$$Leaching = Cwater \times annual\ runoff$$

Annual runoff was set as 200 mm that was used in previous Cd mass balance calculations (Finnish Environment Institute 2000) and annual erosion based on the same source to 500 kg/ha. The amount of eroded element was calculated:

$$Erosion = Csoil \times annual\ soil\ erosion$$

Table 18. Parameters used in the mass balance calculations of Hg.

Model parameters		Source
Soil concentration, mg Hg/kg	0.047	Mäkelä-Kurtto et al. 2007b, Table 1
Deposition, g Hg/ha/a	0.052	Kyllönen et al. 2012
Liming kg/ha/a	400	Recommended liming rate
Concentration in liming materials, mg Hg/kg	0.01	Mäkelä-Kurtto et al. 2007c, Table 17
Fertilizer rate, kg/ha	310	10 P kg/ha, and 3.2 % P concentration
Transfer function, plant/soil	0.025	Sheppard et al. 2011 Table 3 – 7
Yield kg/ha, 14% moisture	3750	Finnish agricultural statistics 2010 – 2014
Kd	3000	Sheppard et al. 2011. Table 3 – 3
Annual runoff, m^3/ha	2000	Finnish Environment Institute 2000
Annual erosion, kg/ha	500	Finnish Environment Institute 2000

After running the model calculations for 100 years using a code programmed by SAS statistical package, following output values were reported: Hg concentration in soil water, annual Hg leaching and erosion, Hg concentration in yield and annual Hg uptake in yield, soil Hg concentration and annual Hg balance.

Table 19. The effect of Hg concentrations in fertilizers on Hg concentrations in soil water, yield and soil, and on leaching, erosion, yield uptake and annual balance of Hg in 100-years mass balance calculations.

mg Hg/ kg fert. DM	Year	Soil water µg/l	Leached g/ha/a	Eroded g/ha/a	Yield µg/kg DM	Yield uptake g/ha/a	Soil mg/kg	Annual balance g/ha
0.01	1	0.016	0.031	0.024	1.18	0.004	0.047	0.005
	100	0.016	0.032	0.024	1.18	0.004	0.047	0.005
1	1	0.016	0.031	0.024	1.18	0.004	0.047	0.311
	100	0.021	0.041	0.031	1.55	0.005	0.062	0.294
2	1	0.016	0.032	0.024	1.18	0.004	0.047	0.621
	100	0.026	0.051	0.039	1.92	0.006	0.077	0.586

In the 100-year time scale, the current realization of Hg inputs would lead to small positive Hg balance and the change in the amounts of Hg leached, eroded and taken up by the crop would be minimal (Table 19). All the other scenarios with higher Hg inputs generate a positive Hg balance. Using the current maximum level of Hg input (1 mg/kg fertilizer) the environmental loading (Hg leached and eroded) and Hg concentrations in crop yields would increase around 32% from the level of the current realization. With the Hg inputs allowed in the EU proposal, the corresponding increases would be clearly higher, 64 %.

6.3 Risk assessment on Hg at increased levels of exposure

Mercury is found in nature both as inorganic compounds and as organic compounds. Organic mercury is the main form in fish and seafood, but it is hardly found in other foods.

These different forms have different toxic effects in the human body. Inorganic Hg is less toxic than organic Hg species, especially methylmercury. Inorganic Hg is most toxic to the kidney while methyl mercury is a strong neurotoxicant and also may cause premature delivery or other reproductive system effects, and developmental immunotoxicity (EFSA 2012c). Inorganic Hg also affects the nervous system, although less strongly than the organic form. Methyl mercury has also been linked to cardiovascular toxicity.

US EPA has determined a safe reference dose for methyl mercury: 0.1 µg/kg bw/day. JECFA has set a provisional tolerable weekly intake value for methyl mercury at 1.6 µg/kg bw/week and EFSA at 1.3 µg/kg bw/week. For inorganic mercury EFSA and JECFA have set the same tolerable weekly intake value: 4 µg/kg bw/week expressed as Hg. (EFSA 2012c) The guidance values of methyl mercury have been determined on the basis of neurological effects (mainly cohort studies of humans) and that of inorganic mercury on the basis of kidney effects (in animal tests).

Ecotoxicity of Hg depends highly on its chemical form, the organic compounds being more toxic than the inorganic species (e.g. Ullrich et al. 2001). Boening (2000) presents the following concentration levels for detrimental effects induced by Hg: harmful effects to microorganisms in culture medium at 5 µg/l of inorganic Hg and 0.5 µg/l of organo-Hg compounds, no-observed-effect-level for freshwater microorganisms 1–50 µg/l inorganic Hg and 10-100 times less for organo-Hg compounds, for aquatic plants 1 mg/l for inorganic Hg and 10-100 less for organic Hg. As for fish, lethal responses occur in freshwater fish kept in static conditions at Hg concentrations exceeding 30 µg/l, and in sensitive aquatic invertebrates, acute toxicity is caused at Hg levels of 1–10 µg/l of inorganic Hg and less than 0.04 µg/l for methyl-Hg. Aquatic organisms readily accumulate Hg and it tends to enrich in the food chain. For terrestrial organisms, Hg is likewise toxic affecting e.g. microbial degradation (Patra and Sharma 2000). The absorption of Hg from soil by plants is restricted and terrestrial plants are rather insensitive to Hg (Boening 2000).

6.3.1 Estimates of dietary intake and its sources

According to Varo and Koivistoinen (1980) the average daily supply of Hg from Finnish foods was 5.7 µg, of which over 60% was derived from fish.

In 2012 EFSA estimated the dietary exposure of European consumers to mercury and methylmercury. In the estimation, relative amounts of inorganic and organic mercury were for the most part estimated as most of the concentration data was available as total mercury. The high-intake consumer groups had methyl mercury exposure at the levels of the TWI (1.3 µg/kg bw/week, based on developmental neurotoxicity), and consumers who eat plenty of fish in Europe may exceed the TWI up to approximately six-fold.

Methyl mercury is mainly found in fish and seafood, and the main component in other food groups is the less toxic inorganic mercury. In the EFSA 2012c estimate, the exposure of Finnish children and adults to inorganic mercury was above the EU median for the 95th percentile of exposure, but the estimated exposure to inorganic mercury from dietary sources does not exceed the TWI (4.0 µg/kg bw/week, based on kidney damage).

According to a recent national risk assessment (Suomi et al. 2015) on the dietary heavy metal intake of Finnish children, the main sources of inorganic mercury exposure were foods for which there were no national concentration data available and mean values reported in the EFSA risk assessment were used instead. The main sources were vegetables, meat and beverages. Also in the national risk assessment, the mercury exposure levels were clearly below the TWI. The 95th percentile of exposure to inorganic mercury was 1.4 µg/kg bw/week for 1-year-old children, and that of older children was still lower.

Effect of change in the Hg concentrations during 100 years

The effect on total dietary exposure of Finnish children was estimated on the assumptions that only the concentration in cereals would change and all other sources of exposure, but otherwise consumption habits would remain unchanged. Comparison was made with the total dietary exposure (including exposure from drinking water) of 3-year-old Finnish children (calculated in Suomi et al., 2015).

Mercury content in most Finnish cereals, including wheat, is currently below the limit of detection. For this reason it is impossible to estimate the effect of an increase in the Hg content by 64%, as calculated from Hg concentration based on the EU proposal. It is likely that this increase would lead to concentrations above the LOD, but their value and distribution are unknown. With the currently available data, an increase of 64% in the Hg content of cereals corresponds to an increase of 2% to the total dietary exposure. The true value would likely be higher, due to the contribution from e.g. wheat.

6.3.2 Estimated maximum acceptable annual load of Hg to a field hectare in Finland

In estimating the maximum acceptable load of a harmful element, degradation of the soil by accumulation of the element, degradation of the environment by increased loading of the element via leaching and erosion and impacts on human health via increased dietary exposure to the element need to be considered. Overall, any increases in these values can be regarded negative. As for Hg, annual inputs exceeding circa 60 mg Hg/ha from mineral fertilizers, liming and deposition lead to increased amounts of Hg leached, eroded and taken up by the crop. Again to the high proportion of acceptable Hg from deposition, only the low Hg concentrations of local fertilizers (Mäkelä-Kurtto et al. 2007c) keep the Hg balance close to zero.

