Cadmium in Arable Crops

The influence of soil factors and liming

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Abstract

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The aims of this thesis were to investigate (i) the influence of soil factors on Cd concentration in carrots, (ii) the effects of lime on Cd solubility in soils and on Cd concentrations in crops, (iii) the correlation between Cd concentrations in crops in liming experiments and soil factors, i.e. Cd species in soil solution and soil extracts.

Common arable crops, carrots and associated soils, soils and saturation extracts from eight liming experiments were studied. The soil pH was the best predictor of carrot Cd concentration. Liming had inconsistent effects on crop Cd concentrations. There was a decrease in crop Cd at sites with high crop Cd concentrations, but at sites with low Cd the Cd concentration in the crop increased. The Cd^{2+} solubility in the soils investigated was mainly controlled by soil pH and there was no detectable increase in Cd solubility due to additions of $Ca(NO_3)_2$ or of lime at higher pH levels. At sites with low crop Cd concentrations, the concentration of Cd in soil solution and batch extracts was also low. This indicates a low availability of metals in the soil, which can lead to micronutrient deficiency and a resultant decrease in biomass or to a release of exudates and a resultant increase in metal bioavailability. There were both visible Mn-deficiency symptoms and/or yield decreases in two of the experiments. It is probable that both plant factors and soil factors affect the solubility and availability of Cd. The Cd concentrations in crops were different between sites and in most cases larger than the effect of liming. The correlation between parameters in the saturation extracts and crop Cd was poor. Hence, analysis of soil solution extracts proved not to be a good tool for predicting crop Cd concentrations at low Cd concentrations in the soil solution.

The recommendation coming out of this thesis is to lime soils that have low soil pH and that are known to give high Cd concentrations in crops. Soils with low pH and low crop Cd concentrations should only be given minor or no additions of lime. The thesis also indicates that site selection may be more effective than liming in managing crop Cd.

Keywords: carrots, cereals, potatoes, pH, soil Cd, soil solution, Cd solubility, Ca^{2+} competition, site selection, saturation extracts.

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List of abbreviations

BS	Base Saturation
BW	Body Weight
Cd_{org}	Organically bound Cd dissolved in water extracts
Cd_{tot}	Total concentration of dissolved Cd in water extracts
DOC	Dissolved Organic Carbon
DW	Dry Weight
EC	Electrical Conductivity
FA	Fulvic Acid
FAAS	Flame Atomic Absorption Spectrophotometry
FAO	Food and Agriculture Organization of the United Nations
FW	Fresh Weight
FYM	Farm Yard Manure
GFAAS	Graphite Furnace Atomic Absorption Spectrophotometry
JECFA	Joint Expert Committee on Food Additives
OSCAR	OSteoporosis, CAdmium as a Risk factor
PTWI	Provisional Tolerable Weekly Intake
WHAM-W	Windemere Humic Acid Model – Water
WHO	World Health Organization

Contents

Appendix

Papers I-IV

The present thesis is based on the following papers, which will be referred to in the text by their Roman numerals:

I. Jansson, G. & Öborn, I. 2000. Cadmium content of Swedish carrots and the influence of soil factors. *Acta Agriculturæ Scandinavica Section B, Soil and Plant Science 50,* 49-56.

II. Jansson, G. & Öborn, I. Effects of liming on cadmium concentrations of potato tubers, cereal grains and straw. *Journal of Environmental Quality* (submitted).

III. Jansson, G., Berggren, D. & Öborn, I. Effects of liming, pH and Ca^{2+} concentration on Cd solubility in four agricultural soils (manuscript).

IV. Jansson, G., Öborn, I. & Smolders, E. Cd concentrations in crops related to different soil factors (manuscript).

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Related papers

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

Johnsson, L., Öborn, I., Jansson, G. & Berggren, D. 2002. Evidence for spring wheat (*Triticum aestivum* L.) uptake of cadmium from subsurface soils. *Journal of Environmental Quality* (submitted).

Öborn, I., Jansson, G. & Johnsson, L. 1995. A field study on the influence of soil pH on trace element levels in spring wheat *(Triticum aestivum)*, potatoes *(Solanum tuberosum)* and carrots *(Daucus carota)*. *Water, Air and Soil Pollution 85,* 835-840.

Introduction

Background

Cadmium (Cd) is a non-essential trace metal naturally occurring in the biosphere. The Cd pollution in our environment due to anthropogenic activities, such as mining, industry, agriculture and waste disposal started in the beginning of the 20th Century and accelerated during the 1960s (Alloway, 1995). Only a few Cd-minerals are known and the abundance of those is very small. Cadmium is chemically very similar to Zn (Zn) and is therefore substituted as an impurity in Zn-minerals and thereby cadmium is obtained as a by-product of the smelting of zinc and other metals. In Sweden, Cd is used in batteries (101 ton yr^{-1}), in alloys (30 ton yr^{-1}), and as a pigment in artistic paints (1.5 ton yr^{-1}) (Hedlund *et al.,* 1997) (data from 1992). Cadmium also occurs as a substitute for Ca in apatite and calcite, which can give rise to impurities in P-fertilisers. The use of Cd in batteries has dramatically increased since the 1980s, but the use of Cd in other products has decreased.

During recent decades, Cd has been the subject of increasing interest as regards human health, crop production and soil science, due to its potential toxicity to man and its relatively high mobility from soil to plant. Cadmium is one of the most soluble trace metals in the soil. Andersson (1977) found in his study that 41% of 2M HNO_3 soluble Cd was released by the relatively weak extractant 1M NH_4OAc pH 4.8. Other trace metals had a much lower solubility *e.g.* zinc (Zn) 5%, manganese (Mn) 7% and nickel (Ni) 3%. The diet is the main source of Cd exposure for non-occupationally exposed humans (non-smokers) in Sweden. Smokers are exposed by the high concentration of Cd in tobacco leaves and the high absorption via the lungs (50%) (IPCS, 1992). Cereals, potatoes and vegetables account for 70% of the dietary intake (Grawé, 1996). The Cd concentration in cereals, potatoes and vegetables is not high compared to that in other food items, such as sunflower seed and linseed, kidney and liver from mammals and hepatopancreas in shellfish (Jorhem & Sundström, 1993), but since the intake of cereals, potatoes and vegetables is rather large, the total Cd intake from those sources is considerable. The average daily intake of Cd in Sweden is in the range of 9 to 12 ug day^{-1} (Becker & Kumpulainen, 1991; Vather *et al.*, 1996; Jorhem *et al.*, 1998). Very little is known about the availability of Cd for humans in food items, but the availability may depend on several factors such as age, nutritional status and diet (Andersen *et al.*, 1992). Iron (Fe) deficiency predisposes individuals to a higher Cd absorption and therefore women are a more vulnerable group since they are more prone to Fe deficiency (Berglund *et al.*, 1994). On average, only a small percentage of the Cd from the diet is absorbed in the gastrointestinal tract.

The absorbed Cd is transported and accumulated in the kidneys and liver and the Cd content in the kidneys increases with age until approximately 50-60 years. The accumulation is due to the life-long intake via the diet and the long half-time of Cd in the kidney. The half-time for Cd is in the order of 10-30 years (Järup *et al.*, 1998). The Cd accumulation in kidneys leads to tubular renal damage, which affects the capacity to reabsorb substances from the primary urine. This kidney damage can progress to a disturbed vitamin D and calcium metabolism, which can cause osteoporosis (Alfven *et al.,* 2000).

A Joint Expert Committee on Food Additives (JECFA) appointed by FAO/WHO has decided that the Provisional Tolerable Weekly Intake (PTWI) of Cd should be 7 μg Cd kg^{-1} body weight (BW) (WHO, 2001). This corresponds to 60 μg Cd day^{-1} at a body weight of 60 kg. An intake of the PTWI over 45 years is calculated to give < 50 mg Cd kg^{-1} in the kidney cortex, which is believed to cause no health effects. However, there are indications that kidney damage occurs at lower intakes of Cd (Buchet *et al.*, 1995; Elinder & Järup, 1996; Alfven *et al.*, 2000; Järup *et al.*, 2000). Recent findings in the OSCAR project (osteoporosis, cadmium as a risk factor) show that tubular proteinuria occurs in environmentally exposed people at lower concentrations of cumulative cadmium dose than was previously realised (Järup *et al.*, 2000). Järup *et al.* (2000) found signs of kidney damage at kidney Cd levels of 50 mg kg^{-1} and about 2% of the Swedish population have concentrations exceeding that value (Barregård *et al.*, 1999). Järup *et al.* (2000) suggest that food Cd should be minimised and that the current standards for intake of cadmium should be lowered. There is also increasing evidence that Cd accumulation can lead to skeletal damage, such as osteoporosis, at low levels of exposure to Cd (Alfven *et al.*, 2000).

Cadmium in agricultural systems

The Cd concentration differs naturally between different kinds of rocks and their corresponding parent materials and soils. Thus the Cd concentration in unpolluted soils differs depending on the parent material from which the soil originates. Söderström & Eriksson (1996) found a significant correlation between the origin of the parent material and the general Cd concentration in the surface soil of agricultural soils in southern Sweden. Soils that originate from alum shales are very likely to contain high concentrations of Cd.

The median Cd concentration in surface and subsurface soils was determined to be 0.20 mg kg^{-1} (n=3067) and 0.10 mg kg^{-1} (n=1717), respectively, in a survey of Swedish arable soils (Eriksson *et al.,* 1997). The Cd concentrations in surface soil were correlated to subsurface soil Cd concentrations, which indicates a strong influence from the parent material. The areas with the highest values were those with alum shales as parent material. The surface soils had on average a 61% higher Cd concentration than the subsurface soils (Eriksson *et al.,* 1997). This difference is probably due to anthropogenic inputs, atmospheric deposition and natural processes. The difference of 61% can be compared to the increase of 33% due to P-fertilisation and atmospheric deposition, which was estimated by Andersson (1992) for the period 1900-1992. The median pH (H_2O, 1:2.5) in Swedish arable surface soils is 6.3 and the minimum and maximum values are 4.2 and 8.7, respectively (*n*=3105) (Eriksson *et al.,* 1997). Twenty-five percent of Swedish arable land has a pH lower than 6.0. However, the most important areas for crop production have median pH values that are higher than the median for the whole country (Eriksson *et al.,* 1997).

