

**Long-term Fate of Sewage-Sludge
Derived Cadmium in Arable Soils**
Laboratory and field experiments, and modelling with
SLAM and WHAM

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Abstract

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The focus of this work was to improve knowledge of the long-term fate of cadmium supplied to arable soils by sewage sludge. Emphasis was placed on measured and modelled changes in the solubility and mobility of cadmium, resulting from long-term turnover of both sludge-derived and inherent organic matter of the soil. Measurements were conducted in a long-term sludge supplied field experiment, situated at Ultuna (60°N, 17°E), started in 1956. Furthermore, batch studies on soil samples and modelling exercises in WHAM were performed in order to study the speciation of cadmium in the soil-solution system. A comprehensive model -the SLAM model- was developed to increase the understanding of the influence of soil and sludge adsorption characteristics on cadmium solubility and bioavailability, and the migration rate of cadmium in soil profiles.

The long-term sludge supplies had increased the solubility of cadmium, measured in crop cadmium concentration, as an effect of enhanced acidification and increased Cd concentration in the soil. A low Cd migration was measured, attributed to non-equilibrium Cd concentration in percolating water, a high cadmium sorption capacity in the subsoil and root driven Cd circulation in the soil profile. No increased Cd sorption capacity was measured in the sludge supplied soil, despite the almost doubled soil organic matter content. This might be partly attributed to the higher iron oxide and hydroxide concentration measured in the sludge, forming more stable complexes with soil humic compounds compared to cadmium complexes with soil humic compounds.

A Monte-Carlo analysis of the SLAM model suggested that the major parameters affecting leaching and crop uptake of cadmium were: the cadmium loading, the partitioning coefficient for sludge-derived inorganic material and parameters controlling the effect of pH on sorption. Long-term scenario simulations in SLAM identified critical factors influencing plant cadmium uptake: the cadmium concentration in the sludge, the adsorption capacity of the sludge in relation to the adsorption capacity of native soil and the proportion of the sludge adsorption capacity contributed by the inorganic fraction.

Key words: Biosolids, adsorption, leaching, crop uptake, bioavailability, modelling, migration, dissolved organic matter, WHAM, partitioning coefficient

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Till Peter, Måns, Jec och Dante

Vattnet som farfar drack

*Vattnet som farfar drack
kom svalt ur sin rena källa.
Åldrig någonsin sade det snack
om vattnet som farfar drack*

*Vattnet som farfar njöt
var oberört av saniteten.
Inga colibakterier flöt
i vattnet som farfar njöt.*

*I vattnet som farfar slök
fanns ej klor eller svavelväte.
endast enstaka grodder dök
i vattnet som farfar slök.*

Ålf Henriksson

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Preface

The thesis presented is based on the following papers, being referred to in the text by their Roman numerals:

- I. Bergkvist, P., Jarvis, N., Berggren, D. and Carlgren, K. 2003. Long-term effects of sewage sludge applications on soil properties, cadmium availability and distribution in arable soil. *Agriculture, Ecosystems, and Environment*, 97, 167-179.
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Introduction

Digested and dewatered sewage sludge, often also referred to as biosolids, is the end product of wastewater treatment. The annual sewage sludge production in Sweden amounted in the year 2000 to ca 230 ktonnes DM. Most wastewater comes from households and industrial activities. Many wastewater treatment plants also still receive excess storm water from roads and paved surfaces, as separate treatment of the storm water is still not satisfactorily developed in Swedish municipalities. Since wastewater is produced from almost all social activities, it also reflects the materials and compounds circulating in society, and so does the produced sewage sludge. Reflecting the composition of the wastewater and treatment practices, sewage sludge is generally rich in plant nutrients, especially phosphorus and sulphur, as well as partly humified organic compounds and it also contains metals.

The worldwide phosphorus (P) containing mining resources are limited and exploiting the resources causes significant negative environmental impacts. The available P resources need therefore to be worked with care. Furthermore, a sensible recirculation of phosphorus may also limit negative environmental impacts, such as eutrophication of water systems. Using sewage sludge as a fertiliser in proper amounts is theoretically one of the most beneficial ways of establishing a circulation of plant nutrients between cities and rural areas. During the last few decades, an intensive debate has taken place in Sweden on the optimal use or destination for the sewage sludge produced, as the sludge beside its content of plant nutrients also represents a concentrated deposit for hazardous chemicals circulating in society, including persistent organic compounds, trace metals and also potential pathogens. This debate has resulted in a reduced use of sewage sludge on arable land and increased deposition in landfills. However, from 2005, landfill deposition of sewage sludge will be prohibited, and alternative solutions are urgently required.

Among the trace metals occurring in sewage sludge, great attention has been paid to cadmium (Cd), as this metal is relatively easily soluble and bioavailable to crops. Sewage sludge additions to arable land eventually lead to an accumulation of Cd in the soil, and thereby an enhanced risk of crop Cd uptake, as well as an enhanced risk for Cd leaching to surface waters and groundwater. There is therefore an urgent need to increase the understanding of the long-term fate of Cd and other trace metals applied to arable soils in sewage sludge. The development of predictive modelling tools integrating existing knowledge of soil and sludge chemistry is necessary for achieving a proper use of sewage sludge on arable land reducing the risks of negative environmental consequences, both in the short and long-term.

Background

Medical aspects of human cadmium intake

Except for smokers and people exposed to Cd through their profession, food intake is the main source of Cd exposure for the Swedish population (Berglund & Vahter 1998). Cereal products and above- ground and root vegetables have been identified as the main contributors to the Cd intake in the Swedish population (Grawé, 1996). Ca 5 % of the Cd intake by food is retained in the gastrointestinal tract and is eventually concentrated in the kidneys. Once toxic levels are reached in the kidneys, Cd may cause dysfunctions by increased secretion of essential low-molecular compounds and calcium, especially if there is an iron deficit as well. (Elinder & Nordberg, 1998). Chronic cadmium poisoning from Cd-enriched rice leading to kidney damage was the reason for the Itai-Itai disease in Japan during the 1950's. The disease manifested itself among the middle-aged female population by a painful skeletal fragility due to calcium losses (Hagina & Kono, 1955).

The Cd concentrations measured in crops cultivated in Sweden are, however, far below the concentrations in cropped products yielding the symptoms mentioned above. The average Cd intake by foodstuffs is calculated at 12 µg /day (Berglund & Vather, 1998). However, in a Belgian study, kidney dysfunctions were reported at a median Cd intake of 15 µg /day in food (Buchet et al, 1990). It is possible that a significant proportion of the Swedish population today reaches or exceeds a safe Cd intake by foodstuffs.

Background Cd concentration in arable soils

The Cd concentrations in Swedish arable soils vary naturally, due to different mineralogical composition of the original bedrock. About 75 % of the Swedish bedrock is granite with relatively low trace metal concentrations (Lewin and Simeonidis, 1998). The average Cd concentration in Swedish arable soils is 0.23 mg Cd kg⁻¹ dry matter (DM) soil. Generally the Cd concentrations are higher in arable soils originated from weathering of sedimentary shale-rich bedrocks, soils of high organic content, as well as loam and clay soils in southern and eastern Sweden, including the district in which this study was performed (Eriksson et al, 1997). The average Cd concentration in topsoils is 0.27 mg Cd kg⁻¹ DM soil in the district of Uppsala, close to the study site in this thesis (Klang & Eriksson, 1997).

Cd supply to arable soils

Historically, Cd has been used in alloys, stabilisers, pigments and more recently in Ni-Cd batteries. The use of Cd was most widespread in the 1980's, but as restrictions were introduced in Sweden, use in stabilisers, alloys and pigments has decreased significantly. Instead, use in rechargeable Ni-Cd batteries has increased in the last decade and represents today 90 % of the Cd used in Sweden (www. Naturvardsverket.se). The Cd concentration in sludge, measured since the mid 1970's clearly shows substantially decreased Cd concentrations. The maximum

sludge Cd concentration in the Uppsala treatment plant was found in the mid-1970's reaching 13 mg Cd kg⁻¹DM, but has thereafter gradually declined to 1.3 mg Cd kg⁻¹ DM (dry matter) by 1995. This concentration is close to the minimum sludge Cd concentration that is possible to reach when regarding the Cd concentration in food and drinking water (SEPA, 1993).

As Cd occurs as a natural trace element in phosphate-rich rocks, fertilizing soils with phosphorus also supplies Cd. P fertilisers are historically the largest source of Cd to arable soils. The Cd concentration in P-fertilisers was highest in the mid-1970's, about 173 mg Cd kg⁻¹ P (Swedish Farmers Association, oral comm.). In 1997, the average Cd concentration in the most common P-fertilizer was 15 mg Cd kg⁻¹ P, (Swedish Board of Agriculture) Since 1995 there is a fee in Sweden on P fertilisers containing more than 5 mg Cd kg⁻¹ P (Swedish Act 1995:616).

Air-borne wet deposition of Cd (mainly from combustion of coal) has also decreased significantly during the last 40 years. In the period 1956-1997, total wet deposition of Cd was estimated to be ca 2 mg Cd m⁻² (Jensen, 1997). The Cd concentration in arable land in Sweden is still increasing by ca 0.01-0.1 % annually from air-borne deposition, use of P-fertilizers, farmyard manure, and CaCO₃ lime (Eriksson, 2000). Use of sewage sludge in arable land leads to enhanced Cd input compared to commercial P-fertilisers, as the Cd /P concentration of sludge is on average four times higher, *i. e.* 40 mg Cd/kg P vs 10 mg Cd/kg P (SCB, 2002).

Wastewater treatment

The aim of wastewater treatment is to separate non- degradable material and easily-degradable organic compounds, nutrients, pathogens and other substances associated to the organic substances, from the effluent. In the first treatment step, larger objects and sand are separated from the liquid phase, while the second step includes biological treatment by active aeration, yielding a rapid growth of microorganisms. Aluminium or iron salts are added in order to precipitate phosphorus, dissolved in the liquid phase. The sediments, containing raw sludge and precipitates, are separated from the basins for biological treatment and are anaerobically digested during ca 30 days. A polymer, facilitating the coagulation of sludge particles, is thereafter added before centrifugation of the sludge in order to separate the liquid phase. The effluent is released into a surface water recipient, while the sewage sludge is stored before final use. In some treatment plants, CaO is added to the digested sludge in order to stabilise the sludge by increasing the pH. Chemical analyses of the nutrient content, organic indicator compounds and metal content of the sewage sludge are routinely carried out with a frequency determined by the population size connected to the treatment plant. The composition of the digested sewage sludge varies between treatment plants, but also within a treatment plant on an annual basis, depending on the composition of the wastewater entering the treatment plant.

Legislation on the use of sewage sludge

The international legislation concerning the use of sewage sludge as a fertilizer and allowable limits for topsoil metal concentration before sludge applications differs widely (Table 1). Sweden is the country with the strictest legislation regarding Cd supply and metal content in arable soils, while regulations in the USA are much less protective (US EPA, part 503). The precautionary principle, underpinning most Swedish environmental legislation has also been applied to the legislation concerning the use of sewage sludge on arable soil.