7 Nickel (Ni)

7.1 Occurrence and behavior in the environment

Ni occurs in nature in oxidation states of +1, +2 and +3, Ni^{2+} being the predominant form in soils (Koljonen et al. 1992). It has five naturally occurring isotopes (^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni, ^{64}Ni), of which ^{58}Ni and ^{60}Ni are the most abundant ones (Reimann et al. 2014f). Ni is both chalcophilic and siderophilic thus it has great affinity to iron and sulphur (Kabata-Pendias 2010). Ni occurs in several minerals like nickeline (NiAs), ullmannite (NiSbS), kullerudite ($NiSe_2$), gersdorffite (NiAsS), millerite (NiS) and pentlandite ($(Fe, Ni)_9S_8$) (Reimann et al. 2014f). Furthermore, it is present as an accessory element in many common minerals (e.g. olivine, mica) and its concentrations in the common sulphide minerals (e.g. galena) can be substantial (Reimann et al. 2014f). In soils, Ni is largely originated from the parent material, the primary anthropogenic sources being mining and smelting and combustion of coal and oil products (Kabata-Pendias 2010, Reimann et al. 2014f). Related to agricultural soils, phosphorus fertilizers can also contain Ni (Nziguheba and Smolders 2008). In Finland, atmospheric emissions have decreased significantly with time. According to Finnish Environment Institute (2014) the atmospheric emissions of Ni have reduced from 63 t to 19 t during the period of 1990 – 2012. In 2012 the main sources were energy production and industrial processes (Finnish Environment Institute 2014).

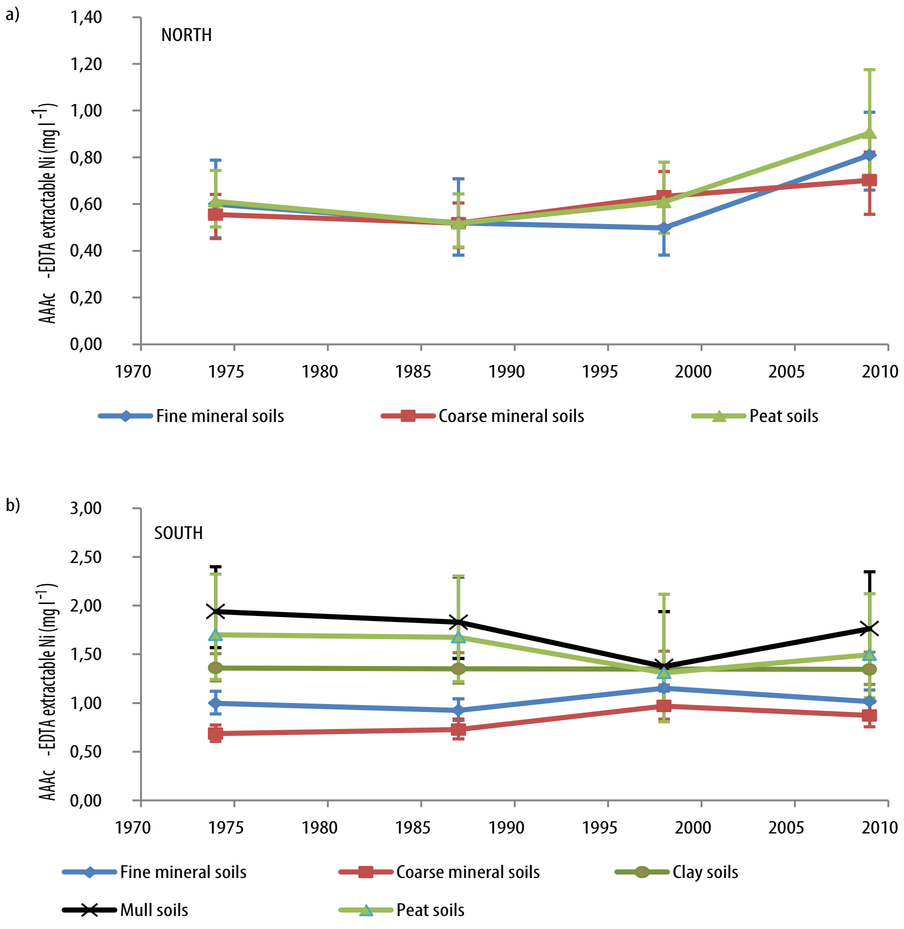
Mean Ni concentrations in different countries in uncontaminated soils have reported to vary between 13 to 37 mg/kg (Kabata-Pendias 2010). In Finland, mean total concentration in till is 27.2 ± 19 ppm (median 24.1 ppm), concentrations being higher in northern Finland due to geological reasons (Koljonen et al. 1992). According to Mäkelä-Kurtto et al. (2007b) average Ni concentration (aqua regia extraction) in Finnish cultivated soils (n=338) is 13.8 mg/kg DM, concentrations varying between 1.2 and 46.4 mg/kg DM, according to region and soil type. Ni concentrations were two times higher in clay soils (28 mg/kg DM) than in coarse-textured mineral soils (11.4 mg/kg DM) or in organic soils (10.9 mg/kg DM). Regionally the highest concentrations were found in southwestern, eastern and northern parts of Finland, which reflects roughly the regional variation of till (Koljonen et al. 1992). According to Tarvainen and Kuusisto (1999) Ni concentrations don't vary significantly between top- and subsoil, median concentrations being 8.08 and 10.6 mg/kg, respectively. Compared to the other Nordic countries, Ni concentrations in Finnish agricultural soils are at the same level (Reimann et al. 2014f). According to Reimann et al. (2014f) Ni concentrations (aqua regia) are much lower in northern Europe (median 8.2 mg/kg) than in southern Europe (median 21 mg/kg) due to geological reasons. At the continental level, Ni concentrations vary greatly between different countries as concentrations in the plough layer (n=2108) range from <0.1 to 2475 mg/kg and in the topsoil of grazing lands (0–10 cm, n=2024) from 0.28 to 2466 mg/kg. Medians for both types of agricultural soils are ca. 15 mg/kg.

The natural background concentrations of Ni in Finnish surface waters are low, the average and median being 1.17 µg/l and 0.44 µg/l (*n=1812*), respectively (Kohijoki 2013). The concentrations vary between 0 – 135 µg/l and are mainly under the environmental quality standard limit in EU's water framework directive (Kohijoki 2013). According to Kohijoki (2013), the highest Ni concentrations result from geology and soil conditions. Also in Finnish drinking water, Ni concentrations are mainly quite low, median concentrations being between 0.4 and 10 µg/l (Ahonen et al. 2008). However, concentrations exceeding the safe concentration limit (20 µg/l) set by the Ministry of Social Affairs and Health have been detected (STM 2000, 2001). According to Lahermo et al. (2002) median and mean concentrations, respectively, were 0.84 and 0.60 µg/l in dug wells (*n=739*), and 3.3 and 1.8 µg/l in drilled bedrock wells (*n=263*). The maximum values for dug and drilled bedrock wells were 277 and 67.5 µg/l, respectively. Only in 2.2 % of measured concentrations in dug wells and 1.1 % of drilled bedrock wells exceeded the safe concentration limit (20 µg/l). In most cases, high Ni concentrations are a consequence of technical appliances used in the wells, although the geological conditions are also an important Ni source in ground waters (Lahermo et al. 2002).

As with other heavy metals, the solubility and bioavailability of Ni depends on various soil factors like soil pH and type, redox-conditions, cation exchange capacity and amount of organic matter and metal oxides (e.g. Kabata-Pendias 2010). The solubility of Ni is very low, when pH is over 6, but increases in acidic conditions (e.g. MacBride 1994, Siebielec and Chaney 2006). Below pH 6, Ni is adsorbed electrostatically by the negatively charged soil constituents (e.g. clays and metal hydroxides), whereas at higher pH values Ni is sorbed more strongly (i.e. chemisorbed) on oxides, noncrystalline aluminosilicates and clays (e.g. McBride 1994). According to Reimann et al. (2014f) Ni is highly mobile under acidic and oxidizing conditions whereas under reducing environment it can form insoluble sulphides, restricting its mobility. On the other hand, Fe and Mn oxides are reduced in reducing conditions thus enhancing the solubility of Ni. Furthermore, organic matter can have either negative or positive effect on Ni availability. Organic matter provides sorption sites, on one hand, but it can also mobilize Ni depending on the organic ligand on the other hand (e.g. McBride 1994). For example, sludge applications have usually found to increase the mobility of Ni in soils mainly because of the complexation with dissolved organic matter

(Kabata-Pendias 2010). Ni can occur in soil solution as Ni^{2+}, $NiOH^{+}$, $HNiO_2^{-}$, $Ni(OH)_3^{-}$ and in complex compounds like $Ni(OH)_2^{0}$ and $NiSO_4^{0}$ (Kabata-Pendias 2010 and references therein).