In Sweden, the most important input sources of Cd in arable soils are atmospheric deposition and commercial phosphorus fertilisers, since sewage sludge is added only to a minor proportion of soils and since urban and industrial activity is still rather low in Sweden (Andersson, 1992) (Fig. 1). Budget calculations made by Andersson (1992) indicate that the Cd concentration of the surface soil had increased by 33% since 1900 and in 1990 the annual change in surface soil Cd concentration was on average 0.21% (Table 1). Eriksson (2000) has made some new Cd balances with updated values from 2000 and calculated the change to be 0.03% in the surface soil (Table 1). The reason for the lower accumulation, which Eriksson (2001) found are that: (i) atmospheric deposition has decreased during the past decade due to measures taken in Europe to reduce heavy metal emissions into the air (ii) smaller inputs of Cd from P-fertiliser are being applied and (iii) leaching was calculated differently (Table 1). In Sweden, there is a tax on Cd in P-fertiliser containing more than 5 mg Cd kg^{-1} and also a restriction against import of P-fertiliser containing more than 100 mg Cd kg^{-1} P. This has led to the use of low Cd containing P-fertiliser and thereby a lowered input of Cd to arable soils. In Andersson's (1992) budget calculation, the leaching was based on Cd concentrations in the drainage water, while in Eriksson's (2001) budget calculations the leaching was based on Cd concentrations in the surface soil solution. The total Cd accumulation was the same in the Finnish budget calculation (Table 1) as in the Swedish one, even though the input and removal values were somewhat different (Moolenaar, 1999). In the Finnish budget, manure was added to the soil, but the atmospheric deposition was lower than in the Swedish budget.

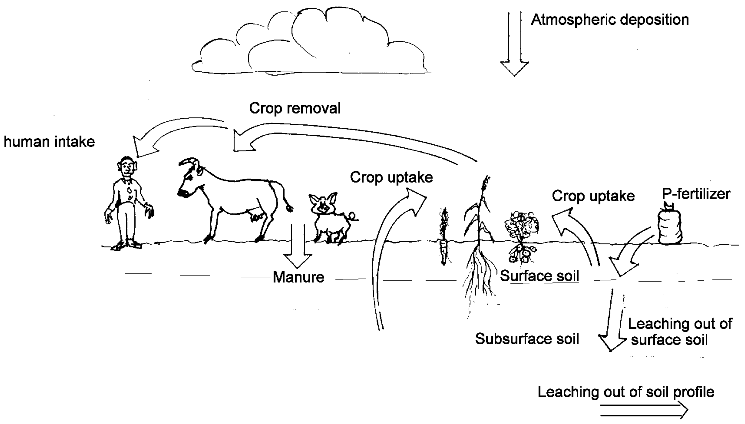

Fig. 1. Cd fluxes in Swedish arable soils.

Table 1. *Cadmium balances for average arable land in Sweden and Finland*

	Sweden 1990[1] no livestock South Sweden	Sweden 2000[2] no livestock South Sweden	Finland[3] countrywide averages
Input, (g ha^{-1} year^{-1})			
P-fertiliser	0.72[4]	0.12[5]	0.10
Manure	-	-	0.22
Deposition	0.78[6]	0.70[7]	0.15
Lime	0.02	0.02	0.03
Sludge	-	-	0.02
Total input	*1.52*	*0.84*	*0.52*
Removal, (g ha^{-1} year^{-1})			
Crops	0.21	0.23	0.14
Leaching	0.06[8]	0.40[9]	0.06
Runoff	-	-	0.11
Total removal	*0.27*	*0.63*	*0.31*
Accumulation	*1.25*	*0.21*	*0.21*
Change in topsoil (%)	*0.21*	*0.03*	-

[1]Andersson, 1992; [2]Eriksson, 2001; [3]Moolenaar, 1999; [4]11 kg P ha^{-1} containing 65 mg Cd kg^{-1} P; [5]10 kg P ha^{-1} containing 12 mg Cd kg^{-1} P, data from 1999; [6] Data from 1990; [7]Data from 1995; [8]Cd in drainage water, 1m depth; [9]Cd in surface (0-25cm) soil solution

Cd concentration in crops: Levels and limit values

The Cd concentration of Swedish winter wheat, oats, barley, carrots and potatoes has been investigated in national surveys (Table 2) (Eriksson, 1990; Eriksson *et al.*, 2000; Jansson & Öborn, 2000; Grawé *et al.*, 2001). The Swedish spring wheat Cd concentration has not been systematically investigated, but spring wheat was included in a field study where the influence of soil pH on crop Cd concentrations was the main focus (Öborn *et al.*, 1995). Eriksson (1990) found that 5-10% of samples of Swedish winter wheat grain had Cd concentrations near or above the limit value for cereals (0.1 mg kg^{-1}) suggested by the CODEX committee on cereals, pulses and legumes (FAO/WHO, 1993). However, they were below the EU limit values for cereals (oats and barley grain 0.1; wheat grain 0.2 mg kg^{-1}) valid from 2002 (EG, 2001; Grawé, 2001). The EU limit value for carrots and potatoes is 0.1 mg Cd kg^{-1} fresh weight (FW), which corresponds to a value of 0.9 mg kg^{-1} dry weight (DW) for carrots and 0.5 mg kg^{-1} DW for potatoes. Swedish surveys conducted in 1993-1994 (carrots) and 1999 (potatoes) found that the EU value was not exceeded in any carrot or potato sample (Jansson & Öborn, 2000; Grawé *et al.*, 2001).

The Cd concentration in wheat grains and carrots was similar in investigations in a number of countries while the Cd concentration in potato tubers was much lower in Sweden and Norway than in Poland, Australia and the United Kingdom (Table 2).

Table 2. *Cd concentrations in crops from different countries (mg kg^{-1} DW)*

Country	Crop	*n*	Median	Min	Max
Sweden[1]	Carrots	72	0.24	0.06	0.82
Denmark[2]	"	18	0.20	0.06	1.73
Netherlands[3]	"	100	0.27	0.045	1.45
USA[4]	"	207	0.15	0.018	1.18
Sweden[5]	Potato tubers	75	0.041	0.004	0.142
Australia[6]	"	359	0.150	0.02	1.05
United Kingdom[7]	"	20	0.150	-	-
Norway[8]	"	79	0.060	<0.010	0.225
Poland[9]	"	6306	0.11	-	-
Sweden[10]	Barley grains	327	0.019	0.002	0.076
United Kingdom[11]	"	233	0.019	-	-
Sweden[10]	Oat grains	208	0.036	0.002	0.505
Poland[12]	Rye	2523	0.03	-	
Sweden[13]	Spring wheat grains	43	0.056	0.014	0.163
Sweden[12]	Winter wheat grains	606	0.044	0.007	0.229
Netherlands[4]	"	84	0.06	0.07	0.35
Poland[12]	Wheat grains	3098	0.07	-	-
United Kingdom[11]	"	250	0.053	-	-

[1]Jansson & Öborn 2000; [2]Andersen, 1979; [3]Wiersma *et al.,* 1986; [4]Wolnik *et al.,* 1985; [5]Grawé *et al.,* 2001; [6]McLaughlin *et al.,* 1997b; [7] Ministry of Agriculture, Fisheries and Food, 1997; [8]Alne & Gjerstad, 1998; [9]Kabata-Pendias *et al.,* 2001; [10]Eriksson *et al.,* 2000; [11]Adams *et al.,* 2000; [12]Terelak *et al.,* 2001; [13]Öborn *et al.,* 1995

Andersson & Bingefors (1985) found a doubling of the Cd concentration in winter wheat grains between the years 1918 to 1980 (Fig. 2). The increased Cd concentration could be due partly to increased solubility of the soil Cd and partly to increased total Cd concentration in the soil. The Cd concentration in wheat grains from a long-term field experiment between (1880 to 1980) at Rothamsted, UK, decreased in plots treated with FYM and increased in control plots and plots treated with P-fertilizer (Jones & Johnston, 1989).

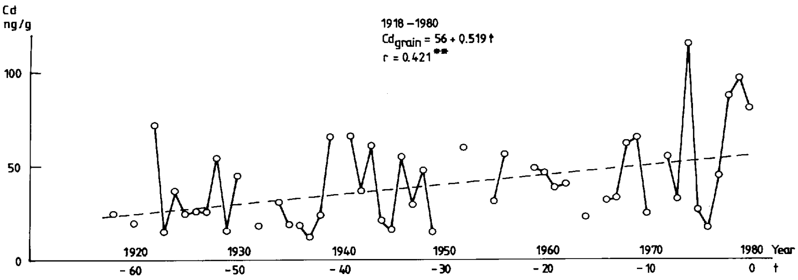

Fig. 2. Cd concentration in winter wheat grains grown between the years 1918 to 1980 in Sweden (from Andersson & Bingefors, 1985).

Cd solubility in the soil environment

In the soil environment, cadmium can occur in three forms: as solid precipitates; associated to solid soil components; and as a solute in the soil solution. In most soils, 99% of the Cd in the soil is associated to soil colloids and only 1% is located in the soil solution (Christensen & Huang, 1999). Cadmium can form precipitates with CO_3^{2-}, S^{2-}, PO_4^{3-} and OH^- in the soil. However, in most soils where arable crops are grown the redox potential is to high and the pH, Cd and anion concentration are too low to form any Cd-precipitates (Christensen & Huang, 1999). Therefore, Cd is most likely controlled by sorption processes in the soil and not by precipitation of Cd minerals.

The Cd sorption to solid particles in the soil depends on several factors, such as pH, clay content, organic matter content, amount of Al- Fe- and Mn-oxides, cationic competition and complexation with ligands in the soil solution. Cd is bound in the soil in two ways; surface complexation or electrostatic adsorption (Tiller *et al.*, 1979; Tiller *et al.*, 1984; McBride, 1994). Cadmium is bound as surface complexes to organic matter (eq. 1), or to OH-groups on the surface edges of oxides and clay minerals (eq. 2).

$$RH_{2(s)} + Cd^{2+}_{(aq)} \leftrightarrow RCd_{(s)} + 2H^{+}_{(aq} \qquad \text{eq. 1}$$

$$FeOH_{(s)} + Cd^{2+}_{(aq)} \leftrightarrow FeOCd^{+}_{(s)} + H^{+}_{(aq)} \qquad \text{eq. 2}$$

Reactions 1 and 2 are strongly pH dependent. The Cd adsorption to OH-groups becomes higher at increasing pH-values (Zasoski & Burau, 1988; Zachara *et al.*, 1992) and surface complexation to organic matter can occur at lower pH-values. The electrostatic adsorption is mainly to clay minerals (2:1 minerals) which have a large proportion of permanent charges (eq. 3).

$$Cd\text{-}Clay + Ca^{2+}_{(aq)} \leftrightarrow Ca\text{-}Clay + Cd^{2+}_{(aq)} \qquad \text{eq. 3}$$

To the electrostatic binding sites, Ca^{2+} as well as Zn^{2+} are strong competitors to Cd^{2+}, which can lead to an increased Cd solubility when Ca^{2+} and Zn^{2+} are applied (Christensen, 1984; Christensen, 1987; Boekhoeld *et al.*, 1993; Temminghoff *et al.*, 1995).