During recent years, a resistance towards use of sewage sludge on arable soil has become widespread especially among the Swedish farming community. In the year 2000 only ca 21% of the produced sludge, fulfilling the Swedish legislation on metal concentrations for arable use, was applied on farmland while the rest was used as a cover material on landfill areas or deposited in landfills (SCB, 2001). According to the actual legislation, sludge for use in arable soils is allowed for e.g. cereals, oleiferous crops for seed production, energy- and industrial crops and ley production, where harvest occurs more than ten months after sludge application (SNFS, 1994).

Table 1. *The maximum permitted Cd concentrations in topsoil prior to sewage sludge applications, the maximum Cd concentration in sewage sludge for arable use and maximum average annual Cd loading by sewage sludge applications in arable land according to the Ordinance 1985/840 and Order SNFS 1994/2 (Swedish Environmental protection Agency, SEPA), the EU sludge directive of 1986 (86/278/EEC) and the US Environmental protection Agency (EPA) Part 503.*

Country	Max. Cd conc. in topsoil, mg Cd kg ⁻¹ DM soil	Max Cd conc. in sewage sludge for arable soils, mg Cd kg ⁻¹ DM sludge	Max average annual Cd load to arable soils, g ha ⁻¹ y ⁻¹
Sweden	0.4	2	0.75
European Community	1-3	20-40	150
United States	20 [#]	39 [¶] / 85 ^{¶¶}	1900 (Cumulative: 39 kg ha ⁻¹)

[#] The value is calculated for maximum cumulative pollutant loading to be mixed into the ploughed soil layer. The background level is excluded.

[¶] Cd concentration in "Extra Quality" sludge, with no limitations in permissible Cd application.

^{¶¶} Ceiling Cd concentration in sludges applied to land.

Cadmium in soils and in sewage sludge

The principal forms of Cd in soils and sewage sludge are (Barrow & Burridge, 1980; Hirsch & Banin, 1990; McBride, 1994, Christensen, 1998):

- i) Exchangeable Cd^{2+} on clay minerals and humic matter (non-specific sorption)
- ii) specific sorption with humic matter and Fe, Mn and Al oxides and hydroxides (surface complexes)
- iii) precipitated and co-precipitated in carbonates, phosphates, hydroxides and sulfides
- iv) in the soil solution, mainly uncomplexed but also complexed to organic or inorganic ligands, especially fulvic acid complexes, CdSO_4^0 , CdCl^+ , and in soils of $\text{pH} > 6.7$, as CdCO_3^0
- v) fixed in crystal lattices of silicate minerals

Factors of importance for Cd binding and solubility in soils

pH

Soil pH is the main factor controlling the solubility and availability of Cd in soils of varying texture and organic matter content (Filius et al, 1998). Christensen (1984) found a linear increase in sorption capacity by ca 3 times for each pH unit increase within the range pH 4.4 - 7. This pH dependence of the sorption capacity is explained by the fact that Cd sorption involves competition between the metallic cation and protons for reactive sorption sites on soil constituents (Lamy et al, 1993). Increasing pH results in increased sorption of Cd to specific sorption sites on humic material as well as oxides and hydroxides, while the almost constant portion of Cd, reversibly sorbed by ion exchange sites on clay and humic matter becomes less significant (Filius et al, 1998). Under alkaline conditions ($\text{pH} > 7.0$) and at very high Cd^{2+} activities, precipitation of Cd may occur; Street et al (1977) calculated that precipitation of CdCO_3 or $\text{Cd}_3(\text{PO}_4)_2$ might be possible at high solution Cd concentrations ($> 0.01 \text{ mg Cd l}^{-1}$), and Holm et al (1996) concluded that carbonates are not likely to govern the Cd concentration, not even at extremely high CO_2 pressures and high pH values, under environmentally relevant conditions.

Total and potentially reactive Cd concentration

Similar to other exchangeable cations present in the soil, the proportion of the total soil Cd concentration found in solution is generally insignificant compared with the amount of exchangeable or complexed Cd^{2+} (Stevenson, 1994). Although several soil variables influence the solubility of Cd, the total Cd content, measured in concentrated acids, is besides pH one of the most important variables affecting solubility and crop Cd content (Eriksson, 1990, He & Singh, 1993, Gray et al, 1999).

The soil Cd fraction extractable in organic chelates, such as EDTA (ethylene diamine tetraacetate) has proved to be a good estimate of the potentially mobilisable and plant available fraction (Roca & Pomares, 1991). EDTA extracts Cd present in the water-soluble, exchangeably sorbed, organically bound and inorganically precipitated soil fractions (Sims & Kline, 1991, Filius et al, 1998,)

but does not attack the silicate lattices (Schulte & Beese, 1994). Hornburg and Brümmer (1993) found a close correlation between the total and the EDTA-extractable Cd contents. Thus, both the EDTA-extractable and the total Cd content can give a good measure of plant available Cd in soils.

As the availability of Cd in soils is closely correlated to the total content, the enhanced Cd concentration generally found in crops cultivated in sewage sludge amended soils is determined not only by the cumulative total amount added by sewage sludge (Berrow & Burridge, 1980; Miller et al, 1995) but must instead be regarded as an effect of the entire Cd concentration in the soil following sludge loading.

Soil organic matter

Stable humic compounds resulting from decomposition of plant residues and soil biota generally comprises > 90 % of soil organic matter (Cresser et al, 1993). A significant fraction of the humified material in soil is strongly associated to inorganic soil compounds, such as clay, or to hydrous oxide complexes if these are coating the clay minerals (Stevenson, 1994). Soil sorption of Cd is therefore generally dominated by the sorption properties of humic compounds, and soil organic matter has been identified as being the crucial soil component determining the overall Cd sorption capacity in soils (Taylor & Theng, 1995; Gao et al, 1997; Wilkens & Loch, 1995; Gray et al, 1999).

The humus fractions involved in trace metal sorption (humic and fulvic acids) exhibit a high content of oxygen-containing functional groups. The functional groups of the humic substances involved in trace metal sorption are the phenolic-OH groups and the carboxylic -COOH groups, and total functional group acidity is thus the sum of carboxyl and phenolic OH groups (Sposito, 1989). The humic acids (HA) are firmly adsorbed or bound to soil particles (Klamberg et al, 1989). Fulvic acids (FA) differ from the HA by a somewhat lower molecular mass, a higher concentration of reactive carboxylic -COOH groups and a higher total acidity and solubility. They form chelates and thereby act as mobilizing agents for most heavy metals, including Cd²⁺ (Kiekens, 1984; Tan, 1993). FA have a higher concentration of reactive groups dissociating at pH < 7 compared to HA (Tipping, 2002), and therefore they exhibit a higher capacity to form stable complexes with metal ions compared to HA. As the humic substances are heterogenous in their composition, the binding affinities for complexation of trace metals range from low-energy bonding (ion exchange) to highly stable coordinate linkages and ring structures (covalent bonding, Stevenson, 1994).

The Cd sorption capacity in soils may not always be positively correlated to the soil humus content, as microbial degradation of fresh organic matter and humic compounds and changes in the ionic composition or pH of the soil solution can cause dissociation of previously immobile organic matter (McBride, 1994; Reemtsma et al, 1999; Fröberg et al, 2003). This facilitates a hydration and release of low-molecular weight organic acids, fulvic acids and related decomposition products, characterized by a higher affinity to Cd compared with the soil solid

phase (Kiekens, 1983; Christensen, 1985; Lamy et al, 1993). The overall solubility of Cd might increase or decrease, depending on the adsorption /desorption equilibrium between dissolved organic material (DOM) and the soil solid phase (Nodvin et al, 1986; Jardine et al, 1989).

Earlier investigations emphasized the environmental hazards following an increased mobility of Cd due to complexation by dissolved organic compounds, arising as a consequence of application of organic amendments to arable soils. Castilho et al (1993) found a positive correlation between the Cd, Cu and Zn concentration in the soil solution and the peak release of DOM in the soil solution ($> 70 \text{ mg DOC l}^{-1}$), following cattle manure application. Biosolid application and wastewater irrigation in arable soils have also been found to increase the solubility of Cd at low concentrations ($< 9 \text{ ug Cd kg}^{-1} \text{ soil}$), due to a “flush” release of easily degradable organic acids and fulvic acids (Neal & Sposito, 1986; Savric et al, 1999). However, Christensen et al (1996) found that the migration velocity of Cd in the soil matrix would be increased due to complex formation by Cd-DOM at dissolved organic carbon concentrations (DOC) up to 230 mg l^{-1} , but would have only minor environmental importance.

CEC

Besides specific sorption of Cd, predominantly to humic compounds and oxide surfaces in soils, cation exchange also contributes to Cd sorption, although it is only of limited significance (Kasap et al, 1999). Specific sorption and cation exchange of Cd in soils occur simultaneously on adsorption sites having different Cd affinities and these reactions are linked, thereby yielding a dynamic equilibrium partitioning of specifically and exchangeably sorbed Cd. The soil humic and clay content explain most of the variation in soil CEC (Christensen, 1989; Eriksson, 1989), and in soils of high clay content electrostatic attraction may control the Cd^{2+} solubility to a greater extent than in soils of high organic matter content (Jansson, 2002). In soils of high Cd concentration, sorption by cation exchange may become more significant compared to specific sorption (Riffaldi et al, 1983).

Cd binding in sewage sludge

Generally, Cd in sewage sludge is more easily extractable compared to Cd in soils, and a range of the exchangeable fraction of 32-48 % (measured as extractable in 1 M MgCl_2) of the total concentration has been reported (Henry and Harrison, 1992). This property also persists after incorporation into soils. Candelaria and Chang (1997) found that most of the applied sludge Cd remained adsorbed in the original phases, and only a minor part was transferred into the soil solution. The mechanisms for Cd binding in sewage sludge are generally the same as in soils. Yet, as the composition of sewage sludge differs from that of soils, the proportions of Cd sorbed to sludge compounds differ. Other exchangeable cations present in sludge were found to be more effective in competition for sorption sites than Cd (Riffaldi et al, 1983). Holzclaw et al (1978) found that Cd and Ni tended to be associated with inorganic fractions, such as precipitable metal phosphates and hydroxides and the fulvic fraction of sewage sludge. Long-term studies of Cd solubility and mobility in previously sludge-amended soils generally indicate no

decrease in the extractability of metals added with the sludge. McGrath et al (2000) concluded that single and repeated sludge applications to soils led to higher percentages of mobile and bio-available Cd (CaCl₂-extractable) also in the long term (50 years). Berrow and Burridge (1980) also suggested a gradual increase in the bioavailable fraction of Cd in soils amended by sewage sludge, at least over the first years following the applications.

Adsorption isotherms

Adsorption isotherms describe the relation between the equilibrium solution concentration and particle-sorbed agents at constant temperature and pressure. A constant soil- solution ratio with an increasing concentration of, for example, Cd²⁺ in the matrix solution is initially employed. At equilibrium, the remaining metal concentration in the solution is measured and the difference is considered as being particle-sorbed. The adsorption reactions involving soils are rapid, as a near equilibrium sorption is usually reached within minutes or hours (Sposito, 1989; Christensen, 1984). Adsorption at increasing solution concentrations can be described by one of four patterns, S, L, H and C type, where each results from differences in affinities between the solvent and the particle surfaces at increasing initial solution concentration (Sposito, 1989).