The easily soluble, AAAc-EDTA extractable concentrations of Ni in the 20-cm surface layer of cultivated soils in Finland have been followed in the national soil survey since 1974 (Sippola and Tares 1978). In the north, the mean easily soluble Ni concentrations have begun to increase over the last decade (Figure 4a). In other parts of Finland, the trends in soil Ni depend on the region and soil type (Fig 4 b–d). In clay soils, no significant changes can be seen in the easily soluble Ni. In the fine and coarse mineral soils of the south, the Ni concentrations have started to decrease after a slightly increasing trend. The organic soils of the south show an opposite trend, though the number of samples is very low. In the east, soil Ni concentrations have increased in mull and coarse mineral soils, but show no significant changes in other soil types. In the west, the soil Ni concentrations are increasing except for the clay soils.



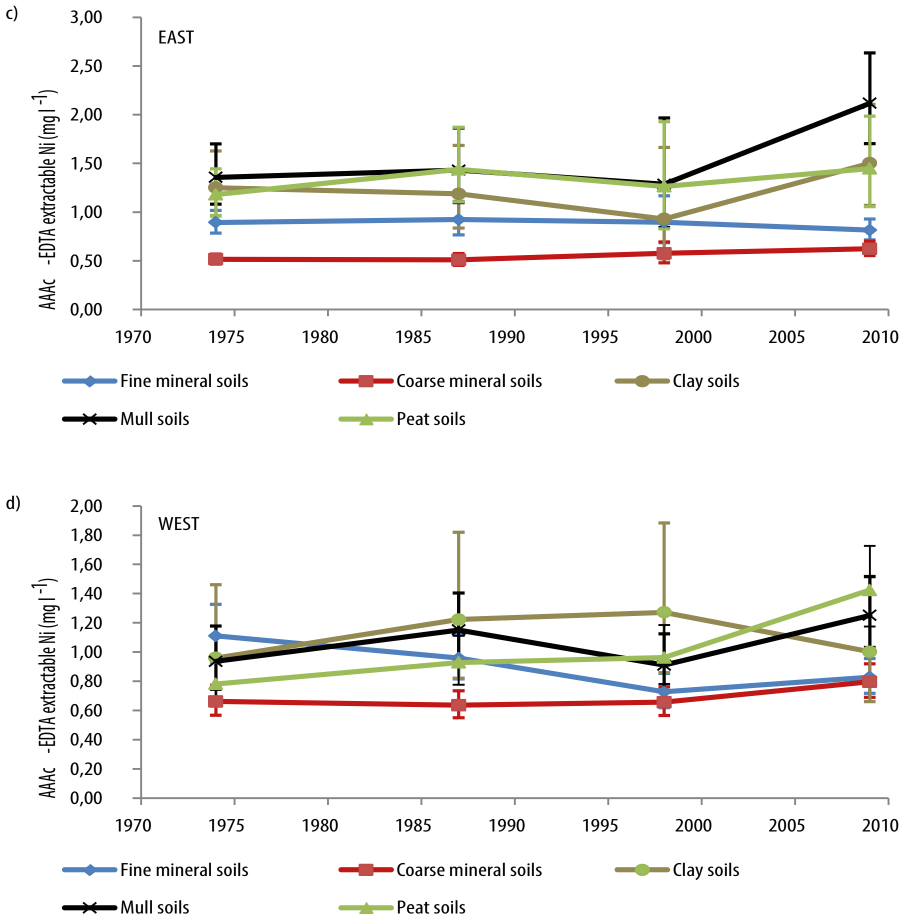


Figure 4. AAAc-EDTA extractable Ni in the 20-cm surface layer of cultivated fine and coarse mineral soils, clay, mull, and peat soils in north (a), south (b), east (c), and west (d) Finland. The graphs show estimated mean concentrations with 95% confidence intervals.

Regional examination of the AAAc-EDTA extractable concentrations of Ni analyzed from the most recent sampling of the Finnish national survey of cultivated soils shows no consistent differences between south, east, west and north Finland (Table 20). The mean soluble Ni concentrations range between 0.6 mg/l in coarse mineral soils and 2.6 mg/l found in clay soils.

Table 20. Easily soluble (AAAc-EDTA extractable) Ni concentrations (mg/l soil) in five soil types and four geographical regions of Finland. The data is from the latest sampling campaign of the Finnish national soil survey conducted in 2009. The figures are mean estimates ± standard error. The number of samples (*n*) are shown in italics.

	South	East	West	North
Fine mineral soils	0.7 ± 0.0 *n = 67*	0.7 ± 0.1 *n = 41*	1.0 ± 0.1 *n = 46*	0.8 ±0.1 *n = 16*
Coarse mineral soils	0.6 ± 0.0 *n = 34*	0.6 ± 0.0 *n = 66*	0.6 ± 0.0 *n = 49*	0.7 ± 0.1 *n = 24*
Clay soils	1.7 ± 0.1 n = 81	1.2 ± 0.1 n = 22	2.6 ± 0.8 n = 3	n = 0
Mull soils	2.4 ± 0.4 *n = 7*	2.4 ± 0.3 *n = 15*	1.6 ± 0.2 *n = 15*	1.6 ± 0.5 *n = 2*
Peat soils	2.0 ± 0.4 *n = 5*	1.3 ± 0.2 *n = 7*	1.5 ± 0.2 *n = 17*	0.8 ± 0.1 *n = 9*

As discussed above, several soil factors (e.g. pH, soil type, redox state) control the solubility and thus phytoavailability of Ni to plants. Furthermore, origin and species of Ni and plant species have an effect on phytoavailability (Sauerbeck and Hein 1991, Kabata-Pendias 2010). In addition, total content of Ni in soils affects the accumulation of Ni into plants (Hooda et al. 1997). However, among the soil factors, pH is considered to be the most significant factor related to the Ni phytoavailability (Hooda et al. 1997, Kabata-Pendias 2010). Because increasing the soil pH reduces the solubility of Ni in soils, liming can decrease Ni concentrations in plants (e.g. Siebielec and Chaney 2006), but this is not always the case. For example in the study of Hooda et al. (1997) liming soils to pH 7 decreased Ni amounts in carrots and spinach but liming to pH 6.5 had no effect on wheat grains. However, phytoavailability is greater in coarse-textured acidic soils than in clayey textured soils with neutral pH values (Hooda et al. 1997). In general, plants take up Ni very easily from soil thus causing potential environmental and health risks (Kabata-Pendias and Mukherjee 2007). Ni^{2+} is thought to be absorbed more readily than its complexes, and Ni^{2+} is also more toxic (Kabata-Pendias 2010). When absorbed to plants, Ni is very mobile and it accumulates in both leaves and seeds (Kabata-Pendias and Mukherjee 2007, Kabata-Pendias 2010). According to Sauerbeck and Hein (1991) and Lübben and Sauerbeck (1991) Ni concentrations are higher in the reproductive than in the vegetative plant parts, highest concentrations being found in plant roots. Like in the case of other heavy metals, sensitivity for Ni concentrations range widely among plant species and cultivars, some of the plants being capable to hyperaccumulate Ni (e.g. Sauerbeck and Hein 1991, Kabata-Pendias and Mukherjee 2007, Kabata-Pendias 2010). According to the review of Kabata-Pendias (2010) the most common Ni phytotoxicity symptom is Fe-induced chlorosis but also gray-green leaves, brown and stunted roots and restricted plant growth can appear especially in cereals which are sensitive to Ni. Elevated Ni concentrations can cause Fe deficiency because Ni inhibits the translocation of Fe from roots to shoots. According to Kabata-Pendias (2010)

Ni concentrations of 1–10 mg/kg in mature leaf tissue are tolerable in agronomic crops, whereas concentrations above that are excessive or toxic in most plants.

7.2 Environmental exposure to Ni

Mass balance for Ni in Finnish agricultural fields has been calculated by Mäkelä-Kurtto et al. (2007c). In their study, data were collected from different sources and Ni concentrations were measured from soil, crop plants and manure.