Soil solution: Cadmium forms and sampling techniques

The composition of the soil solution is very important since the soil solution is closely connected to other Cd-pools in the soil and since plant uptake of Cd and other trace elements takes place in the soil solution (Wolt, 1994). Therefore the composition of the soil solution might be an appropriate indicator for the Cd concentration in crops. The free cadmium ions and potentially the complexed species in the soil solution interact with the Cd species bound to the solid phase by sorption and ion-exchange. Cadmium in soil solution can be present as free, hydrated cations or as species bound to inorganic or organic ligands. Cadmium can also be bound to inorganic or organic colloids suspended in the soil solution. There is no adequate definition on dissolved or particulate Cd and often the size of a membrane filter decides the definition (Helmke, 2000). The suspended particles are organic particles and hydroxy-polymers of Fe and Al. Even if the colloids are mostly not considered to be a part of the soil solution, their intimate association with the solution will affect the behaviour of Cd. It is not only the soil's potential to sorb Cd that determines the Cd concentration in soil solution. High concentrations of ligands in the soil solution, which can be complex bound to Cd, can also increase the total Cd concentration in the soil solution.

There are several different sampling techniques for soil solutions, both laboratory and field methods. Some laboratory methods are high speed centrifugation (undisturbed soil columns), saturation extracts, immiscible displacement, water extracts and column displacement. Field methods are *e.g.* sampling with tension lysimeters and monolith lysimeters (Wolt, 1994). There is unfortunately no perfect method, as all existing methods have disadvantages and affect the soil solution in different ways. In addition, it is not only the sampling of the soil solution that is connected with difficulties. Other factors that can affect the composition of the soil solution are *e.g.* soil sample storage (time, moisture and temperature) (Edmeades *et al.,* 1985; Ross & Bartlett, 1990) and method of Cd speciation.

Crop uptake of cadmium

The Cd concentration in agricultural crops is influenced by soil factors, plant properties, pollution inputs, agricultural management practices and climate. Several studies have shown that important soil factors affecting crop Cd concentration are pH, Cd and Zn concentrations, organic matter, soil texture and complexing ligands. The Cd concentration in crops tends to be highest in soils with a low pH, low organic matter content, high soil Cd concentration and low or high soil Zn concentration (Eriksson, 1990; He & Singh, 1995; Öborn *et al.*, 1995; Eriksson & Söderström, 1996; Wenzel *et al.,* 1996; McLaughlin *et al.*, 1997b; Jansson & Öborn, 2000). Most research has focused on soil factors in the plough layer. However, some plants have deep roots growing into the sub-soil and thus soil factors in those layers are also important. It has been shown that 15-37% of the Cd in wheat grains was taken up from the sub-surface layers (Johnsson *et al.,* 2002).

Some of the plant factors that can affect the Cd concentration are: species, variety, root activity and rooting pattern (Welch & Norvell, 1999). In leafy vegetables Cd accumulates in the leaves, whereas in cereals, accumulation is greatest in the roots and declines towards the top of the plant (Cutler & Rains, 1974). The plant Cd level and the way Cd is distributed within the plant differ between species as well as between cultivars within the same species. The Cd concentration in cereal grains tends to decline in the order: wheat > oat > barley (Eriksson *et al.,* 2000). Differences have been found in Cd concentrations between cultivars of wheat (Pettersson, 1977; Andersson & Pettersson, 1981; Eriksson, 1990; Cieśliński *et al.,* 1996; Wenzel *et al.,* 1996), potatoes (McLaughlin *et al.,* 1994; Grawé *et al.,* 2001), carrots (Harrison, 1986), oats (Eriksson, 1990) and flax

(Cieśliński *et al.,* 1996). Cieśliński *et al.* (1996) also found differences in the distribution of Cd concentrations in plants due to cultivar and soil factors. Different root activities of plants can also affect the Cd solubility in the rhizosphere and thereby influence the Cd concentration in the plant. Root processes can affect the Cd concentration in plants, *e.g.* root efflux of H^+, reductants (phenolic compounds), organic acids (*e.g.* citrate) and non-protein amino acids (*e.g.* phytosiderophores) (Welch & Norvell, 1999).

The Cd concentration in crops grown at the same site is known to differ between years (Andersson & Bingefors, 1985). Andersson & Bingefors (1985) found large annual variations (±30-50%) in winter wheat Cd concentrations (Fig. 2) and there was a close to significant (p=0.053) correlation to precipitation during the growing period (June to August). Eriksson *et al.* (1990) found a significant positive correlation between grain Cd concentration in oat and precipitation. The annual variation in crop Cd concentration as reflected by correlation to precipitation could be due to variations in factors such as atmospheric deposition, redox potential, pH and rooting pattern.

Most research has focused on the uptake of aqueous Cd^{2+} in crops and little attention has been given to other Cd species in the soil solution (Welch & Norvell, 1999). Complexation of cadmium with inorganic ligands (*e.g.* Cl^- and SO_4^{2-}) and organic ligands (*e.g.* humic and fulvic acids) will increase the total amount of Cd in the soil solution and some of these Cd-complexes may be taken up directly by the plant (Smolders & McLaughlin, 1996a,b*;* McLaughlin *et al.,* 1998a,b). Smolders *&* McLaughlin (1996b) found in their studies an increased Cd concentration in Swiss chard when Cl^- concentrations were increased. The crop Cd increase could be due to phytoavailability of the increased $CdCl_n^{2-n}$ concentration or to enhanced Cd diffusion in the areas close to the roots or into the plant roots.

Measures to reduce crop cadmium concentrations

Some measures have been proposed to reduce Cd concentrations in crops, *e.g.* liming, Zn fertilisation, plant breeding and site selection.

Regular liming has been suggested as a measure for decreasing the plant uptake of Cd since soil pH is one of the most important factors influencing the solubility of Cd in soils. However, the effects of liming on Cd concentrations in agricultural crops have been conflicting, with both decreases, increases as well as no effects being reported (Andersson & Simán, 1991; Sparrow *et al*., 1993; Oliver *et al.,* 1996; Maier *et al*., 1997; Sparrow & Salardini, 1997; Tyler & Olsson, 2001; Jansson & Öborn, 2002). There are several possible explanations for these inconsistent results. An increase or zero crop response in Cd concentration could be due to (i) a large proportion of the Cd being taken up by the plants from the subsurface soil, which is unaffected by the lime, and thus the effect of liming is diminished, (ii) competition by added Ca^{2+} on the binding sites in the soil, which leads to higher or unaffected Cd solubility/availability, (iii) increased Cd solubility due to higher dissolution of DOC around lime particles above pH 7.5 and a following complex binding, (iv) micronutrient deficiency induced by the liming, which leads to lower crop biomass and a subsequent enrichment of crop Cd concentration, (v) micronutrient deficiency, which leads to plant release of root exudates and a subsequent increased solubility/availability of Cd or (vi) micronutrient deficiency which leads to reallocation of micronutrients and Cd within the plant. A zero crop response could also be due to relatively high pH in the unlimed plots, which leads to a very small or no difference in Cd solubility/availability between unlimed and limed plots.

There are several theories behind the possible effects of Zn addition on Cd concentration in crops. The decrease in Cd concentration in plants could be due to (i) Zn and Cd competition for binding sites on root surfaces (ii) Zn deficiency leading to disturbed root cell membranes and an uncontrolled mass flow of cations into the cell and (iii) plants releasing exudates at Zn deficiency, which increases the availability of both Zn and Cd (Welch & Norvell, 1999). However, addition of Zn can lead to competition for binding sites on soil particles and thus an increased Cd solubility (Christensen, 1987) and availability. Results in Zn addition studies have been contradictory, with reported increases (Williams & David, 1976), decreases (Oliver *et al.*, 1994; Choudhary *et al.,* 1995; Grant & Bailey, 1997) and zero responses (Grant & Bailey, 1998).

Several studies have shown that there are differences between cultivars in the amount of Cd accumulated and in the pattern of distribution within the plant (Pettersson, 1977; Andersson & Pettersson, 1981; Harrison, 1986; Eriksson, 1990; McLaughlin *et al.,* 1994; Cieśliński *et al.,* 1996; Wenzel *et al.,* 1996; Grawé *et al.,* 2001). Theoretically, this fact makes plant breeding an appropriate measure for reducing Cd concentrations in edible crops. However, the differences in Cd concentrations between cultivars are not very large.

Cadmium concentrations in crops has been shown to vary considerably between regions and sites (Andersson & Pettersson, 1981; McLaughlin *et al.,* 1994; Eriksson *et al.,* 2000). These differences in crop Cd concentrations between regions and sites are probably due to differences in *e.g.* atmospheric deposition, parent material, Cd concentration in soil, pH, soil texture, organic matter, and usage patterns of cultivars and fertilisers. Often the largest difference in crop Cd concentration occurs between sites and not between different soil treatments or cultivars. Thus site selection is sometimes a more powerful tool in reducing crop Cd concentrations than changes in soil or plant factors.

Hypotheses & Objectives

The main objectives of this thesis were to (i) investigate soil factors influencing crop Cd concentrations; and (ii) evaluate liming as a measure for reducing Cd concentrations in arable crops and thereby decrease the intake of Cd via food and lower the health risk of Cd.

The following ***hypotheses*** *were tested in this thesis:*

I. Cd solubility and plant availability are mainly controlled by the soil pH. Therefore liming will decrease the Cd concentration in crops.

II. High additions of lime (calcite) can cause calcium-cadmium competition on the binding sites on the soil particles and thereby increase the Cd solubility and plant availability.

III. Liming decreases both the Cd and micronutrient availability in the soil and thus liming induces micronutrient deficiency. This deficiency leads to smaller biomass and enrichment in Cd concentration.

The specific ***objectives*** *of the studies were:*

- To determine the influence of soil factors on the Cd concentration in carrots grown under field conditions *(Paper I)*.

- To investigate the effects of different lime (calcite) application rates on yield and Cd concentrations in potato tubers, cereal grains and straw in field experiments *(Paper II)*.

- To investigate the effects of liming (calcite) on Cd solubility in soils covering a wide range in clay content and to assess the role of pH relative to the Ca^{2+} competition in controlling the Cd solubility *(Paper III)*.

- To investigate the correlation between Cd concentrations in crops in liming experiments and soil factors, *i.e.* Cd species in soil solution and soil extracts, and to try to find possible explanations to the inconsistent effects of liming on crop Cd concentration found in the field experiments *(Paper IV)*.