For sorption of Cd to soil particles, the L- type isotherm is most often found, and is characterized by a steep slope at low equilibrium concentrations, and a decrease in the slope at increasing concentrations. This isotherm shape reflects the effect of a high affinity of the soil particles for Cd at low surface coverage, indicative of specific sorption, while increasing surface coverage results in a gradual saturation of the specific surface sites, leaving only low-energy sites, *i. e.* electrostatic cation exchange sites to become saturated (Riffaldi et al, 1983, Sposito, 1989). If the adsorption isotherm is measured in the low-concentration range, then it may be apparently linear, as there is still a large excess of potential sorption sites on the soil constituents at increasing equilibrium Cd concentrations. The L-type isotherm with soil as a sorbent is often described by a Freundlich isotherm:

$$S = kc^m \qquad \text{Equation 1}$$

where S is amount of solute retained per unit mass of soil (mg Cd²⁺ kg⁻¹ soil), c is the solution concentration at equilibrium (mg Cd l⁻¹), k is the Freundlich distribution coefficient (mg^{1-m} l^mkg⁻¹) and m is an empirical dimensionless constant., The exponent m is rather constant (Streck & Richter, 1997), varying generally between 0.2 and 0.7 (Tan, 1993). The variability in sorption capacity between soils is mainly reflected in the coefficient k. In the low-concentration range, the Freundlich isotherm may be simplified to a linear isotherm (m=1), and the linear distribution coefficient for cadmium may vary within a wide range, from 57 to 53000 l kg⁻¹ (Alumaa et al, 2002).

The Freundlich isotherm can also be described in an extended form that accounts for the effects of different soil components of differing reactivity and soil pH on

the Cd sorption (Streck & Richter, 1997). For example, including pH and organic carbon content, the Freundlich adsorption isotherm for Cd²⁺ may be extended to:

$$S = k c^m oc^b 10^a pH \quad \text{Equation 2}$$

where oc is the soil organic C content (% by mass), pH is a measure of the hydrogen ion activity, and a and b are exponents introduced for oc and pH.

Features of sewage sludge derived humic substances

Organic matter comprises ca 50% of the total sludge substance (dry matter), while the humic material accounts for ca 17 % of the sludge organic matter (Stevensen, 1986). The HA and FA in sewage sludge show several distinguishing structural and chemical characteristics compared to native soil HA and FA, including a higher N-content, a lower C/N ratio, a higher fraction of aliphatic compounds and lower carboxyl group acidity and a lower concentration of complex binding sites. (Boyd & Sommers, 1990, Soler Rivera, 2002). However, as the differences in the structural composition of composted sewage sludge compared to native soil FA were limited, Esteves da Silva et al (2002) concluded that no qualitative change in the complexation properties of sludge-amended soils should be induced compared with native soils.

Long-term fate of Cd in sewage sludge amended soils

Solubility

A subject of increasing concern in sludge-amended soils is whether the solubility of Cd may change in the long term. Two hypotheses concerning the permanence of Cd have been suggested: The sludge “time bomb” hypothesis (McBride, 1995) stresses the significance of the organic matter of soils and sewage sludge in the immobilisation of Cd. The consequences of mineralisation of soil organic matter, following cessation of sewage sludge applications would therefore be a gradual release of previously sorbed Cd into more soluble forms. Earlier results presented by Hooda and Alloway (1993), support this theory, as an initial increase in the Cd sorption capacity of the soil was measured immediately after sewage sludge applications, an increase which was followed by a gradual decrease in the sorption capacity, which they attributed to the organic matter mineralisation. Petruzzelli et al (1992) studied the organic matter phase in sewage sludge and also ascribed the increased sorption capacity for heavy metals in sludge-amended soils immediately following sludge additions to the increased concentration of sorbing sites, derived from the organic phase of the sludge.

The sludge “protection” hypothesis, on the other hand, stresses the high affinity for Cd to sludge inorganic fractions, such as carbonates, sulphides, phosphates and hydrous oxides, resulting in a permanent increased soil sorption capacity for Cd and other trace metals (Chaney and Ryan, 1993). However, a third possibility also exists, that is an unchanged Cd adsorption capacity in soils despite sewage sludge additions -the constant partitioning hypothesis (McBride, 1995). Merrington et al

(1997) found that sewage sludge amended soils showed no significant change in Cd affinity shortly after sludge additions when compared to control soils, despite an increase in the organic matter content. Up to 23 years following cessation of sewage sludge supply, McGrath et al (2000) also found no change in the solubility of Cd despite a significant decrease in the soil humic content, a result which can be explained either by the sludge “protection” theory or by the constant partitioning theory.

Leaching

Studies of the long-term (6- 19 years) redistribution of Cd in arable soils following sludge applications generally indicate that the downward movement by matrix flow is generally very slow and most often is limited to the zone of a few cm depth immediately below the incorporation zone, while the vast majority remains in the incorporation layer (Chang et al, 1984; McGrath, 1984, Yingming & Corey, 1993). Yet, a significant Cd enrichment was measured in a coarse sandy soil, in the zone below the sludge incorporation depth, eleven years after termination of sludge additions (Larsen & Petersen, 1993). McBride et al (1999) showed that the long-term losses of several trace elements from a sludge-supplied topsoil was closely correlated to their field-based partitioning coefficients, as elements with the smallest k_d -values had the largest loss estimates. Lack of trace metal enrichment below the incorporation layer is however not proof of negligible leaching, as rapid macroporous and preferential flow of Cd might force the downward migration into deeper unsampled soil layers (Camobreco et al, 1996, Richards et al, 1998). This effect may be especially pronounced if transport is facilitated by complexation with dissolved (mobile) organic ligands. However, there is no evidence available from long-term field studies concerning the effects of macropore flow on cadmium leaching.

Changes in soil structure caused by sewage sludge

The topsoil layer affected by sludge amendments may undergo changes in soil coarse structure compared with non-amended soils, reflected by a change in the macroporous flow pattern. The soil macropores are inter-aggregate cracks, root channels and worm holes of > 1 mm equivalent pore diameter range where water flows rapidly by gravity, while water flow in the mesopores and micropores (1- 0.01 mm and < 0.01 mm respectively) is more strongly influenced by capillary forces (Germann & Beven, 1981; Luxmoore, 1981). Solutes exposed to macroporous flow may by-pass the soil matrix so rapidly that the time for equilibration between the soil matrix and solute phase is insufficient (Thomas & Phillips, 1979). Thus, occurrence of macroporous flow of solutes may result in either increased or decreased leaching of pollutants compared with exclusively matrix flow as solutes stored inside the intra aggregate micropores are protected from leaching (Larsson & Jarvis, 1999, Larsson & Jarvis, 2000).

The ability of the soil pore system to conduct water is described by the hydraulic conductivity, K , which decreases at decreasing pressure head (ψ). K varies between soils due to differences in soil texture and structure.

Objectives

The overall aim of this work was to improve knowledge of the long-term fate of cadmium supplied to arable soils by sewage sludge. Emphasis is placed on changes in the solubility and mobility of cadmium, resulting from long-term turnover of both sludge-derived organic matter and the inherent organic matter of the soil. A comprehensive model was developed from existing knowledge and experimental results with the aim to encourage and support investigations on the impact and interactions of those critical processes and conditions in soil and sludge that control the long-term fate of Cd in sewage sludge and other organic soil amendments.

Specific questions investigated in the thesis were the following:

What are the effects of long-term (40+ years) sewage sludge application to arable soils regarding

- i) the sorption capacity for Cd in the resulting sludge/ soil mixture,
- ii) uptake propensity for Cd in cereal crops,
- iii) leaching losses of Cd including the effects of macropore flow and DOC complexation.

These questions were addressed through a combination of field and laboratory experiments and modelling. The work centred on a long-term field experiment (41 years of continuous sludge applications) situated at Ultuna in central Sweden. Table 2 shows the topics studied in this thesis and the methods used.

Table 2. The topics studied and the materials and methods used in this thesis (SS = sewage sludge applied plots and C = control plots)

Topic studied	Specification	Material/method	Soil layers, cm	Paper
Element content	HNO ₃ and EDTA-Cd, Tot- C, org- C, Tot- N, Tot- S	Soil sampled in 1997 and soil stored since 1956	SS: 0-95, C 0-90 1956: 0-60	I
	NH ₄ -oxalate-Al and Fe, Pyrophosphate-Al and Fe, Hydroxylamine- hydrochloride-Mn	Soil sampled in 1997	SS: 0-35, C: 0-50	II
Soil texture	CEC	Soil sampled in 1997	SS: 0-55 C: 0-50	I
Soil physics	Inorganic particle size distribution Dry bulk density	Soil profile sampling, 1997.	SS: 0-95 C: 0-90	I
	Soil structure	Cylinder sampling in the field, 1997 Tension infiltration measurements, 1997	SS: 0-28 C: 0-23 Upper topsoil layers, SS and C	I Complementary study
Sludge analyses	Cd-HNO ₃ , Cd-EDTA, pH, DOC, C,S,N	Sludge samples from the Uppsala treatment plant, stored 1 month, 1999.		I

Table 2, *continued*

Topic studied	Specification	Material/method	Soil layers, cm	Paper
Crop analyses	HNO ₃ - Cd	Barley grain and straw harvested in 1978- 97		I
Batch studies	Cd solubility at equilibrium (24 h)	0.01M Mg(ClO ₄) ₂ , 0.01M Ca(NO ₃) ₂ ,	SS: 0-35 C: 0-50	I I, II
	Adsorption isotherms	Acid and base additions (tot 3 levels) Cd additions (tot 3 levels)		II
	DOC	Acid and base additions (tot 3 levels) Cd additions (tot 3 levels) WHAM-W equilibrium model		I, II I, II
DOC sorption of Cd	Modelling speciation of solute Cd	WHAM-S equilibrium model	SS: 0-35 C: 0-50	I, II
Particle sorption of Cd	Modelling speciation of particle-sorbed and solute Cd	WHAM-S equilibrium model	SS: 0-28 C: 0-23	II
Modeling long term fate of Cd in soil	Agreement in simulations and measurements Sensitivity analysis Scenario simulations	SLAM model		III
Particle sorption of Cd	Modelling speciation of particle-sorbed and solute Cd at varying clay and humus content, CEC and pH	Modelling speciation of particle-sorbed and solute Cd at varying clay and humus content and pH	C: 0-23	Complementary study

Materials and Methods

The experimental site and design

The study was based on an existing field experiment, which was started in 1956, in which different organic and inorganic amendments were supplied in order to study long-term changes in soil fertility. The test field is situated at the Swedish University of Agricultural Sciences, Ultuna (60°N, 17°E). The soil is a structured clay loam and is classified as a Typic Eutrocept (Soil Survey Staff, 1998) or a Eutric Cambisol (FAO, 1998) according to Kirchmann et al (1994). The experimental setup is a randomized block design with four replicates. Each plot is 4 m² in size, separated from adjacent plots by wooden frames, inserted ca 30 cm into the soil and extending ca 10 cm above the surface. Each treatment is fertilized with ca 22 kg phosphorus (P) and ca 36 kg potassium (K) ha⁻¹ yr⁻¹ in the autumn by a combination fertilizer, followed by spade cultivation to a depth of ca 20 cm. The levels of P-fertilizers and sewage sludge were not applied to meet the needs of the cultivated crops, but were deliberately chosen for the purposes of the research. During the years 1956-1997 spring-sown cereals and green rape were the most frequently grown crops in the experimental plots.