In this assessment, mass balance calculations were done by the methodology used with cadmium (see 3.2 Environmental exposure to Cd) and used parameters are listed in Table 21. Soil total concentration was based on *aqua regia* extractions by Mäkelä-Kurtto et al. (2007b). Ni input was summed from fertilization, deposition and liming. Annual liming demand was set to 400 kg/ha (http://www.farmit.net/kasvinviljely/kalkitus-ja-maanparannus/kalkitussanastoa) and Ni concentration in liming materials, 8.3 mg/kg, was taken from Mäkelä-Kurtto et al. (2007b). Deposition was set to 14 g/ha (Mäkelä-Kurtto et al. 2007c). Fertilizer rate was based on the current recommended P rate for spring wheat, 10 P kg/ha. With the average fertilizer P-concentrations (3.2%) reported in Mäkelä-Kurtto et al (2007c), which means that a fertilizer rate of 310 kg/ha leads to 10 P kg/ha.

Following calculations were done:

1. The current dose of Ni from the commonly used mineral fertilizers in Finland was calculated according to average Ni concentrations, 1 mg/kg DM, reported in Mäkelä-Kurtto et al. (2007c). Ni concentration against NP content of fertilizers averaged to 68 mg/kg P and 11 mg/kg N.
2. The current maximum dose of Ni was calculated according to the maximum allowed Ni concentration in fertilizers based on Finnish law of fertilizer products, 100 mg/kg DM.
3. Third possible dose of Ni was calculated according to the EU legislation proposal, where maximum 120 mg/kg DM is accepted for mineral fertilizers.

The output of Ni was summed from uptake in harvested yield and losses via leaching and eroded soil material. Calculation was done for 100 years, using spring wheat as the crop. Plant uptake in harvested organ was based on soil-plant transfer coefficient (SPTC):

$$SPTC = \frac{Cplant}{Csoil}$$

$$Plant\ uptake = Yield \times Cplant$$

Where C*plant* is the total Ni concentration in harvested plant organ per dry matter and C*soil* is the aqua regia extractable Ni concentration per dry matter in 0 – 20 cm top layer of the soil (Mäkelä-Kurtto et al. 2007a). Yield level was set to the average yield during 2010–2014. Transfer coefficient from soil to wheat grains was taken from the results reported by Mäkelä-Kurtto et al. (2007a).

Leaching was based on distribution coefficient (Kd), which shows the relationship between the total (C*soil*, *aqua regia* or HNO_3/HF extractable) concentration in soil and the concentration in soil pore water (*Cwater*). Kd-values for Ni were found from the study of Sheppard et al. 2011 in Sweden, where the Kd value of glacial clay with 10% organic matter content and 35 % clay content was selected. They had extracted total Ni with HNO_3/HCl/HF solution.

$$Kd = \frac{Csoil}{Cwater}$$

$$Leaching = Cwater \times annual\ runoff$$

Annual runoff was set as 200 mm that was used in previous Cd mass balance calculations (Finnish Environment Institute 2000) and annual erosion set to 500 kg/ha (Finnish Environment Institute 2000). The amount of eroded element was calculated:

$$Erosion = Csoil \times annual\ soil\ erosion$$

Table 21. Parameters used in the mass balance calculations of Ni.

Model parameters		Source
Soil concentration, mg Ni/kg	14	Mäkelä-Kurtto et al. 2007b, Table 1
Deposition, g Ni/ha/a	1.63	Mäkelä-Kurtto et al. 2007c, Table 40
Liming kg/ha/a	400	Recommended liming rate
Ni concentration in liming materials, mg Ni /kg	8.3	Mäkelä-Kurtto et al. 2007c, Table 17
Fertilizer rate, kg/ha	310	10 kg P/ha, and 3.2 % P concentration
Transfer function, plant/soil	0.008	Mäkelä-Kurtto et al. (2007a), Table 60
Yield kg/ha, 14% moisture	3750	Finnish agricultural statistics 2010 – 2014
Kd	1500	Sheppard et al. 2011. Table 3 – 3
Annual runoff, m^3/ha	2000	Finnish Environment Institute 2000
Annual erosion, kg/ha	500	Finnish Environment Institute 2000

After running the model calculations for 100 years using a code programmed by SAS statistical package, following output values were reported: Ni concentration in soil water, annual Ni leaching and erosion, Ni concentration in yield and annual Ni uptake in yield, soil Ni concentration and annual Ni balance.

Table 22. The effect of Ni concentrations in fertilizers on Ni concentrations in soil water, yield and soil, and on leaching, erosion, yield uptake and annual balance of Ni in 100-years mass balance calculations.

mg Ni/ kg fert. DM	Year	Soil water µg/l	Leached g/ha/a	Eroded g/ha/a	Yield µg/kg DM	Yield uptake g/ha/a	Soil mg/kg	Annual balance g/ha
1	1	9.33	18.7	7.00	112	0.36	14.0	-20.4
	100	8.69	17.4	6.52	104	0.34	13.0	-18.6
100	1	9.34	18.7	7.01	112	0.36	14.0	9.79
	100	9.65	19.3	7.24	116	0.37	14.5	8.93
120	1	9.35	18.7	7.01	112	0.36	14.0	16.0
	100	9.85	19.7	7.39	118	0.38	14.8	14.6

In the 100-year time scale, the current realization of Ni inputs would lead to negative Ni balance and the change in the amounts of Ni leached, eroded and taken up by the crop would decrease 6.9 % (Table 22). In the other scenarios, high Ni inputs generate a positive Ni balance. Using the current maximum level of Ni input (100 mg/kg fertilizer) the environmental loading (Ni leached and eroded) and Ni concentrations in crop yields would slightly increase and would be 3.4% higher compared to the level of the current realization. With the Ni inputs allowed in the EU proposal, the corresponding increases would be slightly higher, by 5.5 %.

7.3 Risk assessment on Ni at increased levels of exposure

Nickel can cause contact dermatitis. Additional health effects for workers exposed to Ni are nephrotoxic effects and increase of cancer risk, even though WHO considered that there is little or no detectable risk in most sectors of the Ni industry at current exposure level (WHO 1991). Even though Ni compounds are classified as carcinogenic to humans (IARC 2012) through pulmonary exposure, oral exposure has not been shown to be carcinogenic to test animals. Intake of Ni via the gastrointestinal tract can be high, and the estimated average daily dietary intake of Ni was estimated to be around 200 µg (WHO 1991), corresponding to ca. 2.9 µg/kg bw/day for a person weighing 70 kg. High dietary intake of Ni increases its elimination.

Even though Ni is essential for many species of microorganisms, plants and vertebrates, excess Ni causes physiological alterations and diverse toxicity symptoms. An extensive risk assessment on Ni has been compiled in the EU (ECB 2008). The predicted no-effect concentration values in EU soils vary from 4.3 to 96.2 mg Ni/kg (NiPERA 2015). For surface waters, an Environmental Quality Standard value of 4 µg bioavailable Ni/l has been proposed to replace the current level of 20 µg total Ni/l (NiPERA 2014).

EFSA (2015) has estimated a tolerable daily intake value of 2.8 µg/kg bw/day for nickel based on a concentration causing a 10% increase in post-implantation fetal loss in rat tests and a safety factor of 100. Also other studies link nickel exposure to damage to fetus or to genital damage in animals. An acute reference dose for short-term exposure, 1.1 µg/kg bw/day, was determined based on systemic contact dermatitis after dietary exposure in nickel sensitive humans (EFSA 2015). For nickel sensitive individuals, a margin of exposure of 10 (i.e., nickel exposure 0.11 µg/kg bw/day or less) corresponds to an insignificant health risk, according to the EFSA experts. The prevalence of allergic contact dermatitis can be as high as 15% of the population, and it is often undiagnosed. With the current estimates of dietary exposure in Europe, it is possible that some individuals can have eczematous flare-up skin reactions from dietary nickel (EFSA 2015).

7.3.1 Estimates of dietary intake and its sources

Varo and Koivistoinen (1980) reported an average daily supply of 130 µg Ni from Finnish foods. Majority of the Ni supply deriving from cereals (46%) and vegetable foods (33 %).