Materials & Methods

Site and sampling description

Carrot fields (Paper I)

Paired soil and carrot (*Daucus carota* L.) samples were taken in 1993 (*n*=36) and 1994 (*n*=36) from commercial carrot fields within the most important areas of carrot production in Sweden (Fig. 3). The areas are situated between 55°N and 60°N. Carrots from five counties were sampled in the first year. Together, these counties accounted for 87% of the Swedish carrots produced in this year. In the second year, two additional counties were added to the sampling scheme so that the sampled counties accounted for 97% of the total production (SCB, 1988; SCB, 1991). The samples were collected from different fields in the two years.

In each field, a site was selected where paired soil and carrot samples were taken at harvest time. All carrots in a 2-m long section of a row were dug up, weighed and mixed, and a random subsample weighing 2 kg was taken for analysis. In the harvested row, eight sub-samples from the surface soil (plough layer) were sampled, mixed and combined to obtain a single 1-kg sample. The soil samples were taken with an auger to a depth of 25 cm (Ap or Hp horizon).

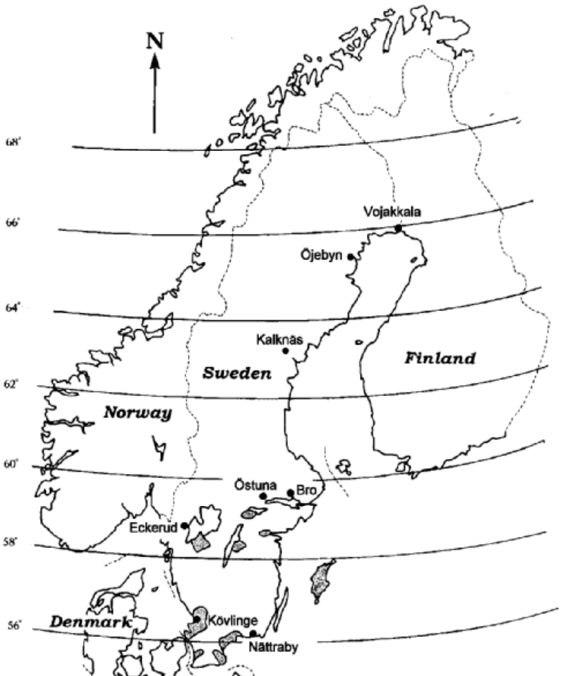

Fig. 3. Map of Sweden showing the sites of liming experiments (●) and the areas sampled in the carrot survey (shadowed areas).

Liming experiments (Papers II-IV)

Seven long-term liming experiments and one newly established liming experiment were sampled. The sites were located in some of the major agricultural regions in the whole of Sweden and represent different parent materials, textures and climatic conditions (Fig. 3). The surface soil (plough layer 0-25cm) in the field experiments was limed to reach different levels of base saturation, *i.e.* unlimed and limed to 55, 70 and 100% BS respectively, except in the recently established experiment where the 100% BS was excluded. The long-term field experiments were limed for the first time in 1983 and thereafter maintenance limed in 1985 and every fourth year. The recently established field was limed at the start in 1996. Finely ground (0-0.5mm) calcite (50% CaO) was used. In all experiments, there were four replicates of each treatment (randomised blocks).

In 1993-1997, potatoes (*Solanum tuberosum* L.) (fresh market) were grown at five different sites, three of which were used for two years. In 1994-1998, cereals, *i.e.* oats (*Avena sativa* L.), barley (*Hordeum vulgare* L.), winter wheat and spring wheat (*Triticum aestivum* L.) were grown at five different sites. At each site, cereals were sampled for one to four years.

Samples of soil, potato tubers, cereal grain and straw were taken from each plot at harvest time. In every plot, 20 sub-samples of the surface soil (0-20 cm) (Ap horizon) and the subsoil (40-60 cm) were taken with an auger. The sub-samples were pooled, thoroughly mixed and a composite sample of 2 kg was saved for analysis.

Crop and soil sample preparation *(Paper I, II and IV)*

Five potato tubers or carrots of median size were randomly selected, brushed, peeled and cut into cubes ($0.5cm^3$) and freeze-dried. Grain and straw were air-dried to ≤15% water content. The straw was chopped into pieces of 0.5-1cm length. Soil samples were (i) frozen (-20 ºC) and/or (ii) air-dried, crushed and sieved at 2-mm and stored in darkness in plastic bags until analysis.

Saturation extracts *(Paper III)*

Surface soil samples from four replicates of the different liming treatments of four field experiments were included in the study. The field experiments used were Kövlinge, Nättraby, Eckerud and Östuna (Fig. 3). The sites were selected to represent a wide range in clay content and crop Cd concentrations (Table 3). To obtain saturation extracts, deionized water was added to thawed soil samples until saturation was reached (van Reeuwijk, 1993). The amounts of added soil and water depended on soil texture and water content in the soil. The soil-water paste was homogenised by hand-stirring with a plastic spoon. The saturated soil was equilibrated for 16h at 12 ºC and thereafter centrifuged, membrane filtered and divided into two subsamples, of which one was acidified (1% HNO_3).

Batch experiments *(Paper III)*

In the batch experiments only surface soil from the unlimed plots from four liming experiments (Kövlinge, Nättraby, Eckerud and Östuna) was used and the four replicates were pooled to give one composite sample. Three grams of thawed soil and 30 ml solution were added to a plastic vessel. The pH levels were set in the soil by adding either HNO_3 or NaOH. Three different experiments were conducted and in each of the experiments different electrolytes were used. The electrolytes used were:
0.01M $NaNO_3$ Expt. "lowNa";
0.01M $NaNO_3$ + 0.01M $Ca(NO_3)_2$ Expt. "Ca";
0.10M $NaNO_3$ Expt. "highNa".
The soil was equilibrated for four days in an end-over-end rotator at 12 ºC. After equilibration the soil was centrifuged and thereafter filtered.

Soil analysis

Characterisation of the sampling areas and sites

In order to characterise the soils included in the studies particle-size distribution, pH (soil-water, 1:2.5), electrical conductivity (EC) (soil:water, 1:2.5), total carbon (C) and 2M HNO_3-extractable trace metal concentrations (Andersson, 1975) were conducted on the soil samples. The trace metal concentrations (Cd, Zn, Mn and Cu) were measured by flame atomic absorption spectrophotometry (FAAS) or graphite furnace atomic absorption spectrophotometry (GFAAS) (Perkin Elmer Zeeman 3030 with an HGA-600 graphite furnace).

Extractions with EDTA pH 4.65, $CuCl_2$ (Juo & Kamprath, 1979), ammonium oxalate ($(NH_4)_2C_2O_2$) pH 3.25 (van Reeuwijk, 1993), and sodium dithionite-citrate (van Reeuwijk, 1993) were made on fresh surface soil samples from four liming experiments (Kövlinge, Nättraby, Eckerud and Östuna) (Fig. 3). Metal concentrations (Al, Fe, Mn and Cd) were measured by FAAS (Perkin Elmer Aanalyst 300) or GFAAS (Perkin Elmer Zeeman 3030 with an HGA-600 graphite furnace).

A sequential extraction was conducted on surface and subsurface soil samples from unlimed plots of some of the liming experiments (Nättraby, Eckerud, Östuna and Öjebyn) (Fig. 3). The extractants used were 1M NH_4NO_3, 0.1M Na_3PO_4, 0.1M ammonium oxalate ($(NH_4)_2C_2O_2$) pH 3.25 and 7M HNO_3. The sequential method used was based on principles suggested by McLaren & Crawford (1973), Elsokkary & Låg (1978) and Swedish Standard 028311 (1997). The method used is described in detail by Alriksson (1997). Cadmium, Zn and Cu were analysed in the extracts by GFAAS (Perkin Elmer Zeeman 3030 with HGA-600 graphite furnace) and FAAS.

Liming treatments

Exchangeable Cd and Zn (1M NH_4NO_3) (only in Kövlinge, Nättraby, Eckerud, Östuna and Öjebyn), pH, EC, total C and 2M HNO_3 extractable trace metal concentrations (Andersson, 1975) were determined in surface soil samples from all treatments in the liming experiments. The trace metal concentrations (Cd, Zn, Mn and Cu) were measured by GFAAS and FAAS as described above.

Saturation extracts and batch experiments

In the saturation extracts and batch experiment extracts pH, EC, concentrations of major cations and anions, dissolved organic carbon (DOC) and Cd were determined. The major cations and anions (only in saturation extracts) were analysed on an ion chromatography (Dionex 2000i/SP), DOC was analysed by Shimadzu TOC-5000A (TC/IC method) and the Cd concentration was analysed by GFAAS with triple injections (Perkin Elmer Zeeman 4110ZL with HGA-600 graphite furnace). In the batch experiment, aluminium was also measured and the cations were analysed using ICP-AES (Perkin Elmer Optima 3000DV).

Plant analysis

For trace metal analysis 2 g carrot cubes (freeze-dried), 2 g potato cubes (freeze-dried), 2 g whole cereal grains or 1 g chopped straw pieces were totally dissolved by digestion in 10+5 ml concentrated HNO_3 (supra pure) at 135 ºC for 17 h using a Tecator Digester equipment. The trace metal concentrations in the crops were analysed by FAAS (Zn, Mn and Cu) (Perkin Elmer Aanalyst 300) and GFAAS (Cd) (Perkin Elmer Zeeman 3030 and 4110ZL with HGA-600 graphite furnace) Addition calibration was used in the analysis of Cd. In the addition calibration, the extract from one sample is used as a matrix to which the standards are added, whereupon a calibration curve is constructed. Reference material, *i.e.* carrot- potato- or wheat-flour from the Agricultural Research Centre of Finland (ARC/CL) and blanks were included in every digestion and each trace metal determination.

Modelling the Cd speciation

Activities and concentrations of the various Cd species in the saturation and batch extracts were calculated using the chemical model WHAM-W (Tipping, 1994). The model describes the protonation and metal binding by humic substances (electrostatic binding and complexation). The standard database WATER 10 (Tipping, 1994) was used in these Cd calculations. All the measured ions, DOC and pH in the extracts were used in the calculations. The model calculates the following Cd species, Cd^{2+}, $CdCl^-$, $CdCl_2^0$, $CdSO_4^0$, $CdOH^-$ and $Cd(OH)_2^0$ and Cd bound to fulvic acids (Cd_{org}). In the calculations we assumed that 50% of the DOC was fulvic acids, having a C content of 50%.

Statistical analysis

The results were analysed by analysis of variance, simple linear regression, multiple regression and stepwise multiple regression using SYSTAT for Windows Versions 5 and 8.0 (SYSTAT, 1992; SYSTAT, 1998). Significance levels used were $p \leq 0.05$ in analysis of variance and simple regression and $p \leq 0.15$ in multiple regression. In the stepwise multiple regression, forward selection was used to find the combination of x variables (predictors) showing the best fit.