Two of the treatments of the main experiments were selected in this study, the sewage sludge treatment (SS treatment) and the control (C). The SS treatment receives sewage sludge from the Uppsala treatment plant in the autumn every other year before spade tillage and each sludge load amounts to ca 13000 kg DM ha⁻¹, containing 4000 kg ha⁻¹ organic C. The sludge is not lime-stabilized. The control is fertilized with 90 kg N ha⁻¹ as calcium nitrate in spring each year. All four replicates were included in the soil analyses.

Soil, sludge and crop analyses

In 1997, after harvest, an initial soil sampling at 0-30 cm depth was carried out in order to calculate the topsoil depth in each treatment, as the supply of sludge during 41 years had increased the topsoil depth. Reference measurements on soil organic C content and dry bulk density prior to the start of the experiment in 1956 were available (see Paper I, table 2). The topsoil depth was calculated from dry bulk density measured in small cylinders in 1956 and 1997, and the known mass of soil organic and inorganic material in 1956 and 1997. Subsequently, a new soil sampling was undertaken of the entire topsoil layer and the subsoil. The subsoil was sampled with an auger from the base of the topsoil down to 67 cm below the base of the topsoil in each treatment. The soil cores were sliced into 7 parts, each 10 cm in thickness, except the uppermost part, which was 7 cm thick.

Soil texture (Paper 1) was measured for the particle fraction < 2mm using standard methods (wet sieving and the pipette method), following dissolution of carbonates by 4 M HCl. Total C, N and S content of the soil samples, before and after dissolution of carbonate-C, was analysed on a LECO[®] CHN 932 analyser. The soil pH was measured in both distilled H₂O and in 0.01 M CaCl₂.

Total Cd concentration in soil was estimated according to Swedish standards by extraction in 7 M HNO₃ (SS 028150), while extraction in 0.025 M Na-EDTA was used to represent the potentially bioavailable Cd fraction. Cd analyses were made on a flame atomic absorption spectrometer (Perking Elmer AA300). CEC was calculated by adding exchangeable Ca²⁺, Mg²⁺, Na⁺, K⁺ and exchangeable acidity by titration of the extracts to pH 7.8. Soil samples stored since 1956 from the 0-20, 20-25, 25-30, 30-40, 40-50 and 50-60 cm depth intervals were also analysed for pH, total N and C, organic C, and HNO₃-extractable Cd.

NH₄-oxalate extractable Al and Fe, representing crystalline and non-crystalline forms and non-crystalline iron oxides (McKeague et al, 1971, McKeague and Day, 1966) were analysed on a Jobin-Yvon JY24 ICP instrument. Pyrophosphate-extracted Al and Fe were assumed to be associated with organic matter, either as complexes and/or as amorphous (oxy)hydroxides (McKeague & Schuppli, 1982; McKeague, 1967). Easily reducible manganese (Mn) oxides and hydroxides were extracted in acidic 0.1 M hydroxylamine hydrochloride according to standard procedures (Chao, 1972), and analysed on a Jobin-Yvon JY24 ICP instrument (paper II). The Cd concentration in stored grain and straw fractions of barley yields cultivated during 1978-1997 were measured by extraction in HNO₃/HClO₄ before analysis on an ICP/MS-DRC - Elan 6100.

No samples of sewage sludge applied during 1958-1997 had been stored. The Cd concentrations in applied sewage sludge were estimated from reports on annual measurements of trace metal content in sewage sludge produced in the actual treatment plant. Sewage sludge, stored outdoors for one month was sampled in October 1999. The HNO₃ and EDTA extractable fractions of Cd, as well as C,N and S content were analysed according to the methods described above.

Batch studies

When actual soil water concentrations of Cd are not available, fair estimates can be obtained using measurements of soil extracts equilibrated in Ca(NO₃)₂ (Holm et al, 1998). In the batch study, 5 g soil was equilibrated in 20 ml 0.01 M Ca(NO₃)₂ solution for 24 h. In order to calculate adsorption isotherms at varying soil pH, the pH of the solutions were initially adjusted by additions of NaOH or HNO₃. Cd was added to the solutions (as Cd(NO₃)₂-solutions) in order to reach three initial Cd concentrations at each pH. The Cd levels were all in the low to medium concentration range (0.14 -35.70 µg l⁻¹), where the lowest concentration in each series was obtained without any Cd additions. Cd concentrations after filtering (0.2µm) were measured with a graphite furnace technique on a 4110 ZL Zeeman atomic absorption spectrophotometer. Dissolved organic carbon (DOC) concentrations were measured in the equilibrium extracts at the lowest and highest Cd concentrations and analysed on a Shimatzu 5000A TOC analyzer.

Modelling Cd speciation in WHAM

Assuming that organic ligands, measured as DOC are the principle complexing anions for Cd^{2+} prevailing in the equilibrium solution, the proportion of uncomplexed and DOC complexed Cd^{2+} ions was calculated using the chemical equilibrium model WHAM (Windemere Humic Aqueous Model) and its submodel for the water phase (WHAM-W) as well as the standard database *Water 10*. The expected partitioning of Cd^{2+} between the solid and the solution phase, disregarding the DOC complexation of Cd^{2+} , was calculated in the WHAM version for soils and sediments (WHAM-S) with the standard database *SSED 10* (Tipping, 1994). The CEC of the mineral fraction in the database was increased from values representative for kaolinite to correspond to illite, as this mineral dominates in the test soil. The model inputs are given in paper II, table 2.

The SLAM model

The main pools and processes of concern for Cd transport, crop uptake and retention in a soil profile of 80 cm depth are described by the SLAM model and are illustrated in fig 1. The model includes four carbon pools (humified and fresh organic material derived from crop residues and sludge respectively), while cadmium in soil is partitioned between the Cd^{2+} ion in the solution and a pool of matrix-sorbed Cd in equilibrium with the solution concentration. Cadmium transport is simulated with the convection-dispersion equation, assuming steady-state water flow. Adsorption is calculated using an extended Freundlich isotherm, accounting for pH and the differing adsorption affinities of six components: an indigenous soil mineral component, inorganic matter derived from sludge and the four carbon pools mentioned above. Crop uptake of Cd is calculated using Michaelis- Menten kinetics as a function of the soil solution Cd concentration and the crop biomass production (Ross & Kaye, 1994). Carbon turnover is modelled using an extended version of the ICBM model (Andrén & Kätterer, 1997). This model postulates first-order kinetics for decomposition of fresh and humified organic material, with separate humification and decomposition constants. These constants describe the rates of microbial respiration, while a 'climatic factor', representing soil moisture and temperature controls carbon flows.

Measurements in the control plots in the long-term field experiment at Ultuna, described in paper I and II, were used to parameterise the SLAM model. This parameterisation served as the basis for a simulation of the sludge-amended treatment at Ultuna, as a preliminary test of the model (paper III).

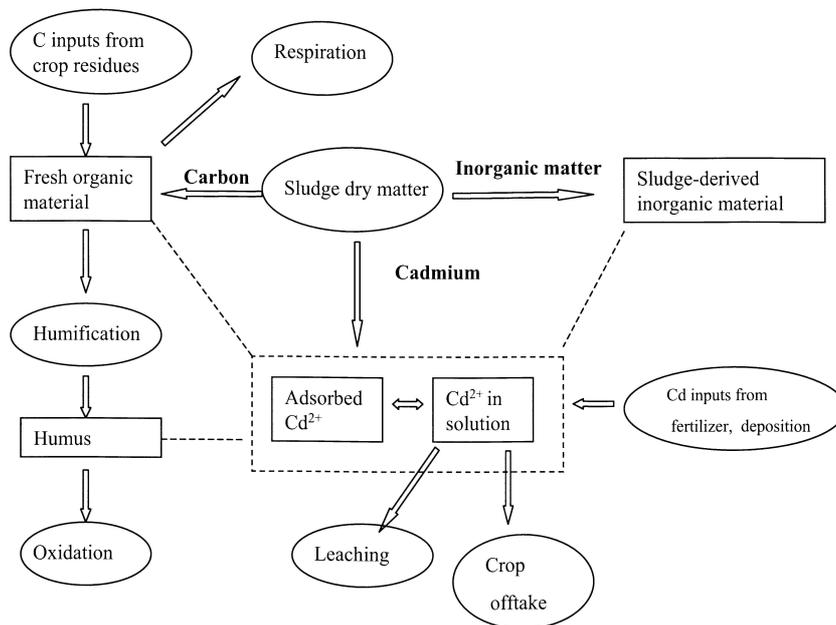


Fig. 1. Schematic picture of the Cd circulation between pools within a sludge-amended arable field. Boxes indicate 'pools', arrows indicate flows, and dashed lines show links or interactions between pools.

The latter simulation served as the basis for a sensitivity analysis of the SLAM model. A Monte Carlo approach using Latin Hypercube sampling was adopted, whereby the parameters were sampled from distributions representing their expected uncertainty and/or variability. In this initial analysis, a uniform distribution for all parameters was assumed, as little is known of the "true" distributions of the parameters. Two target output quantities were investigated separately; cadmium leaching out of the topsoil layer and cadmium in crop offtake. Inputs and outputs were initially ranked in order to minimize the effects of distributional non-linearity or any other skewness (Wonnacott & Wonnacott, 1984).

Scenario-simulations were performed for 150 years, where the basic scenario was a sludge dry matter loading of $1 \text{ kg DM m}^{-2} \text{ year}^{-1}$ for the first 50 years. The sludge inorganic fraction was assumed to be 50% and the crop-derived organic carbon was maintained at steady state during the simulations. The role of sludge adsorption properties controlling the metal solubility and bioavailability and the effects of organic matter decomposition following cessation of applications were explored in these simulations.

Three important system properties were tested using the crop uptake of Cd as the output variable for comparison:

- i) the ratio of sludge k_d to the initial soil k_d ,
- ii) the Cd concentration in the applied sludge (= Cd loading)
- iii) the contribution of the inorganic sludge compounds to the total adsorption capacity of the pure sludge.

The values of the critical system parameters were varied around baseline values. For simplicity, linear adsorption of Cd in the soil was assumed as well as first-order crop uptake of Cd.

Near-saturated hydraulic conductivity, a complementary study

The long-term application of sewage sludge in this test site was assumed to cause changes not only in the soil Cd sorption properties, but also the topsoil structure, which may in turn change the proportion of water flowing in the soil macropores in the topsoil.