The exposure of Finnish adults was estimated to be 2.4 to 3.0 µg/kg bw/day at population mean level and 4.5 to 5.4 µg/kg bw/day at 95th percentile of exposure (EFSA 2015). Even the population mean level can exceed the tolerable daily intake (2.8 µg/kg bw/day) and will exceed the reference dose for contact dermatitis (1.1 µg/kg bw/day). Vegetarians were estimated to have a slightly higher nickel exposure than non-vegetarians, although the estimate was based on less than 60 individuals.

7.3.2 Estimated maximum acceptable annual load of Ni to a field hectare in Finland

In estimating the maximum acceptable load of a harmful element, degradation of the soil by accumulation of the element, degradation of the environment by increased loading of the element via leaching and erosion and impacts on human health via increased dietary exposure to the element need to be considered. Overall, any increases in these values can be regarded negative. As for Ni, annual inputs of roughly 34 g/ha from mineral fertilizers, liming and deposition increase the amounts of Ni leached, eroded and taken up by the crop only slightly. This input level is reached with the current limit of Finnish Fertilizer product act, 100 mg/kg. Ni balance would be close to zero, when Ni limit is 70 mg/kg fertilizer.

8 References

Ahonen, M.H., Kaunisto, T., Mäkinen, R., Hatakka, T., Vesterbacka, P., Zacheus, O. and Keinänen-Toivola, M.M. 2008. Suomalaisen talousveden laatu raakavedestä kuluttajan hanaan vuosina 1999-2007. Vesi-Instituutin julkaisuja 4. In Finnish. Available on the internet: http://www.samk.fi/download/27075_VI-julkaisu4.pdf.

Amundsen, C.E., Almås, Å. and Singh, B.R. 2000. Risk assessment of Cd in mineral fertilizers in Norway using model calculations. Norwegian Centre for Soil and Environmental Research. Report no. 85/00. 39 p.

Anderson, R. A. 1997. Chromium as an essential nutrient for humans. Regualtory Toxicology and Pharmacology 26:35-41.

ATSDR 2012. U.S. Department of Health and Human Services, Agency for Toxic Substances and Disease Registry. Toxicological Profile for Cadmium. URL http://www.atsdr.cdc.gov/toxprofiles/tp5.pdf

Backman, B., Luoma, S., Ruskeeniemi, T., Karttunen, V., Talikka, M. and Kaija, J. 2006. Natural occurence of arsenic in the Pirkanmaa region in Finland. Geological Survey of Finland, Miscellaneous Publications. 82 p. Available on the internet: http://tupa.gtk.fi/julkaisu/erikoisjulkaisu/ej_057.pdf

Boening, D. W. 2000. Ecological effects, transport, and fate of mercury: a general review. Chemosphere 40:1335-1351.

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

Byrne, C., Divekar, S.D., Storchan, G.B., Parodi, D.A., Martin, M.B. 2009. Cadmium - a metallohormone? Toxicology and Applied Pharmacology 238:266-271.

Christensen, T.H. 1984. Cadmium soil sorption at low concentrations: I. Effect of time, cadmium load, pH, and calcium. Water, Air, and Soil Pollution 21: 105-114.

Christensen, T.H. 1989. Cadmium soil sorption at low concentrations: VIII. Correlation with soil parameters. Water, Air, and Soil Pollution 44: 71-82.

Clemens, S. 2006. Toxic metal accumulation, responses to exposure and mechanisms of tolerance in plants. Biochimie 88: 1707-1719.

Demayo, A., Tatlor, M. C., Taylor, K. W., Hodson, P. V. and Hammond, P. B. 1982. Toxic effects of lead and lead compounds on human health, aquatic life, wildlife plants, and livestock. CRC Critical Reviews in Environmental Control 12:257-305.

Dixit, S. and Hering, J. G. 2003. Comparison of arsenic (V) and arsenic (III) sorption onto iron oxide minerals: Implications for arsenic mobility. Environmental Science and Technology 37: 4182-4189.

ECB 2008. European Union Risk Assessment Report, Nickel. CAS No: 7440-02-0, EINECS No: 231-111-4.

EFSA 2009a. Panel on Contaminants in the Food Chain (CONTAM); Scientific Opinion on Arsenic in Food. EFSA Journal 7(10):1351. [199 pp.]. doi:10.2903/j.efsa.2009.1351. Available online: www.efsa.europa.eu

EFSA 2009b. Scientific Opinion of the Panel on Contaminants in the Food Chain on a request from the European Commission on cadmium in food. The EFSA Journal 980:1-139.

EFSA 2012a. European Food Safety Authority; Cadmium dietary exposure in the European population. EFSA Journal 2012;10(1):2551. [37 pp.] doi:10.2903/j.efsa.2012.2551. Available online: www.efsa.europa.eu/efsajournal

EFSA 2012b European Food Safety Authority; Lead dietary exposure in the European population. EFSA Journal 2012; 10(7):2831. [59 pp.] doi:10.2903/j.efsa.2012.2831. Available online: www.efsa.europa.eu/efsajournal

EFSA 2012c. Panel on Contaminants in the Food Chain (CONTAM); Scientific Opinion on the risk for public health related to the presence of mercury and methylmercury in food. EFSA Journal 10(12):2985. [241 pp.] doi:10.2903/j.efsa.2012.2985. Available online: www.efsa.europa.eu/efsajournal

EFSA 2014. Panel on Contaminants in the Food Chain (CONTAM); Chromium in food and drinking water. EFSA Journal 12:3595. [261 pp.] doi:10.2903/j.efsa.2014.3595. Available online: www.efsa.europa.eu/efsajournal

EFSA 2015. Panel on Contaminants in the Food Chain (CONTAM); Nickel in food and drinking water. EFSA Journal 13:4002. [202 pp.] doi:10.2903/j.efsa.2015.4002. Available online: www.efsa.europa.eu/efsajournal

Eriksson, J., Öborn, I., Jansson, G. and Andersson, A. 1996. Factors influencing Cd-content in crops. Results from Swedish field investigations. Swedish Journal of Agricultural Research 26: 125-133.

Finnish Environment Institute 2000. Cadmium in fertilizers, Risks to human health and the environment. Study report for the Finnish Ministry of Agriculture and Forestry. 120 p.

Finnish Environment Institute 2014. Air pollutant emissions in Finland. Available in: http://www.ymparisto.fi/en-US/Maps_and_statistics/Air_pollutant_emissions

Flora S.J.S., Pachauri, V., and Saxena G. 2011."Arsenic, cadmium and lead". Chapter 23 in: Gupta RC (ed.), Reproductive and Developmental Toxicology, Elsevier.

Gabriel, M.C. and Williamson, D.G. 2004. Principal biogeochemical factors affecting the speciation and transport of mercury through the terrestrial environment. Environmental Geochemistry and Health 26: 421-434.

Ghoshesh, A, Bashir, S., and Dabbas, L. (1996). Managing the cadmium content of phosphate rock: A contribution to environmental impact mitigation. *In* Fertilizers as a source of cadmium. OECD proceedings. pp 13-20.

Hakala, E. and Hallikainen, A. 2004. Suomalaisten arseenialtistuminen, arseenin vaikutukset ja terveysriskit. Abstract in English: Exposure of the Finnish population to arsenic, effects and health risks. In publication: Loukola-Ruskeeniemi, K. and Lahermo, P.(eds.), 2004. Arseeni Suomen luonnossa, ympäristövaikutukset ja riskit. Abstract in English: Arsenic in Finland: Distribution, Environmental Impacts and Risks. Geological Survey of Finland. 137 p.

Hatakka, T., Mäkelä-Kurtto, R., Tarvainen, T. Laakso, P., Laitonen, A. and Eurola, M. 2007. Trace elements in top- and subsoil on selected crop and dairy farms in Finland in 2004. Agrifood Research Reports 108. 80 p.

Hatakka, T. (ed.), Tarvainen, T., Jarva, J., Backman, B., Eklund, M., Huhta, P. Kärkkäinen, N. and Luoma, S. 2010. Pirkanmaan maaperän geokemialliset taustapitoisuudet. Summary in English: Geochemical baselines in the Pirkanmaa region. Geological Survey of Finland. Report of Investigation 182. 104 p.

Heikkinen, P. 2000. Haitta-aineiden sitoutuminen ja kulkeutuminen maaperässä. Summary: Retention and migration of harmful substances in the soil. Geological Survey of Finland. Report of Investigation 150.