Results & Discussion

Survey of Swedish carrots and paired soils *(Paper I)*

Commercially produced carrots (*Daucus carota* L.) were sampled in 1993 and 1994 from the most important areas of carrot production in Sweden. There was a wide variation in the Cd concentration in the sampled carrots, with a minimum of 0.06 mg kg^{-1} DW (0.007 mg kg^{-1} FW) and a maximum of 0.87 mg kg^{-1} DW (0.09 mg kg^{-1} FW) (Fig. 4). The median Cd concentration of the carrots was 0.24 mg kg^{-1} DW (0.03 mg kg^{-1} FW) (Table 2). There was no significant difference between the median values from the two years. Twenty-four percent of the samples exceeded 0.05 mg kg^{-1} FW (0.45 mg kg^{-1} DW), which is the limit value used in the production of infant food in Sweden, but none of the samples exceeded 0.10 mg kg^{-1} FW (0.9 mg kg^{-1} DW), which is the present limit value in the EU (EG, 2001). The values in this study were similar to values in other studies reported from Denmark, the Netherlands and the USA (Anderssen, 1979; Wolnik *et al.*, 1985; Wiersma *et al.*, 1986) (Table 2).

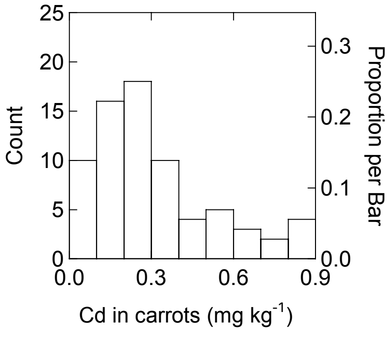

Fig. 4. Cd concentrations in carrots sampled during 1993 and 1994 in Sweden (mg kg^{-1} DW).

The sampled soils were either sandy soils or organic soils. The median surface-soil pH was 6.3 and the pH values varied greatly (from 5.0 to 8.1) both between and within counties (Fig. 5a,b). The median concentration of Cd (2M HNO_3) in the surface soil was 0.30 mg kg^{-1} and the range was between 0.15 and 0.58 mg kg^{-1}. The median Cd concentration in this study was somewhat higher than the median concentration (0.20 mg kg^{-1}) found in a survey of Swedish agricultural soils (Eriksson *et al.,* 1997).

Since there was no significant difference in carrot Cd concentration between the two sampling years, carrot and soil samples from the two years were pooled for statistical analysis. The soil samples and corresponding carrot samples were divided into two groups: soils with an organic C content lower than 7% (mineral soils) (n=37) and soils with an organic C content equal to or higher than 7% (organic soils) (n=35). Simple linear regressions and stepwise multiple linear regressions relating the $\log_{10}$ Cd concentration of carrots to surface soil factors such as pH, organic C content, and Cd concentration, were carried out. I used the $\log_{10}$ since the Cd concentration of carrots was more close to a normal distribution after log transformation.

In both soil groups there was a significant negative correlation between surface soil pH (0-25 cm) and the Cd concentration in carrots. The regression coefficient (R^2) was 0.51 in mineral soils and 0.77 in organic soils (Fig. 5a,b). The relation between soil organic C and Cd in carrots was not significant in any of the soil groups. The Cd concentration in carrots was significantly and positively correlated to Cd in soil (2M HNO_3) in organic soils (R^2=0.35), but there was no significant correlation in mineral soils.

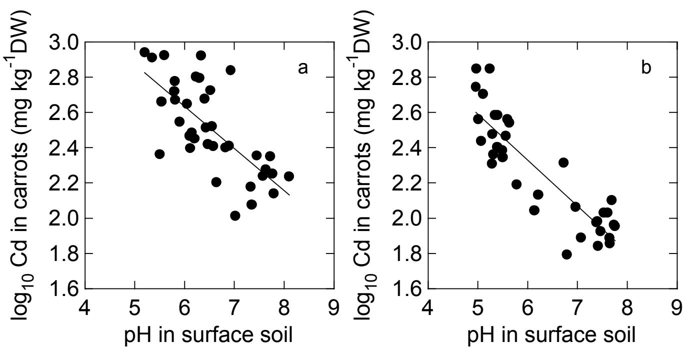

Fig. 5. Relation between surface-soil pH and $\log_{10}$ Cd concentration of carrots sampled in two consecutive years; *(a)* in mineral soils (R^2=0.51, n=37) and *(b)* in organic soils (R^2=0.77, n=35).

A stepwise multiple regression was carried out in which the $\log_{10}$ Cd concentration of carrots was related to pH, organic C and Cd concentrations of the surface soil. In the group with mineral soils, the pH and Cd concentration of the surface soil were included in the model and explained 62% of the variation in the Cd concentration of carrots (eq. 4). In the group with organic soils, all three soil factors were included in the model and explained 85% of the variation in the Cd concentration of carrots (eq. 5).

$\log_{10}Cd_{carrot} = 4.16 - 0.29*pH + 1.00*Cd_{soil}$ (mineral) $R^2=0.62$ eq. 4

$\log_{10}Cd_{carrot} = 4.11 - 0.28*pH - 0.007*org\text{-}C + 0.34*Cd_{soil}$ (organic) $R^2=0.85$ eq. 5

Soil properties in liming experiments *(Paper II-IV)*

The clay content in the plough layer (A_p) varied widely between sites, 8-62%. The pH in the unlimed A_p-horizons was acid to slightly acid (5.0-6.2). The B-horizons included both highly acid and neutral conditions, which led to a wide range in subsurface soil pH from 3.3 to 7.0. The soil Cd concentration extracted by 2M HNO_3 was in the range of 0.10 to 0.41 mg kg^{-1} (Table 3). These values are both lower and higher than the Swedish average level (0.22 mg kg^{-1}) (Eriksson *et al.,* 1997). Cadmium concentrations in soil samples from unlimed plots in the liming experiments extracted by 1M NH_4NO_3 were 0.008-0.063 mg kg^{-1}, which corresponds to 6-38% of the HNO_3-extractable fraction.

Table 3. *Characterisation and classification (FAO, 1988) of the soil profiles at the fields outside the liming experiments*

Soil/ horiz	Depth (cm)	Clay[1] (%)	Org C (%)	pH H_2O 1:2.5	CEC_{pH7} $cmol_c$ kg^{-1}	Cd[1] NH_4NO_3 mg kg^{-1}	Cd	Zn	Mn
							HNO_3 mg kg^{-1}		
Kövlinge, Dystric Regosol									
A_p	0-37	8	3.3	5.7	25	0.009	0.10	18	-
B_{w1}	46-68	4	-	5.3	-	-	-	-	-
Nättraby, Eutric Cambisol									
A_p	0-27	21	1.8	6.0	15[2]	0.013	0.14	49	370
B_{w2}	37-62	52	0.4	7.0	-	0.003	0.10	43	450
Eckerud, Eutric Cambisol									
A_p	0-20	40	3.1	6.2	22[2]	0.008	0.18	58	380
B_{gw3}	45-60	47	0.5	6.6	-	0.005	0.07	47	430
Östuna, Gleyic Cambisol									
A_p	0-25	56	2.2	5.4	26[2]	0.050	0.21	95	310
B_{gw2}	40-60	66	0.8	4.9	-	0.020	0.13	96	450
Bro, Gleyic Cambisol									
A_p	0-25	62	3.4	5.6	31[2]	-	0.41	-	330
BC_g	55-100	59	0.9	4.6	-	-	0.24	-	430
Kalknäs, Eutric Regosol									
A_p	0-20	20	2.5	6.2	20[2]	-	0.13	-	500
B_{gw}	33-60	19	0.4	6.3	-	-	0.08	-	850
Öjebyn, Thionic Gleysol									
H_p	0-23	21	13.1	5.0	41[2]	0.063	0.19	34	270
B_{gjw2}	47-58	26	2.9	3.3	-	0.005	0.01	24	117
Vojakkala, Dystric Regosol									
A_p	0-28	16	3.0	5.0	24[2]	-	0.09	-	143
BC_g	48- 69	17	1.4	4.7	-	-	0.07	-	180

[1] Clay<2µm; [2] Soil from unlimed plots in the liming experiments; [3] Haak & Simán, 1992

Effects of liming on soil properties and crop Cd concentration *(Paper II)*

The pH was significantly increased by liming at all eight sites. In six experiments the pH range was 5.3/5.5-6.6/7.0, while at two sites it had higher initial pH level and thus a more narrow range 6.2-7.0 and 5.7-6.3, respectively (Table 4; Fig. 6a,b; Fig. 7a,b). Exchangeable Cd (1M NH_4NO_3) values in surface soil samples from unlimed plots and plots with the highest liming rate were 9-48 µg kg^{-1} and 1-9 µg kg^{-1}, respectively. The exchangeable Cd and Zn were significantly decreased by liming at five and three sites, respectively. There was a strong significant and positive correlation between pH and exchangeable Cd at all five sites, R^2=67-90%. A multiple regression was carried out in which the exchangeable Cd was related to pH and clay content of the surface soil of all sites together (eq. 6). Clay content and pH explained 81% of the variation. Clay content and Cd extracted by 2M HNO_3 were positively and significantly correlated, R^2=67%.

$$\text{exchangeable Cd} = 134 - 22*\text{pH} + 0.4*\text{clay content} \qquad R^2 = 0.81 \qquad \text{eq. 6}$$

Table 4. *Electrical conductivity (EC), pH, exchangeable Cd, Zn and Ca in surface soil samples from liming experiments. The treatments are: unlimed; and limed to: 55% base saturation (BS); 70% BS; and 100% BS*

Site	pH[1]	EC[1]	Exchangeable[1,2]		
	(H_2O, 1:2.5)	(H_2O, 1:2.5)	Cd (mg kg^{-1})	Zn (mg kg^{-1})	Ca (g kg^{-1})
Kövlinge	5.8-6.4*	-	0.009-0.004*	-	0.7-1.0*
Nättraby	5.7-6.3*	187 –247*	0.019-0.006*	0.55-0.05*	1.8-2.2*
Eckerud	6.2-7.0*	156-159	0.012-0.001*	0.20-<0.05[3]	1.8-3.1*
Östuna	5.5-6.6*	184-230	0.048-0.009*	0.95-0.05*	2.0-3.2*
Bro	5.5-6.7*	231-302*	-	-	-
Kalknäs	5.7-7.0*	175-281*	-	-	-
Öjebyn	5.3-6.8*	524-705*	0.031-0.003*	2.10-<0.05[3]*	2.4-5.2*
Vojakkala	5.5-6.9*	127-170*	-	-	-

[1] First numbers are mean values for samples from unlimed plots and second numbers are from plots with highest liming rate; [2] Exchangeable cations extracted with 0.25M $BaCl_2$ in soils from Kövlinge; other soils extracted with 1M NH_4NO_3; [3] Below detection limit of 0.05 mg Zn kg^{-1}; *Significant difference between liming rates or different pH ($p \leq 0.05$)

The Cd concentration of potato tubers varied widely between the experimental sites and average Cd concentration in potatoes from the different liming experiments was in the range 29-360 µg kg^{-1} DW (Table 5; Fig. 6a,b). The Cd concentrations in potatoes were significantly different between sites and in most cases larger than the effect of liming. At Nättraby, the Cd concentration was considerably higher than at the other sites. The Cd concentration in potatoes was both positively (two experiments) and negatively (two experiments) significantly related to surface soil pH in four of the five experiments (Fig. 6a,b). In the fifth experiment was there a non-significant increase. In four of the experiments where samples were collected in two consecutive years, the response of tuber Cd to liming was similar in both years, although the Cd concentrations differed significantly between years at two sites (Nättraby and Kalknäs) (Table 5). This observation suggests that the pattern of crop response to liming is mostly influenced by site and less by annual variations.