In October 1997, steady state infiltration rates were measured using tension infiltrometers (Zavattaro et al, 1999) in each of the four replicate plots of the SS treatment and the control. Two replicate measurements were performed in each plot, yielding eight replicates for each treatment. The test plots had been harvested, above-ground crop residues had been removed, but no spade tillage had been performed. Messing & Jarvis (1993) have extensively described the methods used in the field and theoretical considerations underlying this method. Infiltration measurements were performed at laboratory-calibrated supply water potentials of -5, -4, -2 and -1 cm. Each measurement started at the lowest potential and increased stepwise in order to exclude air entrapment within the soil pores. A linear regression model was used to describe the changes in log K (hydraulic conductivity) across the supply potential range.

Statistics

The significance of differences in soil parameters between the SS treatment and control was tested by one-way analysis of variance (ANOVA) with one treatment factor on two levels (SS treatment and control), where the different soil layers in each soil core sampling were regarded as repeated measurements. To account for correlations in properties between the different soil layers, an autoregressive covariance structure of order one, AR (1), and the GLM procedure were used in the ANOVA analysis. The SAS[®] software was used for these calculations (SAS, 1996). To calculate significance of differences between treatments in the correlation between log k_d and pH, and also between hydraulic conductivity and supply potential, analysis of covariance with one factor fixed and one covariate was used (SAS, 1996). Linear regression analysis was executed using Microsoft[®] Excel.

Results and discussion

Cd amount supplied by sludge, P-fertilizer and aerial deposition

The total supply of Cd to the upper 20 cm in the soil by sludge, P-fertilizer and wet deposition amounted to ca 153 mg Cd m⁻² in the SS treatment, and ca 13 mg Cd m⁻² in the control in the years 1956-1997 (Paper I, table 5). As the levels of sewage sludge supply were chosen for scientific purposes, the loadings exceeded by far the limits set by Swedish legislation. The total Cd amount applied during the 41 test years corresponded to 1900 years of maximum allowed Cd application by sewage sludge. However, the applied amounts were still within the limits according to the EU legislation (Table 1). The highest Cd concentrations in sewage sludge and P-fertilizers were measured during the first years of the experiment, with 50% of the total amount applied within the first 13 years. From a maximum Cd concentration of 13.2 mg Cd kg⁻¹ sewage sludge (1971) and 173 mg Cd kg⁻¹ P (1965-1970), the levels were reduced to 1.7 mg Cd kg⁻¹ sewage sludge and 50 mg Cd kg⁻¹ P in 1996-1997.

Soil carbon, nitrogen and sulfur content

Measurements of the organic C, N, and S contents in the soil profiles of both treatments in 1956 and 1997 showed similar patterns: similar C, N and S concentrations in the topsoil and upper 15 cm subsoil layers, and a reduction with depth due to decreasing root biomass input into the soil organic pool. In 1997, the control and SS treatments both showed a significant decrease in the subsoil C, N and S concentrations compared to 1956. This was explained by increased mineralization of soil organic matter (SOM), due to installation of drainpipes in 1956. Nevertheless, in 1997 the SS treatment profile showed higher C, N and S concentrations compared to the control throughout the soil profile, and also compared to topsoil samples stored since 1956. The increase in the topsoil layer is explained by the sewage sludge additions, containing ca 60 % by weight of organic matter and also a high S concentration compared to the native soil (table 3).

The increased C and N concentrations in the subsoil layers of the SS treatment were due to higher root residue input, as the harvest yields in the SS treatment exceeded the control by ca 20 % on average during the experiment (Paper I). As the C/S and C/N ratios of the applied sludge were < 200 and < 20 respectively, S and N mineralization of the applied sewage sludge probably occurred in the aerobic topsoil (Havlin et al, 1999; Brady and Weil, 1999) and some leaching of mineralized SOC, NO₃²⁻ and SO₄²⁻ may also have contributed to the higher measured C, N and S concentrations in the SS treatment subsoil compared to the control. Modeling the changes in soil organic carbon content in the SS treatment in the period 1956 –1997 using the SLAM model showed that this model well matched the measured data (Fig 2). The ICBM model, which was originally parameterized for carbon turnover in the topsoil layer, also predicted the decrease in subsoil organic carbon contents satisfactory.

The C/N ratio decreased with depth in both treatments, in the control from 10.4 to 7.8 (Paper II, table 1), indicating a shift towards more humified compounds, which possess a larger concentration of surface reactive groups compared to younger organic matter (Brady & Weil, 1999). This shows that in the subsoil the input of root residues was of little significance compared to the content of highly humified organic matter, while the contribution of fresh crop litter of high C/N ratio (ca 80) incorporated into the topsoil increased the average C/N ratio significantly. A considerably smaller proportion of humified organic matter in the surface soils therefore seems more probable. The C/N ratio in a soil profile might therefore be a useful indicator of the affinity for trace metal sorption in the organic phase of natural soils.

Table 3. *Chemical properties in sludge samples from the Uppsala treatment plant, stored one month outdoor. Values within brackets denote standard errors (N=4).*

Property	Value
Total C, % by mass	30.8 (1.4)
Total N, % by mass	3.8 (0.1)
Total S, % by mass	1.3 (0.1)
C/N ratio	7.9 (0.1)
pH	8.0 (0.3)
EDTA-Cd, $\mu\text{g kg}^{-1}$ ts	648.3 (78.9)
HNO ₃ -Cd, $\mu\text{g kg}^{-1}$ ts	836.8 (49.0)
DOC, mg l^{-1}	479.4 (9.5)

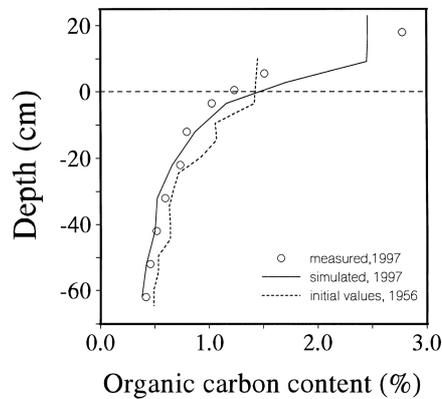
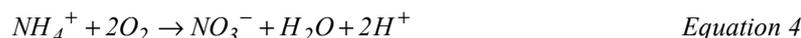
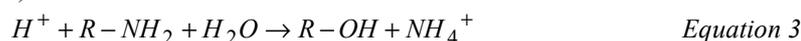


Fig. 2. Comparison of measured and simulated organic carbon content in the sludge-amended soil, Ultuna, 1956-1997. The zero depth in the soil profile is given as the base of the topsoil in 1956, since the topsoil thickness changes with time.

pH

The 40 years of mineralization of the organic compounds supplied by sludge had resulted in a decrease in the pH of the topsoil layer in the SS treatment due to:

a) nitrification:



b) oxidation of organic S:



Kirchmann et al (1996) showed however that acidification due to oxidation of sulphur rich compounds of the topsoil in the SS amended soil was more important than the acidification from N-mineralization in this experiment. Furthermore, the organic material in the applied sludge was also partly decomposed in the digestion step of the wastewater treatment, which resulted in a buildup of recalcitrant humus compounds (Boyd & Sommers, 1990; Witter, 1996). Altogether, these processes resulted in a continuous reduction in pH in the topsoil layer of the SS treatment, reaching pH 4.9 in the SS treatment, compared to 6.3 in the topsoil of the control.

As the soil profile is increasingly calcareous in the subsoil layers, the leaching of organic acids from the topsoil was buffered by $CaCO_3$ in the upper subsoil layer, and the sub soil pH remained the same in both treatments, increasing by depth from ca 6.4 to 7.4 (see Paper I, table 1).

Changes in soil Cd solubility resulting from sludge applications

In 1997, the equilibrium concentration of Cd in the SS treatment topsoil layer, measured in 0.01 M $Ca(NO_3)_2$, exceeded the control by > 30 times, while the increase in HNO_3 -extractable Cd exceeded the control by a factor of 3. The explanation for the difference between these two values is to be found in the properties of the pure sewage sludge and the processes following the mineralization of the sludge in the soil: a large proportion of Cd in sewage sludge stays in easily mobilisable fractions. The EDTA/ HNO_3 -extractable Cd ratio in pure sewage sludge was 77 % in the sludge samples studied in 1999, while the ratio was slightly lower in the sludged topsoil (66%), which can be compared to the ratio in non-sludged soil, 53 %. Thus, the properties in the sludged topsoil in this study had gradually approached the solubility measured in pure sewage sludge. This result is also in agreement with previous comparisons of sludged and native soils (Sims and Kline, 1991; Juste & Mench, 1992). Another, and perhaps the strongest, reason for the increased solubility in the SS treatment compared to the soil was the strong reduction in pH in the topsoil layer compared to the control. The batch studies on the test soils at varying pH values confirmed the role of pH as the dominant

variable determining the solubility of Cd, as pH explained > 95 % of the variation in the partitioning coefficients for Cd in each measured soil layer (Fig 3A).

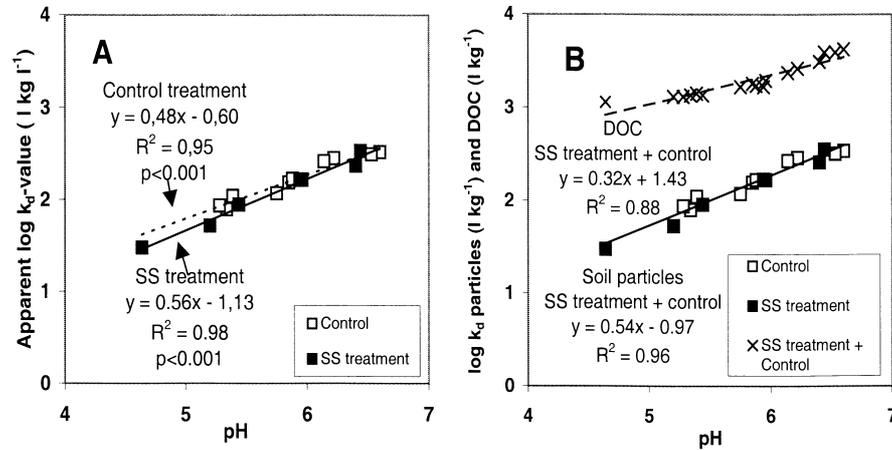


Fig 3A. The apparent Cd partitioning coefficients, $-K_{d-app}$ at increasing pH. B) The calculated partitioning of Cd between soil particles and Cd^{2+} in the solution- K_{d-part} accounting for the competition effect of DOM-complexation and the partitioning coefficient between DOM and Cd^{2+} in the solution- K_{d-DOC} .

Soil physical properties, a complementary study

Figure 4 depicts the decreasing hydraulic conductivity (K) in both treatments at decreasing supply potentials (ψ) within the range -1 to -5 cm. Taking the logarithms of the K values showed a strong linear dependence on the supply potential in both the SS treatment and the control ($R^2 = 0.999$ and 0.992 , respectively).