Heikkinen, J., Ketoja, E., Nuutinen, V. and Regina, K. 2013. Declining trend of carbon in Finnish cropland soils in 1974-2009. Global Change Biology 19:1456-1469.

Hooda, P.S., McNulty, D., Alloway, B.J. & Aitken, M.N. 1997. Plant availability of heavy metals in soils previously amended with heavy applications of sewage sludge. Journal of the Science of Food and Agriculture 73: 446-454.

Huang, J-H., Hu, K-N. and Decker, B. 2011. Organic arsenic in the soil environment: Speciation, occurrence, transformation, and adsorption behavior. Water, Air and Soil Pollution 219: 401-415.

IARC, International Agency for Research on Cancer. 2012. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Vol. 100C. A Review of Human Carcinogens: Arsenic, Metals, Fibres, and Dusts. WHO Press.

Jain, A. and Loeppert, R.H. 2000. Effect of competing anions on the adsorption of arsenate and arsenite by ferrihydrite. Journal of Environmental Quality 29: 1422-1430.

JECFA, Joint FAO/WHO Expert Committee on Food Additives. 2011. Safety evaluation of certain contaminants in food. Arsenic (addendum). Prepared by the 72nd meeting of the Joint FAO/WHO Expert Committee on Food Additives. WHO Food Additives series 63.

Juntunen, R., Vartiainen, S. and Pullinen, A. 2004. Arseeni Pirkanmaan porakaivovesissä. Abstract: Arsenic in water from drilled bedrock wells in Pirkanmaa, southern Finland. In publication: Loukola-Ruskeeniemi, K. and Lahermo, P.(eds.), 2004. Arseeni Suomen luonnossa, ympäristövaikutukset ja riskit. Abstract in English: Arsenic in Finland: Distribution, Environmental Impacts and Risks. Geological Survey of Finland. 137 p.

Kabata-Pendias, A. 2010. Trace elements in soils and plants. Fourth edition. CRC Press/Taylor and Francis Group. 520 p.

Kabata-Pendias, A. and Mukherjee, A.B. 2007. Trace elements from soil to human. Springer. 550 p.

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

Keskinen, R., Ketoja, E., Heikkinen, J., Salo, T., Uusitalo, R. and Nuutinen, V. 2016. 35-year trends of acidity and soluble nutrients in cultivated soils of Finland. Geoderma Regional 7:376-387.

Kimbrough, D.E., Cohen, Y., Winer, A.M., Creelman, L. and Mabuni, C. 1999. A Critical Assessment of Chromium in the Environment. Critical Reviews in Environmental Science and Technology, 29(1):1–46.

Kohijoki, V. 2013. Suomen pintavesien lyijyn ja nikkelin taustapitoisuudet ja niiden biosaatavuus. Abstract in English. University of Helsinki. Department of Geosciences and geography. Master's thesis. 51 p.

Koivuhuhta, A. and Nikkarinen, M. 2006. Kirjallisuuskooste kromin ympäristögeokemiallisesta luonteesta ja tutkimusmenetelmistä – painoalueena Suomi. Geological Survey of Finland, Archival Document, 37 p. Abstract in English: Literary Review about Chromium Natural Occurence, Geochemical Character in Waters and Soils and Research Methods – Focusing in Finland.

Koljonen, T. (ed.), Elo, S., Gustavsson, N., Huhma, H., Kauranne, L.K., Koljonen, T., Noras, P., Pesonen, L.J., Ruotoistenmäki, T, Saltikoff, B., Sillanpää, M., Tanskanen, H., Vaasjoki, M. and Vuorela, P. 1992. The Geochemical Atlas of Finland, Part 2: Till. Geological Survey of Finland. Espoo, 218 p.

Kyllönen, K., Hakola, H., Hellén, H., Korhonen, M. and Verta, M. 2012. Atmospheric mercury fluxes in a southern boreal forest and wetland. Water, Air & Soil Pollution 223:1171-1182.

Kyllönen, K., Karlsson, V. and Ruoho-Airola, T. 2009. Trace element deposition and trends during a ten year period in Finland. Science of the Total Environment 407: 2260-2269.

Kyllönen, K., Paatero, J., Aalto, T. and Hakola, H. 2014. Nationwide survey of airborne mercury in Finland. Boreal Environment Research 19 (suppl. B): 355–367**.** Lahermo, P., Väänänen, P., Tarvainen, T. and Salminen, R., 1996. Geochemical Atlas of Finland, Part 3 – Environmental Geochemistry-Stream waters and sediments. Geological Survey of Finland. Espoo, 149 p.

Lahermo, P, Tarvainen, T., Hatakka, T. Backman, B., Juntunen, R., Kortelainen, N., Lakomaa, T., Nikkarinen, M., Vesterbacka, P., Väisänen, U. and Suomela, P. 2002. Tuhat kaivoa – Suomen kaivovesien fysikaalis-kemiallinen laatu vuonna 1999. Summary: One thousand wells – the physical-chemical quality of Finnish well waters in 1999. Geological Survey of Finland. Report of Investigation 155. 92 p.

Lahdenperä, A-M. 2014. Geochemical and physical properties, distribution coefficients of Soils and Sediments at the Olkiluoto Island and in the Reference Area in 2010–2011. Working Report 2013-66. Posiva. 84 p. http://www.posiva.fi/tietopankki/tyoraportit/geochemical_and_physical_properties_distribution_coefficients_of_soils_and_sediments_at_the_olkiluoto_island_and_in_the_reference_area_in_2010-2011.1769.xhtml?xm_col_report_year=2013andxm_col_language=3andxm_col_type=5andcd_order=col_report_numberandcd_offset=0

Lilja, H., Uusitalo, R., Yli-Halla, M., Nevalainen, R., Väänänen, T. and Tamminen, P. 2006. Finnish soil database – soil map at scale 1:250 000 and properties of soil. MTT:n Selvityksiä 114, 70 p.

Lübben, S. and Sauerbeck, D. 1991. The uptake and distribution of heavy metals by spring wheat. Water, Air & Soil Pollution 57-58: 239-247.

Mahimairaja, S., Bolan, N.S., Adriano, D.C. and Robinson, B. 2005. Arsenic contamination and its risk management in complex environmental settings. Advances in Agronomy 86: 1-82.

Manning, B.A. and Goldberg, S. 1996. Modeling competitive adsorption of arsenate with phosphate and molybdate on oxide minerals. Soil Science Society of America Journal 60: 121-131.

Markus, J. and McBratney, A. B. 2001. A review of the contamination of soil with lead II. Spatial distribution and risk assessment of soil lead. Environment International 27:399-411.

Matschullat, J. 2000. Arsenic in the geosphere – a review. The Science of the Total Environment 249: 297-312.

McBride, M.B. 1994. Environmental chemistry of soils. Oxford University Press, New York. 406 p.

Mukherjee, A.B. 1998. Chromium in the environment of Finland. The Science of the Total Environment 217:9-19.

Mäkelä-Kurtto, R. and Kemppainen, E. 1993 Karjanlannassa vähäisiä määriä raskasmetalleja (Low concentrations of Cd in farm yard manures). Koetoiminta ja käytäntö 50:7.

Mäkelä-Kurtto, R. and Sippola, J. 2002. Monitoring of Finnish arable land: changes in soil quality between 1987 and 1998. Agricultural and Food Science in Finland 11:273-284.

Mäkelä-Kurtto, R., Louekari, K., Nummivuori, S., Sippola, J., Kaasalainen, M., Kuusisto, E., Virtanen, V., Salminen, R., Tarvainen, T. and Malm, J. 2003. Kadmium Suomen peltoekosysteemeissä: pitoisuuksia, taseita ja riskejä. Abstract in English: Cadmium in Finnish agroecosystems: concentrations, balances and risks. Maa- ja elintarviketalous 27, 51 p. In Finnish.

Mäkelä-Kurtto, R., Eurola, M., Justén, A., Backman, B., Luoma, S., Karttunen, V. and Ruskeeniemi, T. 2007a. Arsenic and other elements in agro-ecosystems in Finland and particularly in the Pirkanmaa region. Geological Survey of Finland, Miscellaneous Publications, 119 p.

Mäkelä-Kurtto, R., Eurola, M. and Laitonen, A. 2007b. Monitoring programme of Finnish arable land. *Aqua regia* extractable trace elements in cultivated soils in 1998. Agrifood Research Reports 104. 61 p.