Tuber yield significantly decreased at the Vojakkala site (Table 5) and there were visible Mn deficiency symptoms on the leaves in the limed plots. Liming also significantly reduced the Mn concentration and the total Mn uptake. The Mn deficiency was probably induced by the low total Mn concentration in the plough layer (Table 3) and the increased pH in the surface soil.

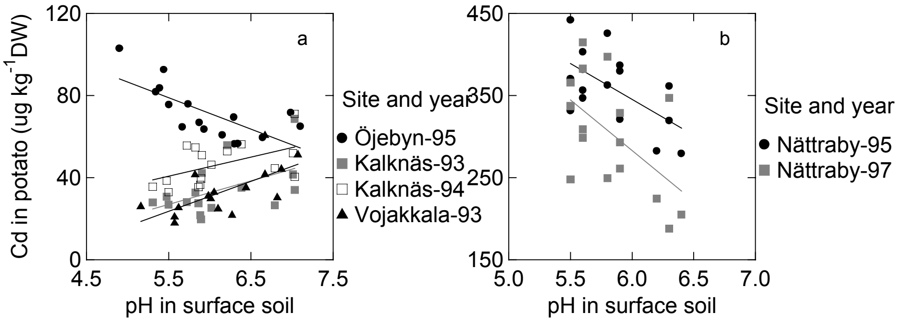

Fig. 6. Relation between surface soil pH and cadmium concentrations in potato tubers from four liming experiments during one or two years. Only significant results are shown. *(a)* Vojakkala (-93 R^2=0.47), Öjebyn (-95 R^2=0.51) and Kalknäs (-93 R^2=0.30) (-94 R^2=0.26) (*b)* Nättraby (-95 R^2=0.35) (-97 R^2=0.31).

At four sites, spring wheat cv. Dragon was grown and the average Cd concentrations of grain and straw were significantly different between sites, with site averages of 36-101 and 87-227 μg kg^{-1} DW, respectively (Table 5; Fig. 7a, b). The Cd concentration in grains from the study sites differed significantly with the concentration order Östuna > Bro > Eckerud, Kövlinge and in straw in the order Östuna, Bro > Eckerud, Kövlinge. The Cd concentration in cereal grains was consistently lower at Eckerud, Kövlinge and Nättraby and consistently higher at Östuna (Table 5) than the Swedish average concentration, which has been reported to be 69 μg kg^{-1} DW in spring wheat, 51 μg kg^{-1} DW in winter wheat, 36 μg kg^{-1} DW in oats and 19 μg kg^{-1} DW in barley grain (Eriksson, 1990; Öborn *et al.*, 1995; Eriksson *et al.*, 2000).

Statistical analyses of the liming effect for each site and year separately (seven experiments in total), showed that in three of the experiments, the Cd concentration of grain was negatively correlated with the pH in surface soil or the lime treatment and in three of the experiments the correlation was positively (Fig. 7a). Only in one experiment there was no response of the liming. The Cd concentration in straw was negatively and significantly correlated with pH or lime treatment in most of the experiments (six out of eight) (Fig. 7b). In the other two experiment increased the Cd concentration in straw with liming, but only one experiment had a significant result.

Table 5. *Yield and Cd concentrations in crops from liming experiments*

Site	Year	Crop	Cultivar	Yield[1, 2] ton FW ha^{-1}		Cd in crop[1, 2,3] µg kg^{-1} DW	
				tuber or grain	straw	tuber or grain	straw
Kövlinge	96	Potatoes	King Edward	48-51	-	33 - 42^{a}	-
Nättraby	95	“	Bintje	18-16	-	380-311^{b}*	-
“	97	“	Bintje	17-19	-	300-240*	-
Kalknäs	93	“	Hertha	24-24	-	30 - 42^{a}*	-
“	94	“	Hertha	9-11	-	42 - 50*	-
Öjebyn	94	“	Jätte-Bintje	24-21	-	67 - 58^{4}	-
“	95	“	Jätte-Bintje	22-17*	-	86 - 66^{c}*	-
Vojakkala	93	“	Hertha	21-14*	-	28 - 47^{a}*	-
“	94	“	Hertha	13 - 9*	-	30 - 41	-
Kövlinge	98	S. wheat	Dragon	-	-	34 - 37^{a}*	114-130^{a}
Nättraby	96	W. wheat	Konsul	7.8-6.4	3.1-3.3	33 - 34	143-121*
Eckerud	94	S. wheat	Dragon	2.6-2.8	1.7-1.9	41 - 51^{a}*	81-102^{a}*
“	95	W. wheat	Kosack	5.9-6.3	-	33 - 50^{4}	-
“	96	“	Kosack	5.2-5.4	3.3-3.1	20 - 26*	58 - 52*
Östuna	94	S. wheat	Dragon	2.2-2.5	1.3-1.5	108 - 83^{b}*	232-165^{b}*
“	96	Oats	Sang	4.3-4.3	2.7-3.1	103 - 69*	253-161*
“	97	Barley	Scarlett	3.2-4.4*	1.1-1.5*	37 - 26*	163 - 61*
Bro	95	S. wheat	Dragon	1.9-2.1	-	88 - 46^{c4}	250-131^{b}*

[1] Different letters = sig. difference between sites with the same species (potatoes) or cultivar (cv. Dragon) ($p \le 0.05$)

[2] First numbers are mean values for samples from unlimed plots and second numbers are from plots with highest liming rate

[3] *= sig. difference between different pH or liming rates ($p \le 0.05$)

[4] Replicates were merged and no statistical analysis concerning differences in pH effects was possible

The crop Cd response to liming and pH showed the same trend in each season at one site (Eckerud) where the same cultivars of winter wheat were grown for more than one year. However, the crop Cd levels differed significantly between the two years. The Cd concentration in winter wheat grains at Eckerud was 37 µg kg^{-1} DW in the first year and 22 µg kg^{-1} DW in the second year.

Effects of pH and Ca^{2+} on Cd solubility *(Paper III)*

The pH in the saturation extracts was significantly increased by liming at all four sites included in this study (Table 6). The largest pH difference in the saturation extracts was between unlimed and limed plots from Östuna while at Eckerud and Kövlinge the pH was overall rather high >6.0. Unfortunately, the pH values in the saturation extracts are slightly unreliable, since the degassing of CO_2 from the saturation extracts was not controlled. Degassing of CO_2 can lead to a higher pH than the actual pH in the soil solution during field conditions (Lorenz *et al.,* 1997).

The saturation extracts from the Nättraby soil showed the highest Cd^{2+} and Cd_{tot} concentrations, while the extracts from the Eckerud soil showed the lowest concentrations (Table 6). The dissolved total Cd concentration in the saturation extracts from Östuna and Nättraby was significantly decreased by an increase in pH (liming) (Table 6; Fig. 8). The Cd^{2+} concentration was decreased by liming at all sites except Eckerud. The higher Cd solubility at Nättraby was probably caused by the combination of a relatively low pH in the saturation extracts, content of organic matter and clay content, since the HNO_3 and NH_4NO_3-extractable Cd were in same range as in the other soils (Tables 3, 4 and 6). The Cd concentrations at Eckerud were very low in all plots and this is probably due to the high pH. The additions of Ca^{2+} did not cause any detectable increase in Cd solubility. However, at Eckerud was there a small but non-significant increase in the Cd^{2+} concentration and in total dissolved Cd. The non-significant result could be due to the low concentrations of Cd having lead to difficulties in the analysis, but there was probably no competition between Cd and Ca for binding sites since there are large amounts of these at this high pH (6.8-7.8). The Cd^{2+} and Cd_{tot} concentrations in this study were in the lower end or much lower than Cd concentrations in other studies (Lorenz *et al.,* 1997*;* McLaughlin *et al.,* 1997a; Sauvé *et al.,* 2000). However, the soils used in those studies were moderately to heavily metal-contaminated or saline.

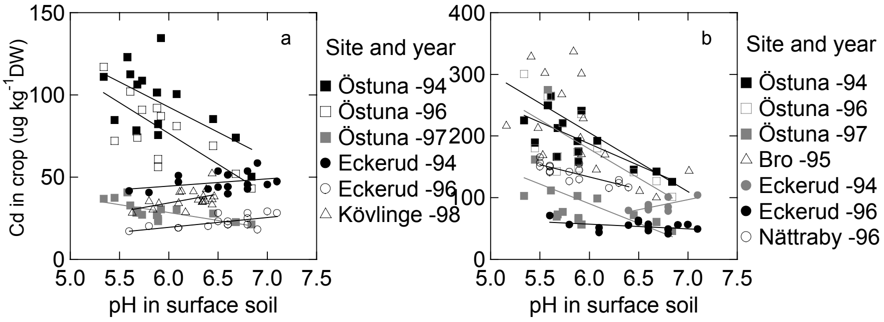

Fig. 7. Relation between surface soil pH and cadmium concentrations in cereals from five liming experiments during one or two years. Only significant results are shown. *(a)* grain Kövlinge (-98, S. Wheat R^2=0.23), Eckerud (-94 S. Wheat), (-96 W. Wheat R^2=0.41) and Östuna (-94 S. Wheat R^2=0.38) (-96 Oats R^2=0.51) (-97 Barley R^2= 0.52) *(b)* straw Nättraby (-96 W. Wheat R^2=0.68), Eckerud (-94 S. Wheat), (-96 W. Wheat), Bro (-95 S. Wheat R^2=0.38), Östuna (-94 S. Wheat R^2=0.56), (-96 Oats R^2=0.51) and (-97 Barley R^2=0.40).