At all supply potentials, $K(\psi)$ was larger in the SS treatment than in the control, but the differences between the treatments were small at each supply potential, which indicates that only small changes in the macropore system had resulted from the sludge additions. Pairwise comparisons of $K(\psi)$ between the treatments showed, however, significant or nearly significant differences at supply potentials between -2 and -5 cm ($p = 0.08, 0.01, 0.08$), while no significant difference at the largest supply potential, -1 cm ($p = 0.64$) was found. These results indicate that the sludge amendments have resulted in a slightly better developed fine structural pore system, while the large macropore system (i. e the coarse structure) was unaltered. The consequence of this development of the fine soil structure is that smaller macropores and mesopores contribute more significantly to infiltration in the SS treatment, while the larger macropores would contribute more in the control. Thus, under steady-state infiltration a rainfall of 4 mm h^{-1} would generate a “supply potential” of -2.60 and -2.09 cm at the soil surface in the SS treatment and the control respectively, according to the linear regression equations for each treatment shown in fig 4. As the radius of the equivalent pore that is able to conduct water is inversely proportional to the supply potential, according to:

$$h_t = -\frac{0.3}{d_v}$$

Equation 6

where h_t is the supply potential (cm) and d_v is the equivalent pore diameter (cm), the largest equivalent pore diameter contributing to the water flow at a rainfall rate of 4 mm h^{-1} would theoretically be 1.43 mm in the control, but 1.15 mm in the SS treatment. Although this difference is small, it shows that a smaller proportion of the precipitation would be conducted by larger macropores in the SS treatment. Therefore, the contact time and surface area between by-passing water and the intra-aggregate soil matrix would be greater in the SS treatment, giving more time to equilibrate the Cd concentration between soil matrix and solution, leading to a slightly higher leaching of matrix-incorporated Cd (Jarvis, 1998).

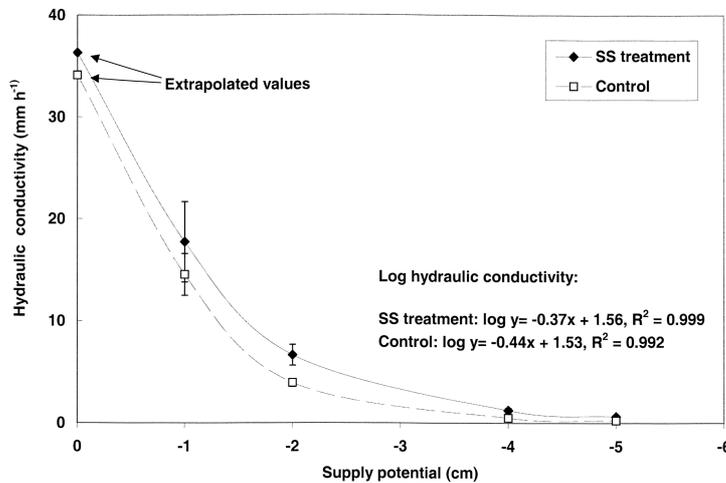


Fig 4. Data points and a regression model fits for $K(\psi)$ in the sewage sludge amended and the control treatment. Ranges indicate standard errors of mean.

As the soil texture is similar in both treatments, the difference in $K(\psi)$ between the treatments is attributed to the higher organic matter content in the SS treatment topsoil, which results in a higher biological activity and thus a better developed smaller macropore-and mesopore system. Since the total soil porosity was also significantly larger in the SS treatment compared to the control (59.5 vs 48.5 %, $p=0.04$), the physical conditions for crop establishment and growth are also better compared to the control. The greater contribution of mesopores in the SS treatment also suggests a higher water holding capacity at field capacity compared to the control. Thus, the significantly higher yields in the SS treatment compared to the control during the experiment can at least partly be attributed to a significant improvement in soil physical conditions resulting from an increase in organic matter content (Arvidsson, 1998) due to the sewage sludge additions.

Crop Cd uptake

Despite the measured increase in the EDTA-extractable concentration in 1997 in the SS treatment topsoil, measurements of the Cd concentration in barley crops cultivated during 1978 to 1997 showed no increase in Cd concentration in the grain fraction in the SS treatment ($p=0.46$, fig 5), and the grain concentrations measured during 1978-1997 were generally well below the limit value for cereals for human consumption (Commission Regulation 466/2001). In the straw fraction, however, the higher soil Cd solubility in the SS treatment resulted in an almost twice as high Cd concentration compared to the control ($p=0.078$) on average during 1978-1997. Numerous studies (*e. g.* Miller et al, 1995) corroborate this Cd uptake pattern. The present study was conducted in a soil with good conditions for deep rooting and a significant share of the mature root system may have occupied soil volumes not mixed with sludge. McBride (1995) postulated that roots avoided Cd uptake from sludge-amended topsoils and that this might reduce the metal uptake in crops cultivated in field trials. Thus, the crop Cd concentration might have been further increased in a soil less favorable for deep rooting compared to this test soil.

The continuous additions of sewage sludge had also resulted in increased soil fertility, as measured in harvest yields. The total above-ground yield in the SS treatment during 1956-1997 was thus ca 20 % higher compared to the control. This increase in soil fertility could be attributed to the supply of macro- and micro nutrients and improved physical properties, for example increased total porosity. Thus, the total offtake of Cd in sludge-applied soils was enhanced by a combination of increased crop Cd concentration and increased harvest yields. During 1956-1997, Cd offtake was on average twice as high in the SS treatment compared to the control.

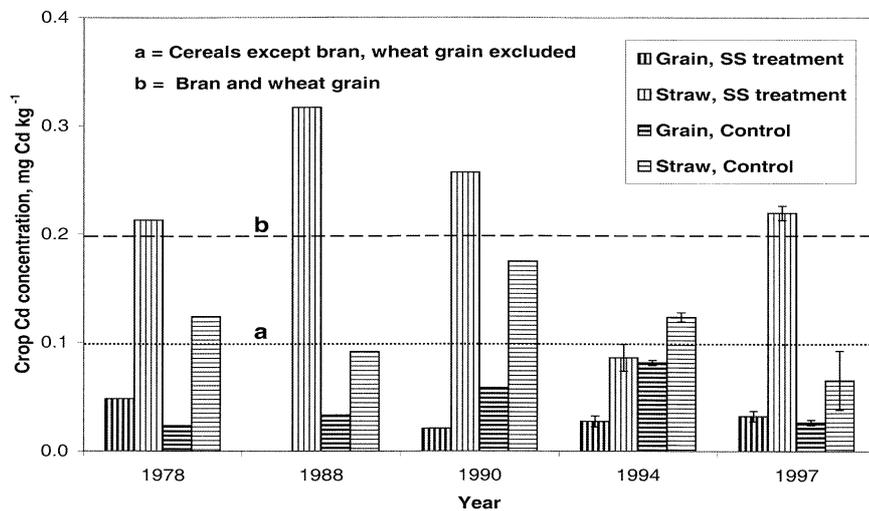


Fig 5. Cd concentration in barley grain and straw fractions during 1978-1997. Letters a and b denote the maximum Cd concentration tolerated for human consumption according to Regulation (EC) No 466/2001

The impact of DOC complexation on Cd solubility

The DOC concentration in the SS treatment exceeded the control by ca 3 times, measured at equal pH values (Paper II, table 3). This difference was explained by a combination of repeated additions of sewage sludge and the higher content of harvest residues exposed for mineralization in the SS treatment. Surprisingly, the regression line for $\log k_d$ vs pH for the SS treatment fell slightly below the control soils at equal pH values (fig 3A), although the soil organic matter content was almost twice as high. This indicates that the overall affinity for Cd in the insoluble soil phase was apparently lower in the SS treatment. As this might be an indication of competition for Cd ions with ligands in the solution, the partitioning of Cd in the soil solution was modeled in WHAM-W in order to explore this possibility. Measured data was used as model input (table 4), assuming that Cd complexation to inorganic ligands was negligible.

The modeling suggested that in this experiment, only 2-5 % of the Cd would be complexed by organic ligands at the DOC concentrations present in the solution. Since two years had passed since the last application of sewage sludge, it is possible that an initial peak release of DOC had been missed and DOC in the soil solution had now become so low that its impact on the total solubility of Cd was minor.

Table 4. Measured total Cd and DOM concentrations in 1997 in equilibrium extracts (0.01 M $\text{Ca}(\text{NO}_3)_2$) at zero Cd additions and three solution pH values, and the share of Cd complexed by DOM calculated using WHAM-W. Bold letters indicate suspensions with no acid or base added in sewage sludge (SS) and control (C) treatments

Soil layer, cm	pH		DOC, mg l^{-1}		Tot-Cd, $\mu\text{g l}^{-1}$		Cd bound by DOM, %	
	SS	C	SS	C	SS	C	SS	C
Topsoil								
0-28/0-23	4.6	5.4	22.5	8.6	7.11	0.67	2.5	1.2
	5.2	5.9	22.9	7.3	4.71	0.33	2.9	1.4
	6.4	6.6	24.3	7.1	1.08	0.14	7.0	2.9
Subsoil								
0-7	5.4	5.4	14.0	10.0	0.50	0.29	2.0	1.4
	5.9	5.8	12.3	10.2	0.24	0.25	2.3	1.8
	6.4	6.2	13.4	10.2	0.13	0.19	4.3	2.6
7-17		5.3		6.0		0.36		0.8
		5.7		6.1		0.17		1.0
		6.5		6.6		0.05		2.5
17-27		5.3		5.9		0.47		0.1
		5.9		7.7		0.05		0.1
		6.1		8.7		0.01		0.2

The partitioning coefficients between the Cd^{2+} ions in the solution and the soil matrix of both treatments were calculated at increasing pH disregarding the DOC-complexed Cd concentrations in the adsorption isotherms (fig 3B). In this case, the regression lines for k_d -part and pH merged for the two treatments, indicating an equal sorption affinity for Cd in the sludge-amended treatment and the control despite the difference in organic carbon content within and between the treatments.

As pH was identified as the most important control on the solubility of Cd in this experiment, the most effective way to decrease the solubility in the sludge-applied topsoil would be to add lime, in order to increase the pH to 6-6.5. However, as the solubility of DOM also increases at increasing pH values (McBride, 1994), this might also promote an increased share of Cd^{2+} complexed by organic ligands. In this experiment, the proportion of Cd complexed to DOM was actually highest at the highest pH in the SS treatment topsoil, but as the effect of pH itself exerts a much stronger control on the solubility of Cd than the DOM concentration, liming the SS treatment topsoil to ca pH 6.4 would decrease the solution Cd concentration drastically, and thereby reduce the crop Cd uptake significantly.

Changes in the soil humic phase by sludge supply

The humic fraction of the SS treatment topsoil consists of a mixture of organic compounds derived from decomposed sewage sludge and native humic matter. Besides pH, the trace metal sorption is assumed to be governed mainly by the soil humic content. Therefore, a modeling exercise in WHAM –S (Tipping, 1994) was conducted in order to calculate the expected increase in the partitioning coefficient, due to the higher humic content in the SS treatment topsoil. The model outcome indicated that the Cd sorption capacity of the particulate phase should be nearly twice as high in the SS treatment compared to the control at equal pH value ($k_{d, \text{pred}} = 151$ vs 76 l kg^{-1} , Paper II, fig 3). Instead, the sorption capacities were very similar at corresponding pH (339 and 353 l kg^{-1} , respectively). As the WHAM-W calculations indicated only a minor increase in the Cd solubility due to complexation by organic ligands in the soil solution, the lack of increase of sorption capacity in the SS treatment topsoil must be explained by other factors.