Mäkelä-Kurtto, R., Laitonen, A., Eurola, M., Vuorinen, A., Pasanen, T., Rankanen, R., Suominen, K., Laakso, P., Tarvainen, T., Hatakka, T. and Salopelto, J. 2007c. Field balances of trace elements at farm level on selected crop and dairy farms in Finland in 2004. Agrifood Research Reports 111. 87p.

Mäntylahti, V. and Laakso, P. 2002. Arsenic and heavy metal concentrations in agricultural soils in South Savo province. Agricultural and Food Science in Finland 11: 285-300.

NiPera. 2014. The derivation and implementation of an environmental quality standard for nickel in European surface waters. Special issue fact sheet addressing the nickel environmental quality standards under the Water Framework Directive (WFD, 2000/60/EC). Available online at: http://www.nipera.org/en/EnvironmentalScience/FSSI1-EQS.aspx

NiPera. 2015. Data compilation, selection, and derivation of PNEC values for the soil compartment. Special issue fact sheet addressing issues specific to the environment section of the European Union's Existing Substances Risk Assesment of nickel (EU RA). Available online at: https://www.nickelinstitute.org/en/HealthScienceEnvironmentalScienceAndSafeUse/EnvironmentalScience/SoilCompartment.aspx

Nziguheba, G. and Smolders, E. 2008. Inputs of trace elements in agricultural soils via phosphate fertilizers in European countries. Science of the Total Environment 390: 53-57.

Ottesen, R. T., Birke, M., Finne, T. E., Gosar, M., Locutura, J., Reimann, C., Tarvainen, T. and the GEMAS Project Team. 2013. Mercury in European agricultural and grazing land soils. Applied Geochemistry 33: 1-12.

Pantsar-Kallio, M., Reinikainen, S-P. and Oksanen, M. 2001. Interactions of soil components and their effects on speciation of chromium in soils. Analytica Chimica Acta 439:9-17.

Patra, M. and Sharma, A. 2000. Mercury toxicity in plants. The Botanical Review 66: 379-422.

Peralta-Videa, J:R., Lopez, M.L., Narayan, M., saupe, G. and Gardea-Torresdey, J. 2009. The biochemistry of environmental heavy metal uptake by plants: Implications for the food chain. The International Journal of Biochemistry and Cell Biology 41:1665-1677.

Pietarila, H., Salmi, T., Saari, H. and 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.

Reimann, C., Matschullat, J., Birke, M. and Salminen, R. 2009. Arsenic distribution in the environment: The effects of scale. Applied Geochemistry 24: 1147-1167.

Reimann, C., Flem, B., Fabian, K., Birke, M., Ladenberger, A., Negrel, P., Demetriades, A., Hoogewerff, J. and The GEMAS Project Team. 2012. Lead and lead isotopes in agricultural soils of Europe – The continental perspective. Applied Geochemistry 27: 532–542.

Reimann, C., Demetriades, A., Birke, M., Filzmoser, P., O'Connor, P., Halamic, J., Ladenberger, A. and the GEMAS Project Team 2014a. Distribution of elements/parameters in agricultural and grazing land soil of Europe. Arsenic (As). In: Reimann, C., Birke, M., Demetriades, A., Filzmoser, P. and O'Connor, P. (eds.). 2014. Chemistry of Europe's agricultural soils. Part A. Methodology and interpretation of the GEMAS data set. Geologisches Jahrbuch, Reihe B, Heft 102. 528 p.

Reimann, C., Demetriades, A., Birke, M., Filzmoser, P., O'Connor, P., Halamic, J., Ladenberger, A. and the GEMAS Project Team 2014b. Distribution of elements/parameters in agricultural and grazing land soil of Europe. Cadmium (Cd). In: Reimann, C., Birke, M., Demetriades, A., Filzmoser, P. and O'Connor, P. (eds.). 2014. Chemistry of Europe's agricultural soils. Part A. Methodology and interpretation of the GEMAS data set. Geologisches Jahrbuch, Reihe B, Heft 102. 528 p.

Reimann, C., Demetriades, A., Birke, M., Filzmoser, P., O'Connor, P., Halamic, J., Ladenberger, A. and the GEMAS Project Team 2014c. Distribution of elements/parameters in agricultural and grazing land soil of Europe. Chromium (Cr). In: Reimann, C., Birke, M., Demetriades, A., Filzmoser, P. and O'Connor, P. (eds.). 2014. Chemistry of Europe's agricultural soils. Part A. Methodology and interpretation of the GEMAS data set. Geologisches Jahrbuch, Reihe B, Heft 102. 528 p.

Reimann, C., Demetriades, A., Birke, M., Filzmoser, P., O'Connor, P., Halamic, J., Ladenberger, A. and the GEMAS Project Team 2014d. Distribution of elements/parameters in agricultural and grazing land soil of Europe. Lead (Hg). In: Reimann, C., Birke, M., Demetriades, A., Filzmoser, P. and O'Connor, P. (eds.). 2014. Chemistry of Europe's agricultural soils. Part A. Methodology and interpretation of the GEMAS data set. Geologisches Jahrbuch, Reihe B, Heft 102. 528 p.

Reimann, C., Demetriades, A., Birke, M., Filzmoser, P., O'Connor, P., Halamic, J., Ladenberger, A. and the GEMAS Project Team 2014e. Distribution of elements/parameters in agricultural and grazing land soil of Europe. Mercury (Hg). In: Reimann, C., Birke, M., Demetriades, A., Filzmoser, P. and O'Connor, P. (eds.). 2014. Chemistry of Europe's agricultural soils. Part A. Methodology and interpretation of the GEMAS data set. Geologisches Jahrbuch, Reihe B, Heft 102. 528 p.

Reimann, C., Demetriades, A., Birke, M., Filzmoser, P., O'Connor, P., Halamic, J., Ladenberger, A. and the GEMAS Project Team 2014f. Distribution of elements/parameters in agricultural and grazing land soil of Europe. Nickel (Ni). In: Reimann, C., Birke, M., Demetriades, A., Filzmoser, P. and O'Connor, P. (eds.). 2014. Chemistry of Europe's agricultural soils. Part A. Methodology and interpretation of the GEMAS data set. Geologisches Jahrbuch, Reihe B, Heft 102. 528 p.

Roberts, T.L. 2013. Cadmium and Phosphorous Fertilizers: The Issues and the Science. Procedia Engineering 83: 52 – 59.

Ruoho-Airola, T., Hatakka, T., Kyllönen, K., Makkonen, U. and Porvari, P. 2014. Temporal trends in the bulk deposition and atmospheric concentration of acidifying compounds and trace elements in the Finnish Integrated Monitoring catchment Valkea-Kotinen during 1988–2011. Boreal Environment Research 19: 31–46.

Sadiq, M. 1997. Arsenic chemistry in soils: An overview of thermodynamic predictions and field observations. Water, Air and Soil Pollution 93: 117-136.

Sauerbeck, D.R. & Hein, A. 1991. The nickel uptake from different soils and its prediction by chemical extractions. Water, Air, and Soil Pollution 57-58: 861-871.

Schuster, E. 1991. The behavior of mercury in the soil with special emphasis on complexation and adsorption processes – A review of the literature. Water, Air, and Soil Pollution 56: 667-680.

Shanker, A. K., Cervantes, C., Loza-Tavera, H. and Avudainayagam. 2005. Chromium toxicity in plants. Environmental International 31:739-753.

Sheppard, S., Sohlenius, G., Omberg, L-G., Borgiel, M.m Grolander, S. and Norden, S. 2011. Solid/liquid partition coefficients (Kd) and plant/soil concentration ratios (CR) for selected soils, tills and sediments at Forsmark. 77 p. SKB R-11-24. http://www.skb.se/upload/publications/pdf/r-11-24.pdf.

Siebielec, G. and Chaney, R.L. 2006. Manganese fertilizer requirement to prevent manganese deficiency when liming to remediate Ni-phytotoxic soils. Communications in Soil Science and Plant Analysis 37: 163–179.

Singh, H.P., Mahajan, P., kaur, S., Batish, D.R. and Kohli, R.K. 2013. Chromium toxicity and tolerance in plants. Environmental Chemistry Letters 11:229-254.

Sippola, J. and Tares, T. 1978. The soluble content of mineral elements in cultivated Finnish soils. Acta Agriculturae Scandinavica, Suppl. 20.