Dissolved organic carbon was increased by liming at Eckerud and Östuna, while at the other two sites there was no significant effect of liming. The increase in DOC was probably accounted for a combination of deprotonation of organic acids and an increase in biological activity.

Table 6. *Ionic strength (I), pH, DOC and concentrations of* Ca^{2+}, Cd^{2+}, Cd_{org} *and* Cd_{tot} *in saturation extracts from four liming experiments. Treatments are unlimed; and limed with calcite to 55% BS; limed to 70% BS; limed to 100% BS*

Site/ Treatm.	I mol l^{-1} *10^{-6}	pH	DOC g l^{-1}	Ca mol l^{-1} *10^{-3}	Cd^{2+} mol l^{-1} *10^{-9}	Cd$_{org}$ mol l^{-1} *10^{-9}	Cd$_{tot}$ mol l^{-1} *10^{-9}
Kövlinge							
unlimed	7.4^{a}	6.0^{a}	0.108^{a}	0.71^{a}	0.68^{a}	0.85^{a}	1.78^{a}
55% BS	8.4^{a}	6.6^{b}	0.081^{a}	1.04^{a}	0.48^{b}	0.66^{a}	1.30^{a}
70% BS	9.1^{a}	6.7^{b}	0.069^{a}	1.00^{a}	0.57^{ab}	0.74^{a}	1.54^{a}
Nättraby							
unlimed	11.5^{a}	5.6^{a}	0.064^{a}	1.84^{a}	1.72^{a}	0.66^{ab}	2.69^{a}
55% BS	11.0^{a}	5.7^{ab}	0.076^{a}	1.62^{a}	1.34^{ab}	0.68^{ab}	2.29^{a}
70% BS	9.3^{a}	5.9^{b}	0.089^{a}	1.47^{a}	1.15^{ab}	0.91^{a}	2.30^{ab}
100% BS	13.2^{a}	6.9^{c}	0.060^{a}	1.96^{a}	0.35^{b}	0.38^{b}	0.81^{b}
Eckerud							
Unlimed	1.5^{a}	6.8^{a}	0.034^{a}	0.26^{a}	0.19^{a}	0.31^{a}	0.51^{a}
55% BS	2.4^{ab}	6.8^{a}	0.036^{a}	0.56^{a}	0.20^{a}	0.30^{a}	0.50^{a}
70% BS	2.3^{ab}	7.5^{b}	0.043^{ab}	0.66^{a}	0.16^{a}	0.59^{a}	0.76^{a}
100% BS	3.6^{b}	7.8^{b}	0.051^{b}	1.24^{b}	0.23^{a}	0.57^{a}	0.80^{a}
Östuna							
unlimed	1.7^{a}	5.5^{a}	0.030^{a}	0.31^{a}	0.94^{a}	0.57^{a}	1.58^{a}
55% BS	2.0^{a}	6.4^{a}	0.035^{a}	0.38^{a}	0.27^{ab}	0.32^{b}	0.61^{b}
70% BS	3.0^{a}	7.2^{a}	0.045^{b}	0.71^{a}	0.23^{ab}	0.48^{ab}	0.73^{b}
100% BS	6.2^{b}	7.8^{b}	0.054^{c}	2.05^{b}	0.18^{b}	0.35^{ab}	0.54^{b}

[1] Different letters = significant difference between liming treatments at the same site ($p \leq 0.05$)

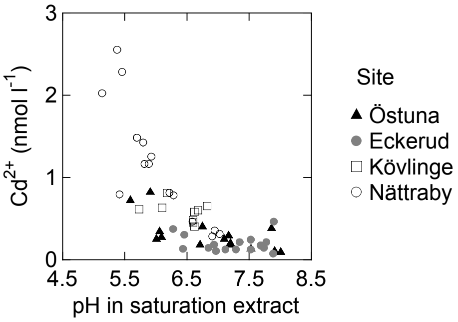

Fig. 8. The Cd^{2+} concentration as a function of pH in saturation extracts from four liming experiments.

In the three batch experiments ("lowNa", "Ca" and "highNa"), the Cd^{2+} solubility was strongly affected by the soil pH. The Cd^{2+} solubility was decreased with increasing pH in all three experiments. (Fig. 9a-d). The slightly higher Cd^{2+} solubility in Expts. "Ca" and "highNa" at pH<7 as compared to "lowNa" is probably due to the increased ionic strength caused by the higher salt concentration of $Ca(NO_3)_2$ and $NaNO_3$. Christensen (1984) also found a higher Cd solubility in soils at pH 6 due to an addition of Ca. The Östuna site had the highest Cd^{2+} solubility and Eckerud had the lowest solubility in all three experiments. Kövlinge and Nättraby had almost the same Cd^{2+} solubility in all experiments.

In Expts. “lowNa” and “highNa”, the total Cd solubility increased at pH values higher than 7.0. This was due to a higher dissolution of organic carbon and a subsequent complex binding of Cd to DOC (Fig. 10). The effect was most pronounced in Expt. “lowNa” and not at all or to a very small degree in Expt. “Ca”. The addition of Na^+ enhances the dissolution of organic matter, but not the addition of Ca^{2+}. The Ca^{2+} is bound to the negatively charged organic molecules and thus causes the organic matter to flocculate (Andersson *et al.*, 2000).

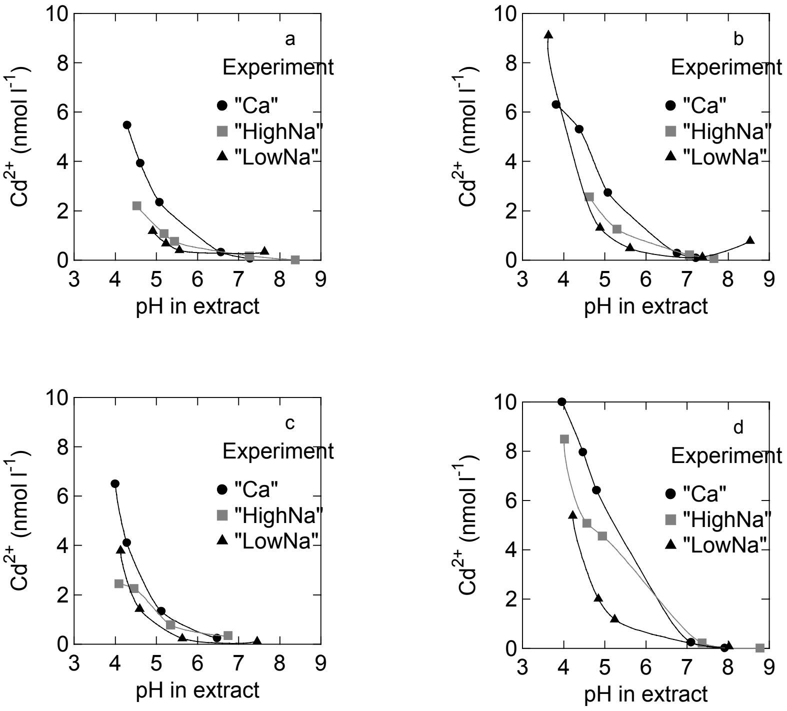

Fig. 9. The Cd^{2+} as a function of pH in three batch experiments and saturation extracts in four soils. *(a)* Kövlinge *(b)* Nättraby *(c)* Eckerud *(d)* Östuna.

The rather small difference between Cd solubility in Expts. “lowNa” and “highNa“ in the Kövlinge and Nättraby soils suggests that surface complexation reactions probably played the major roll in controlling the Cd solubility even at pH<6 (Fig. 9a,b). The specific bonding to organic matter or oxides is probably the most important factor when considering Cd sorption in those soils. If electrostatic interactions played the most important role in controlling Cd solubility, increasing the NaNO₃ concentration by a factor of ten would be expected to increase the Cd solubility to a larger degree. In the Eckerud and Östuna soils, which have high amounts of clay, the electrostatic bonding to the clay and organic particles probably plays the greatest role.

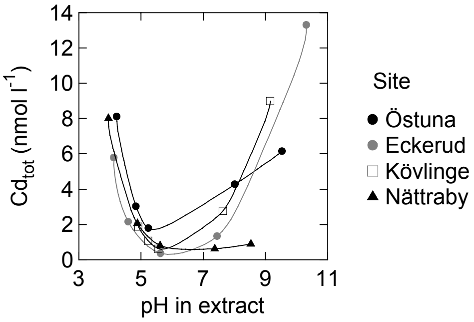

Fig. 10. The Cd^{2+} solubility as a function of pH in Expt. "lowNa" and in four soils: Eckerud, Östuna, Nättraby and Kövlinge.

Cd in crops from limed fields correlated to soil parameters

(Paper IV)

Cadmium concentrations in potato tubers, cereal grain and straw from Kövlinge, Nättraby, Eckerud, Östuna and Öjebyn were included in this study. There were positive and significant correlations between exchangeable Cd in surface soil and Cd concentrations in crops at three of the sites (Nättraby -95, Östuna -94 and Öjebyn -95) and at one site the correlation was negative (Eckerud, grain and straw). At the Kövlinge site (potato tubers -96) the correlation was non-significant. Exchangeable Cd explained 24 to 82% of the variation in crop Cd concentrations (Fig. 11a,b). The negative correlation was observed at Eckerud, where the grain and straw Cd concentration was increased by liming (Table 5). This increase could have been due to several factors, *e.g.* increased Cd solubility/availability due to addition of Ca^{2+} or a micronutrient deficiency induced by liming.

I found a significant correlation between Cd concentrations in crops (cereal straw and potato tuber) and pH in saturation extracts in three experiments, Kövlinge -96 (potato), Nättraby -95 (straw) and Eckerud -96 (straw). The correlation at two sites (Nättraby and Eckerud) was negative, but at the third site (Kövlinge) the correlation was positive and an increase in straw Cd concentration was observed (Table 5). There was a positive significant correlation between Cd concentration in wheat straw and Cd species in the saturation extract, *i.e.* Cd^{2+}, CdCl^{-}, CdSO$_4^0$, Cdorg and Cd$_{tot}$ at Nättraby ($R^2 = 35$-53%) (Fig. 12).