Phosphorus precipitation salts

As Al^{3+} (aluminium) and Fe^{3+} (iron) ions compete more effectively in forming metal-organic associations on humic substances compared to Cd^{2+} (Kerndorff and Schnitzler, 1980) the association of the Fe and Al salts, added for phosphorus (P) precipitation in the treatment plant, to soil organic matter were further studied. The total supply of Fe, Al and Mn (manganese) during 1956-1997 from sewage sludge amounted to 1.5 , 0.7 and 0.01 kg m^{-2} respectively (Uppsala municipality, personal comm.), which yielded a measurable increase in the pool of Fe associated to soil organic compounds by a factor three compared to the control topsoil (3.23 and $1.07 \text{ mmol Fe g}^{-1} \text{ org C}$), while the organically associated Al-pool remained unchanged (1.12 and $1.20 \text{ mmol Al g}^{-1} \text{ org C}$). These figures indicate that Fe salts added to the wastewater during the water purification competed more effectively

for complexation sites on humic compounds compared to the added Al. These results also confirm the suggestion of Pandeya and Singh (2000) that formation of stable complexes of Fe with humic matter are to be expected upon incorporation of sewage sludge in soil due to the high stability constants of Fe³⁺-fulvic acid complexes. The consequence of this might be a reduced capacity for sorption of metals other than Fe (Cowan et al, 1992). Thus, the reduction in the Cd binding capacity in the organic phase in the sludge-derived topsoil might at least partly be attributed to the addition of Fe salts by precipitation chemicals. This would be due to blocking access to the reactive sites in humus compounds as the metals are assumed to share common binding sites (Tipping et al, 2002).

Changes in the sorption properties of the humic compounds

Although not investigated in this study, the increased proportion of sewage sludge derived humic substances compared to native soil humic compounds is also likely to have changed the humic matter composition in the SS treatment topsoil towards the properties found in pure sewage sludge, (e.g. Gigliotti et, 2001; Soler Rivera, 2002) leading to changed sorption properties for Cd and other trace metals in the soil humic fraction. Thus, the change in organic carbon content due to sludge additions could not explain the Cd sorption capacity in the SS treatment. This result emphasizes that it is not solely the content of organic matter, but rather the properties of the humic compounds and their content of reactive functional groups as well as the presence of strongly chelating cations, such as Fe and Al, that critically determine the Cd sorption capacity of a sludge-amended soil.

Cd migration induced by sludge additions

Bio-circulation

Despite the higher solubility of Cd in the topsoil layer of the SS treatment, caused by a combination of increased Cd loading and reduced pH, the losses of Cd out of the soil profile were small, based on a mass balance calculated for Cd in the SS treatment and Control soil profiles during 1956 to 1997 (paper 1). Storage in the soil profile (0-60 cm) had increased by 149 mg Cd m⁻² in 1997 in the SS treatment, which corresponds closely to the calculated supply. Thus, the losses of Cd out of the soil profile by leaching and crop offtake seemed to be negligible. Most of the applied Cd still remained in the topsoil (Table 5). However, indirect evidence of Cd migration out of the topsoil layer was found, as the upper subsoil layer in the control (23-30 cm) indicated a depletion in the Cd content in 1997, compared to the levels measured in 1956, while this was not found in the equivalent soil layer of the SS treatment. The depletion in the control must be regarded as evidence for root uptake of Cd from the subsoil, resulting in translocation into the upper soil layers by mineralization of crop residues. Johnsson et al (2002) showed that 15 to 45% of the cadmium uptake by wheat plants grown in lysimeters originated from the subsoil. No depletion of the Cd content was measured in the upper subsoil layer of the SS treatment, indicating that the amount corresponding to root uptake from and biocirculation in crop roots from this soil layer must have been replaced by leaching out from the topsoil layer. The effect of this assumed bio-circulation of Cd in the SS treatment was therefore an apparently low migration rate of Cd out of the

topsoil layer and might also be a contributory factor explaining the generally low migration rates of Cd found in previously reported long-term experiments on Cd mobility in sludged soils (McBride et al, 1999). In SLAM, crop offtake was regarded as a Cd sink, but crop-driven Cd recirculation was not considered. This is probably the reason why the leaching of Cd into the upper subsoil from the topsoil was overestimated (Fig 6). Therefore, crop-driven recirculation of Cd appears to be significant at this site.

Table 5. Cadmium budget in the test period 1956-1997, based on measurements and estimations. Figures within brackets denote standard errors of means. $N = 2$ in soil analysis but $N = 19$ in sewage sludge supply.

	Treatment	
	Sewage sludge amendment	Control
	mg Cd m ⁻²	
Cadmium supply:		
<i>Sewage-sludge</i> [#]	140 (2)	0
<i>P-fertilizer</i> [□]	11	11
<i>Aerial deposition</i> [§]	2	2
Total Cadmium supply:	153 (2)	13
Estimated Cadmium losses:		
<i>Crop uptake</i> ^{**}	4	2
<i>Leaching losses</i> [¶] :	0 (14)	1
Initial Cadmium content in soil profile 0-60 cm:	130	130
Total Cadmium content 1997 in soil layers 0-60 cm	275 (12)	140 (0)
Measured change in storage 1956-1997:		
Soil profile, corresponding to 0-60 cm in 1956	+149 (12)	+10 (1)
<i>Topsoil, corresponding to 0-20 cm in 1956</i>	+141 (6)	+17 (1)
<i>Upper subsoil, corresponding to 20-37 cm in 1956</i>	0 (3)	-11 (1)
<i>Lower subsoil, corresponding to 37-60 cm in 1956</i>	+7 (2)	+4 (0)

[#] Depth corresponding to initial soil profile depth.[#] Cadmium supply by sewage sludge according to Kirchmann et al. 1994 and the Uppsala municipality, 1998.

[□] Cd-supply by P-fertilizer according to personal communication with Hydro-Agri Company and Swedish Farmers Supply and Crop Association.

[§] Aerial wet and dry Cd deposition according to Jensen, 1997.

^{**} Cd uptake according to barley yields and Cd concentrations in straw and grain fractions in 1978-1997.

[¶] Leaching losses calculated in balance calculations are based upon soil content in 1956, Cd supply 1956-1997 and crop Cd content 1978-1997.

Physical non-equilibrium

The lack of Cd leaching from the topsoil layer found in this study might also be partly attributed to physical non-equilibrium in Cd concentrations between matrix pores and macropores. Cd applied to soils in sewage sludge is almost exclusively sorbed or associated to the particulate phase. The clay loam soil in this field experiment cannot be considered as a homogenous flow domain, because of the presence of macropores, such as cracks and root/earthworm channels. This soil structure causes rapid macropore flow, leading to a physical non-equilibrium with

the solution concentration in the soil matrix (Jarvis, 1998). The incorporation of sewage sludge into the soil by spade tillage may therefore have resulted in a physical protection of Cd in soil/sludge aggregates. Within these aggregates, the prerequisites for equilibrium of Cd concentrations between the soil particles and the micropores may be fulfilled, while the time to reach equilibrium between the - solute phase and the macropores is not attained, resulting in much smaller Cd concentrations in the macropores (Jarvis, 1998).

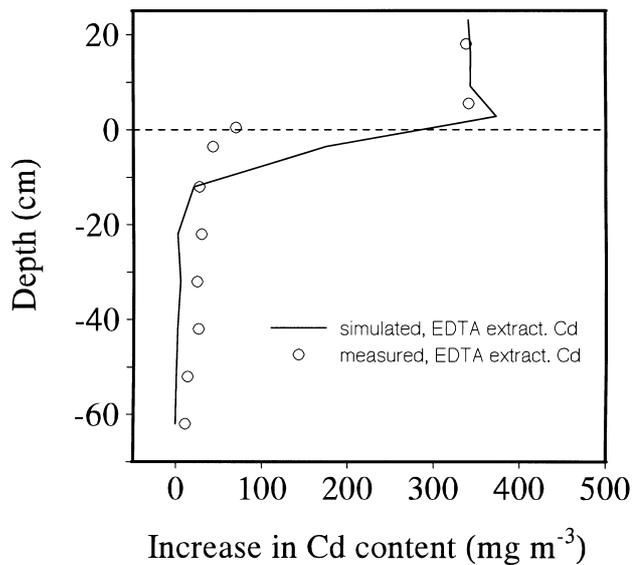


Fig 6. Comparison of measured and simulated increases in EDTA-extractable cadmium contents in sludge-amended soil, Ultuna in 1956-1997. The zero depth in the soil profile is given as the base of the topsoil in 1956, since the topsoil thickness changes with time.

The effects of non-equilibrium macropore flow on the Cd migration pattern was also apparent from a comparison of the SLAM model predictions with measurements of changes in the EDTA-extractable Cd-pool during 1956-1997 in the SS treatment (Fig 6). As also indicated by the measurements, the model predicted insignificant leaching out of the investigated soil profile, but it overestimated the leaching into the upper subsoil layer. Besides root uptake driven biocirculation of Cd, non-equilibrium macropore leaching may also have contributed to this overestimation. This process is not accounted for in the SLAM model, but is likely to be significant in this soil which has a strong structure with many coarse and fine tubular pores (Messing & Jarvis, 1990). The occurrence of macropores in this structured soil is therefore likely to have contributed to the low leaching amounts of Cd measured in this test site. The apparent slight increase in the EDTA-extractable Cd concentration in the subsoil in 1997 is a further indication that macropore flow might have influenced the transport of Cd (fig 5).

Dissolved organic ligands

The higher partitioning coefficient for Cd to DOC, $K_{d,DOC}^{Cd}$ compared to the soil particles calculated from the batch data (fig 3B), in combination with the low measured DOC concentration, gave only a negligible increase in the predicted effective Cd migration velocity, v^* , given by:

$$v^* = v(1 + k_{d,DOC}^{Cd} * \rho_{DOC}) \quad \text{Equation 7}$$

where ρ_{DOC} is the DOC concentration (g DOC l⁻¹). Equation 7 represents an upper estimate of the enhanced transport velocity since it assumes that DOC itself entirely behaves as a non-reactive tracer. Christensen et al (1996) concluded that the enhanced migration introduced by DOC complexation of Cd at a DOC concentration exceeding that found in this study by one order of magnitude (232 mg DOC l⁻¹) was still negligible, as the transport velocity was 1 % of the matrix water velocity. Thus, the influence of DOC on Cd leaching was regarded as insignificant at the Ultuna field site and migration of DOC complexed Cd was therefore not considered in the SLAM model simulations presented in this thesis.