Smolders, E. 2001. Cadmium uptake by plants. International Journal of Occupational Medicine and Environmental Health 14: 177–183.

Smolders, E. 2013. Revisiting and Updating the Effect of Phosphorus Fertilisers on Cadmium Accumulation in European Soils. Proceeding 724. Royal Fertliliser Society. 60 p.

Sorvari, J., Schultz, E., Rossi, E., Lehtinen, H., Joutti, A., Vaajasaari, K. and Kauppila, T. 2007. Risk assessment of natural and anthropogenic arsenic in the Pirkanmaa region, Finland. Geological Surcey of Finland, Miscellaneous Publications. 126 p.

Sternbäck, J., Eriksson, J. and Österås, A.H. 2011. The role of mineral fertilisers for cadmium in Swedish agricultural soils and crops. Commission E. Ares (2011) 532940 – 17(´/05/2011.

STM 2000. Sosiaali- ja terveysministeriön asetus talousveden laatuvaatimuksista ja valvontatutkimuksista. 461/2000.

STM 2001. Sosiaali- ja terveysministeriön asetus pienten yksiköiden talousveden laatuvaatimuksista ja valvontatutkimuksista. 401/2001.

Suomi, J., Tuominen, P., Ranta, J., Savela, K. 2015. Risk assessment on the dietary heavy metal exposure of Finnish children (in Finnish). Evira Research Reports 2/2015. 141 pp. ISBN 978-952-225-145-9

Tanskanen, H., Lahermo, P. and Loukola-Ruskeeniemi K. 2004. Arseeni Kittilän pohjavesissä Keski-Lapissa. Abstract: Arsenic in groundwater in Kittilä , Finnish Lapland. In publication: Loukola-Ruskeeniemi, K. and Lahermo, P.(eds.), 2004. Arseeni Suomen luonnossa, ympäristövaikutukset ja riskit. Abstract in English: Arsenic in Finland: Distribution, Environmental Impacts and Risks. Geological Survey of Finland. 137 p.

Tarvainen, T. 2004. Arseeni maaperässä. Abstract in English: Arsenic in soils. In publication: Loukola-Ruskeeniemi, K. and Lahermo, P. (eds.). 2004. Arseeni Suomen luonnossa, ympäristövaikutukset ja riskit. Abstract in English: Arsenic in Finland: Distribution, Environmental Impacts and Risks. Geological Survey of Finland. 137 p.

Tarvainen, T. and Kuusisto, E. 1999. Baltic soil survey: Finnish results. Geological Survey of Finland, Special Paper 27: 69-77.

Tarvainen, T. and Mannio, J. 2004. Arseeni pintavesissä ja purosedimenteissä. Abstract: Arsenic in surface waters and stream sediments. In publication: Loukola-Ruskeeniemi, K. and Lahermo, P. (eds.) 2004. Arseeni Suomen luonnossa, ympäristövaikutukset ja riskit. Abstract in English: Arsenic in Finland: Distribution, Environmental Impacts and Risks. Geological Survey of Finland. 137 p.

Tarvainen, T., Albanese, S., Birke, M., Poňavič, M., Reimann, C. and The GEMAS Project Team. 2013. Arsenic in agricultural and grazing land soils of Europe. Applied Geochemistry 28: 2-10.

Ullrich, S. M., Tanton, T. W. and Abdrashitova, A. 2001. Mercury in the aquatic environment: A review of factors affecting methylation. Critical Reviews in Environmental Science and Technology 31:241-293.

Varo, P. and Koivistoinen, P. 1980. Mineral element composition of Finnish Foods XII General discussion and nutritional evaluation. Acta Agriculturae Scandinaviva Suppl. 22: 165-171.

Verta, M., Kauppila, T., Londesborough, S., Mannio, J., Porvari, P., Rask, M, Vuori, K-M. and Vuorinen, P.J. 2010. Metallien taustapitoisuudet ja haitallisten aineiden seuranta Suomen pintavesissä – Ehdotus laatunormidirektiivin toimeenpanosta. Abstract in English: Background levels for metals and monitoring of priority substances in Finnish surface waters – Proposal for the implementation of Directive on Environmental Quality Standards. Suomen ympäristökeskuksen raportteja 12. 45 p. In Finnish. Available on the internet: https://helda.helsinki.fi/bitstream/handle/10138/39683/SYKEra_12_2010.pdf?sequence=1.

WHO. 1991. International Programme on Chemical Safety. Environmental Health Criteria 108. Nickel. World Health Organizarion, Geneva.

Yläranta, T. 1996. Uptake of heavy metals by plants from airborne deposition and polluted soils. Agricultural and Food Science 5:431-447.

Zayed, A. M. and Terry, N. 2003. Chromium in the environment: factors affecting biological remediation. Plant and Soil 249:139-156.

Zhao, F-J., McGrath, S.P. and Meharg, A. A. 2010. Arsenic as a food chain contaminant: Mechanisms of plant uptake and metabolism and mitigation strategies. Annual Review of Plant Biology 61: 535-559.

Appendix 1. Mass balance calculations for Cu an Zn

Similar mass balance calculation for wheat in 100-year rotation was conducted for Cu and Zn comparable to other heavy metals. The parameters used are shown in table A1 and results for Cu in table A2 and for Zn in table A3.

Table A1. Parameters used in the mass balance calculations of Cu and Zn.

Model parameters	Cu	Zn	Reference
Soil concentration, mg/kg	21	55	Mäkelä-Kurtto et al. 2007b, Table 1
Deposition, g/ha/a	5.54	26.6	Mäkelä-Kurtto et al. 2007c, Table 40
Liming kg/ha/a	400	400	Recommended liming rate
Concentration in liming materials, mg/kg	3.5	23.0	Mäkelä-Kurtto et al. 2007c, Table 17
Fertilizer rate, kg/ha	310	310	10 P kg/ha and 3.2 % P concentration
Transfer function, plant/soil	0.23	0.24	Median from Mäkelä-Kurtto et al. 2007a, Tables 39 and 58
Content of mineral fertilizers in Finland, mg/kg	6	285	Mäkelä-Kurtto et al. 2007c, Table 13
Suggested content in the prepared EU legislation, mg/kg	600	1500	Finnish law of fertilizer products and the proposal of fertilizing products
Yield kg/ha, 14% moisture	3750	3750	Finnish agricultural statistics 2010-2014
Kd	650	6000	Cu: Lahdenperä 2014; Zn: Sheppard et al. 2011, Table 3-3.
Annual runoff, m^3/h	2000	2000	Finnish Environment Institute 2000
Annual erosion, kg/ha	500	500	Finnish Environment Institute 2000

Table A2. Output values for 100-years mass balance calculations of Cu.

mg Cu/ kg fert. DM	Year	Soil water µg/l	Leached g/ha/a	Eroded g/ha/a	Yield µg/kg DM	Yield up-take g/ha/a	Soil mg/kg	Annual balance g/ha
6	1	32.3	64.6	10.5	4830	18.1	21.0	-84.2
	100	26.6	53.1	8.63	3969	14.9	17.2	-67.6
600	1	32.5	64.9	10.6	4851	18.2	21.1	98.9
	100	39.2	78.4	12.8	5863	22.0	25.4	79.4

Table A3. Output values for 100-years mass balance calculations of Zn.

mg Zn/ kg fert. DM	Year	Soil water µg/l	Leached g/ha/a	Eroded g/ha/a	Yield µg/kg DM	Yield uptake g/ha/a	Soil mg/kg	Annual balance g/ha
285	1	9.17	18.4	27.5	13209.	49.5	55.0	15.0
	100	9.29	18.6	27.9	13380	50.2	55.7	13.8
1500	1	9.21	18.4	27.6	13256	49.7	55.2	404
	100	12.40	24.8	37.2	17858.7	67.0	74.4	371

Maa- ja metsätalousministeriön julkaisuja 2018

1/2018	Toimintaohjelma maatalouden ammoniakkipäästöjen vähentämiseksi Suomessa
1a/2018	Operativt program för att minska jordbrukets ammoniakutsläpp i Finland
1b/2018	Action plan for reducing ammonia emissions in Finland

ISBN 978-952-453-961-6 (Verkkojulkaisu)
ISSN 1797-397X (Verkkojulkaisu)

www.mmm.fi
PL 30, 00023 VALTIONEUVOSTO