The non-significant correlation between Cd in saturation extracts and related crops can have several possible explanations, resulting from both technical problems with the method as well as factors/processes in the rhizosphere or within the plants. One technical problem could be related to mimicking the soil solution in the root environment by saturation extracts, especially in heavy clays (Eckerud and Östuna), since the aggregates are crushed when the bulk soil sample is homogenized. There are certainly different soil environments (*i.e.* pH, ionic strength, redox potential) inside and outside soil aggregates, a fact that is not reflected by the saturation extracts. Hence, the saturation extracts in strongly structured soil may not represent the root bathing solution. Secondly, the Cd concentrations in the saturation extract of Kövlinge and Eckerud were close to the detection limit, which may also explain a lack of correlation with crop Cd. In other studies, where crop Cd concentrations have been significantly correlated to the soil solution Cd concentrations, the soils used have been contaminated by heavy metals or have been rather saline, with resulting higher Cd concentrations in soil solutions than in our study (Lorenz *et al.,* 1994; Hamon *et al.,* 1995; Lorenz *et al.,* 1997; McLaughlin *et al.,* 1997a).

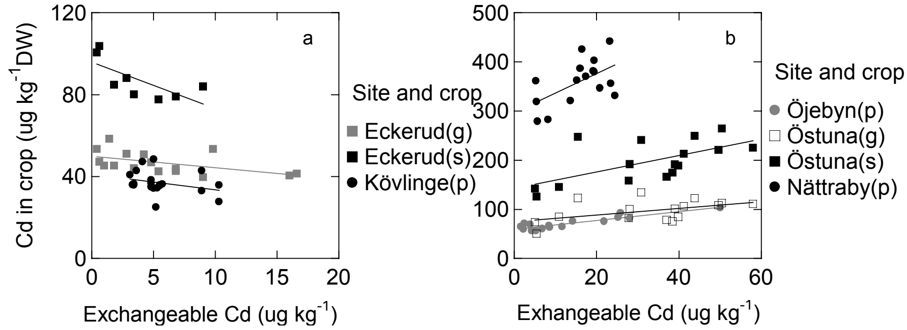

Fig. 11. Correlation between exchangeable Cd and crop Cd concentrations at five sites. Degree of explanation (R^2). *(a)* Kövlinge -96 (potatoes) not significant, Eckerud -94 (grain) 26% and Eckerud -94 (straw) 40% *(b)* Nättraby -95 (potatoes) 32%, Östuna -94 (grain) 24%, Östuna -94 (straw) 40% and Öjebyn -95 (potatoes) 82%.

A third problem could be that the soil solution composition changes during the growing period, which leads to a need to sample and measure the soil solution composition several times during the growing season in order to reflect the crop Cd concentration. Lorenz *et al.* (1994) found in their pot experiment that applications of excess fertilizer cations affected the pH and Cd concentrations in soil solutions. There was a weak correlation between Cd concentrations in crops and soil solutions, but a strong correlation between mass flow of Cd and Cd concentration in plants. This suggests that there is a need to collect soil solutions on several occasions during a growing period when management practices and plant factors affect the soil solution composition. McLaughlin *et al.* (1997) found in their study a significant correlation between the activities of $CdCl_n^{n-1}$ in soil solutions and Cd concentrations in potato tubers. The soil solutions were made from bulked soil samples, which were only collected once during the growing season. The Cd and Cl concentrations in soil solutions had a wide range and the median concentrations were considerably higher (on average 30 and 40 times higher) than those found in this study. The rather high salinity in those soils could have diminished any effect of management practices and plant factors in the rhizosphere.

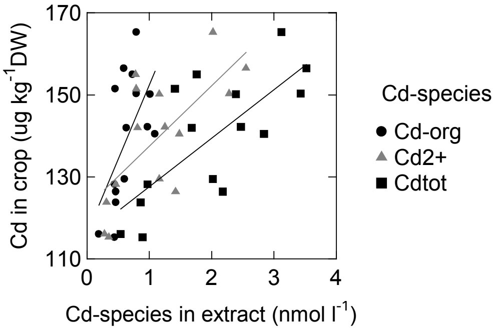

Fig. 12. Correlation between Cd species in saturation extracts and Cd concentration in straw from Nättraby. The variation in crop Cd at Nättraby was explained by Cd^{2+} to 46%, Cd_{org} to 35% and Cd_{tot} to 53%.

Concluding discussion

In the studies presented in this thesis, it was shown that soil pH mainly controlled the solubility of surface soil Cd and that liming decreased the exchangeable Cd and increased the pH. It was also found that liming decreased the Cd^{2+} concentration in saturation extracts in two out of four experiments. It was concluded in the batch experiments that Ca^{2+} competes with Cd for binding sites only at low pH values. Thus, liming according to agricultural practice which leads to an increase in pH should not lead to an increased Cd solubility due to Ca competition.

I found in my study that liming increased, decreased or had no effect on the crop Cd concentration and that there was a clear correlation between pattern of response to liming and crop Cd levels. At sites with low crop Cd concentrations (below Swedish average levels), liming increased or had no effect on the crop Cd concentrations, while at sites with high crop Cd levels, liming decreased the crop Cd. Low crop Cd concentrations indicate a low availability of Cd in the soil and *vice versa* at sites with high crop Cd concentrations. At sites with low Cd availability, one might also expect a low availability of several other trace metals since their solubility is regulated by similar factors as for Cd, *i.e.* pH being of major importance. In addition, total trace metal contents are correlated in Swedish arable soils, reflecting the geochemistry of the parent material, which means that soils high in Cd are usually high in other trace elements such as Cu and Zn and *vice versa* (Eriksson *et al.,* 2000). In most of the Swedish long-term liming experiments, liming increased the yield but at some locations significant negative yield responses or no yield response have been observed (Simán, 1989; Haak & Simán, 1992). In order to explain the inconsistent liming effects on yield response, pot experiments with barley (*Hordeum vulgare* L.) were performed. Liming decreased Mn uptake on all soils and Zn uptake on all except one soil (Hylander, 1995). It was shown in *Paper III* that the Cd solubility (batch experiments and saturation extracts) at low pH was lower at sites with low crop Cd levels (Eckerud and Kövlinge) than at sites with high crop Cd levels (Östuna and Nättraby). The differences in Cd solubility could be due to several soil factors, *e.g.* content of clay, organic matter, trace metals and Fe or Mn-oxides.

At sites with already low Cd and trace metal availability, one might expect that a further decrease in availability due to liming would lead to micronutrient deficiency, especially since the solubility/availability of other trace metals has been shown to be more closely related to pH than that of Cd (Öborn *et al.,* 1995; Eriksson *et al.,* 2000; Grawé *et al.,* 2001). Micronutrient deficiency can lead to a decrease in biomass production or an induced plant release of root exudates (Treeby *et al.*, 1989). Exudates have been shown to increase both micronutrient and Cd availability (Merckx *et al.*, 1986; Mench & Martin, 1991; Nigam *et al*, 2001) and the effects of liming are thereby diminished. Reductions in plant biomass and visible micronutrient deficiency symptoms are rather easy to detect, but it is more difficult to detect release of exudates and any resultant increase in trace metal availability. In my study (*Paper II*), I found both visible Mn deficiency symptoms and reductions in biomass at one experimental site (Vojakkala). The Mn deficiency at this site was probably due to a low total concentration of Mn in the soil and a subsequent low solubility/availability, which was further decreased by liming. At Eckerud, liming increased the concentration and total amount of Cd in winter wheat grain, but the concentration and total amount of Cd in winter wheat straw was decreased. This led to the total Cd accumulation (grain and straw) in winter wheat being unaffected by liming. There could have been a reallocation of Cd within the plant due to liming and perhaps a subsequent micronutrient deficiency in the limed plots. In their report from these liming experiments, Haak & Simán (1992) discuss Cu deficiency in oats in the Eckerud experiment. I could not detect any other deficiency symptoms or biomass reductions at the other sites with low crop Cd concentrations and an increased crop Cd due to liming. However, this does not exclude the possibility that the crops in the limed plots had increased the trace metal solubility/availability in the root environment by releasing exudates and thereby neutralizing the effect of liming.

The relationship between soil solution parameters and crop Cd at low Cd concentrations is poor. However, other authors have shown that soil solution Cd can be a good predictor of crop Cd at high Cd concentrations (contaminated soils or soils with high amounts of ligands) (*Lorenz et al.,* 1997; McLaughlin *et al.,* 1997). The non-significant correlation between Cd in saturation extracts and related crops can have several possible explanations deriving from both technical problems with the method as well as factors/processes in the rhizosphere or within the plants. The saturation extracts reflect the whole bulk soil solution and the soil solution in the rhizosphere could be different from this, since plants can affect the Cd solubility by changing the pH and DOC and by releasing root exudates (Merckx *et al.,* 1986; Treeby *et al.,* 1989; Mench & Martin, 1991; Hamon *et al.,* 1995; Nigam *et al.,* 2001). This theory is supported by the findings of Lorenz *et al.* (1997) in a pot experiment, where the Cd concentrations in non-rhizosphere soil solutions were poorly correlated to Cd concentrations in crops, but the Cd concentrations in rhizosphere soil solutions were better correlated to the crop Cd concentrations.

Conclusions

- The Cd^{2+} solubility in the soils investigated was mainly controlled by soil pH. There was no detectable increase in Cd solubility in batch experiments or saturation extracts due to addition of Ca^{2+} or of lime at higher pH levels.

- Liming decreased the Cd concentrations in crops with high Cd levels, but at sites with low Cd levels in crops the Cd concentration increased. At those sites it was not only the crop Cd concentration that was low, but also the concentrations of Cd in soil solution and batch extracts. This indicates a low availability of trace metals in the soil, which can lead to micronutrient deficiency and a resultant decrease in biomass or to a release of root exudates and a resultant increase in metal bioavailability. There were visible Mn-deficiency symptoms and yield decreases in some of the experiments. The conclusion is that it is most probable that plant factors as well as soil factors affect the Cd solubility and bioavailability.

- The correlation between parameters in the saturation extracts and crop Cd was poor due to difficulties in sampling, preparing and measuring soil solution extracts at low Cd levels. Hence, use of soil solution extracts was not a good tool to predict crop Cd concentrations at low Cd concentrations in soil solution, although it might be useful at high soil solution Cd concentrations (polluted soils or soils with high amounts of ligands).

- The recommendation from this thesis is to lime soils that have low soil pH and that are known to give high Cd concentrations in crops. However, the amount of lime added should be a normal standard agricultural rate. Soils with low pH and low crop Cd concentrations should only be given minor or no additions of lime. Larger additions of lime can increase crop Cd concentrations in these soils due to micronutrient deficiency.

- Differences in crop Cd concentrations were larger between sites than the effects of liming within a specific site. It is concluded that managing crop Cd by site selection rather than by liming may be more effective. Crops aimed for human consumption should be grown on suitable fields known to give low crop Cd concentrations.

- Further research is needed to fully understand the effects of liming on crop Cd concentrations. At sites where liming increases the Cd concentration in crops, the effects of root exudates on micronutrient dynamics and on Cd solubility/availability need to be further investigated.

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