Sorption hysteresis

It is generally observed that adsorption and desorption isotherms employed during short-term to medium-term experiments (days -months) for Cd and other trace metals in soils are not identical, but exhibit hysteresis (Filius et al, 1998; Tran et al, 2002). Adsorption processes for trace metals on soils are generally fast, reaching equilibrium within ca one day (Lee et al, 2001), while desorption of trace metals is slower and also less complete, and is therefore to be regarded as highly non-reversible, at least in the short-term perspective (McBride, 1994). However, knowledge on the long-term effects of sorption hysteresis on trace metal migration velocity is still scanty. If sorption/ desorption hysteresis of Cd also occurred in the long-term (> 40 years), the SLAM model would consequently over-estimate the desorption rate and thereby the Cd migration velocity. Sorption hysteresis might therefore be a process exerting a significant impact on the leaching of Cd, resulting in a lower measured Cd migration out from the upper subsoil layer, compared to the model predictions, as shown in fig 6.

Applying the SLAM model on the long-term field experiment

Sensitivity analysis

Tables 6 and 7 show the results of the Monte-Carlo sensitivity analysis for leaching from the topsoil layer and crop offtake. The overall R² values of the multiple linear regressions of the ranked variables were 92 and 95% respectively, which was considered as being sufficiently large to allow a unequivocal interpretation of the results (Janssen et al, 1992). The results indicate that four model parameters were of great significance for both target output quantities, namely the Cd concentration in sludge, explaining 65% of the overall variation in Cd leaching and 16 % of the Cd offtake, and three parameters related to the Cd adsorption properties of soil and

sludge, namely the inorganic fraction in the sludge ($1-f_o$), the partitioning coefficient of the sludge inorganic fraction k_{ms} and the exponent a regulating the pH sorption effect.

Other parameters identified affecting Cd leaching were two transport properties, reflecting the pore water velocities in the profile; the soil water recharge and the dispersivity. These two parameters together explained 23% of the variation in Cd leaching. The parameters of greatest importance for Cd offtake were Michaelis-Menten equation parameters describing the maximum plant concentration (C_{p-max}) and the half-maximum soil Cd concentration (k_p). Together, they explained 72% of the variation in uptake.

Table 6. *Partial rank correlation coefficients (PRCC) between model input parameters and total simulated Cd leaching below 28 cm depth and their contribution to the total R². All variables significant at p<0.05 are included.*

Parameter	PRCC	Contribution R-sq
Correlation R ² /R ² adj		0.950/ 0.941
Cd concentration in sludge	0.963***	0.648
Soil water recharge	0.885***	0.183
Dispersivity	0.700***	0.049
Partition coefficient (sludge inorganic fraction)	-0.653***	0.037
Freundlich exponent	-0.403***	0.010
Exponent for pH sorption effect	0.375***	0.008
Partition coefficient (sludge organic fraction)	-0.371***	0.008
Humification constant	-0.255**	0.004
Inorganic fraction in sludge	-0.254**	0.004
Half-maximum soil Cd concentration	0.222*	0.003

*** p<0.001
 ** p<0.01
 * p<0.05

Table 7. *Partial rank correlation coefficients (PRCC) between model input parameters and total crop offtake of cadmium and their contribution to the R²-value. All variables significant at p<0.05 are included.*

Parameter	PRCC	Contribution R ²
Correlation R ² / R ² adj		0.920/ 0.906
Max. plant Cd concentration	0.927***	0.489
Half-maximum soil Cd concentration	-0.863***	0.234
Cd concentration in sludge	0.819***	0.163
Inorganic fraction in sludge	-0.401***	0.015
Partition coefficient (sludge inorganic fraction)	-0.327***	0.010
Exponent for pH sorption effect	0.284***	0.001

*** p<0.001

Since the sludge rates were kept constant in the sensitivity analysis, the Cd concentration in sludge is also equivalent to the total Cd amount in the soil, resulting from Cd loading by sewage sludge. The sensitivity analysis thus stressed the importance of the total applied amount of Cd in controlling the long-term

effects on both leaching and crop uptake, while the fraction of EDTA-extractable Cd in sludge seemed to be of little significance.

As sludge application leads to an accumulation of persistent inorganic compounds in the long-term, their contribution to the overall soil Cd sorption capacity becomes significant, while the organic compounds derived from sewage sludge and crop residues continuously undergo mineralization and therefore contribute proportionally less to the soil sorption capacity. The difference in persistence of the inorganic and organic soil compounds in the long-term perspective investigated (150 years) explains the strong contribution of the partitioning coefficient of the inorganic fraction, k_{ms} , to the regression, while the partitioning coefficient for the organic fraction of the sludge, k_{hs} , contributed less.

Only one of the parameters describing the supply and turnover of organic matter in the soil profile originating from crop residues: the humification constant (h), was found to have a significant contribution to the variation in the target output quantities. This is explained by the smaller contribution of native humic compounds to the total soil humic content compared to the sludge-derived humic content. However, a shorter-term sensitivity analysis, carried out for the buildup phase of soil humic content due to sludge applications, might have resulted in a more significant contribution by k_{hs} to the over-all sorption capacity of the soil.

When interpreting the outcome of the sensitivity analysis it is important to consider the assumptions and limitations involved. Extending or narrowing the ranges for the parameters in the sensitivity analysis might significantly change the contribution of the parameters to the significance level and their contribution to the over-all correlation coefficient. The estimates of the significance of the parameters controlling crop offtake and leaching cannot therefore be considered as precise estimates, but rather indicate trends in terms of which parameters make a significant contribution. In contrast to this basic sensitivity analysis, uncertainty analysis is more firmly based in measured distributions of parameters for a given site or region (Janssen et al, 1992).

As rank transformation of data introduces linearity in the correlation between input parameters and the output data, the contribution of previously non-linear relations (to the overall regression coefficient) might also become overestimated. The partial rank correlation coefficients (PRCC) listed in tables 5 and 6 show however generally high values for the model input parameters contributing to a high extent to the regression correlation. Therefore, the ranking of data prior to the analysis probably increased the clarity of the underlying relations.

Scenario simulations

Figure 7a shows that the ratio of sludge k_d to initial soil k_d exerts a strong influence on the plant Cd concentration; a sludge k_d value equal to the initial soil k_d would give no change in the sorption capacity of the soil-sludge mixture with time, and a more or less linearly increasing solution Cd concentration due to the increased Cd concentration in the soil. This would result in a corresponding increase in crop Cd

concentration, if first order crop Cd uptake rate is assumed due to the increasing Cd content in the soil. This can be demonstrated by Equation 1 in paper III, which may be re-arranged and simplified in the case of linear sorption:

$$c = \frac{A}{\theta + \gamma k_d} \quad \text{Equation 8}$$

where c is the total Cd concentration in the solution (mg Cd l^{-1}), A is the total soil Cd content (mg Cd m^{-3}), θ is the volumetric water content ($\text{m}^3 \text{ water m}^{-3} \text{ soil}$) and γ is the soil bulk density ($\text{kg m}^{-3} \text{ soil}$). This constant partitioning corresponds to the results achieved in this batch study on soils of the Ultuna soil fertility experiment, as no increased sorption capacity was measured following sludge additions, while crop Cd concentration increased due to the increased total Cd content in the soil and the reduction in the topsoil pH.

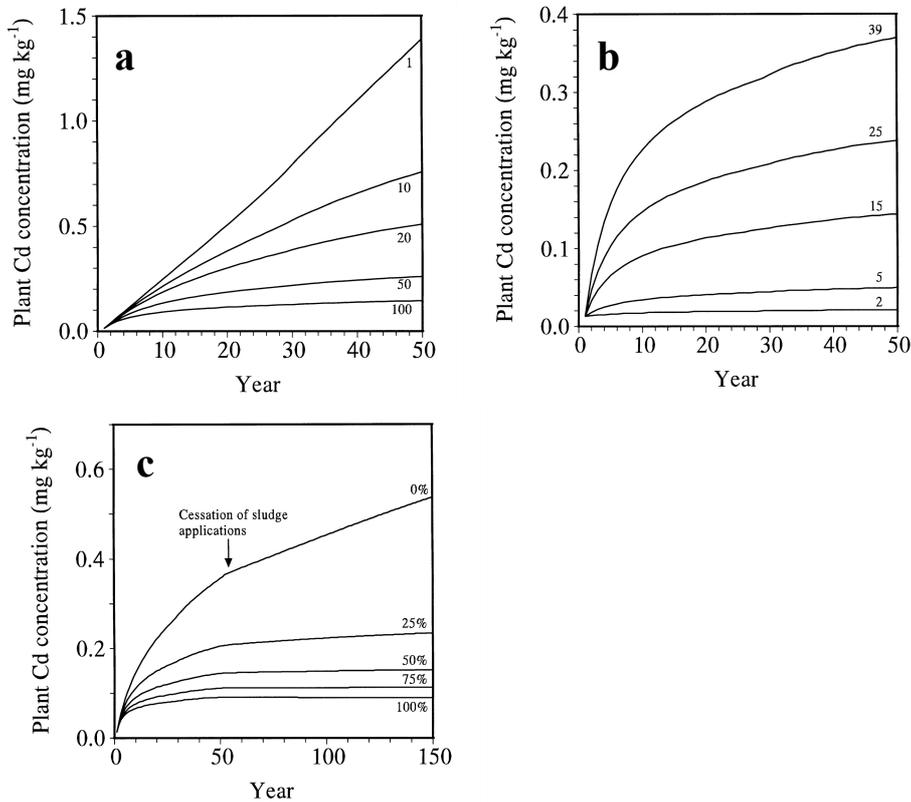


Fig 7. Simulated plant Cd concentrations. The figures on the curves denote in a) the ratio of sludge k_d to initial soil k_d value, in b) the Cd concentration in sludge in $\text{mg kg}^{-1} \text{ DM}$ in c) the proportion of sludge k_d contributed by the inorganic components.

A sorption capacity of the sludge that exceeds that of the native soil by orders of magnitudes will result in a higher total sorption capacity in the sludge-amended soil, such that the crop Cd concentration would asymptotically approach a “plateau”, despite the continuously increased soil Cd content. Although sludge “protection” was not found in the Ultuna experiment, it has been reported in other studies (Petruzzelli et al, 1997, Li et al, 2001). Fig 7b shows that applying sludges of low Cd concentration would exert only a minor impact on the crop Cd concentration, even if the sludge K_d is lower than the initial soil k_d , as the background soil Cd concentration would remain the dominant source for crop Cd uptake.

Sludge of very low Cd concentration, or rather a low Cd loading, and with a higher k_d value than the native soil could therefore in principle reduce the solubility and crop uptake of Cd, as the effect of the increase in the soil k_d value would be proportionally larger than the Cd loading (see equation 8). On the other hand, high Cd loadings might overshadow the “protection” effect of a high sorption capacity of the added sludge, resulting in an increased solubility of Cd (not shown), as demonstrated by Chaudri et al (2001).

The scenario simulations indicated two prerequisites for a sludge “time bomb” effect to occur: the sludge must be characterized by a high initial sorption capacity compared to the native soil and the organic compounds of the sludge must contribute most of the adsorption capacity (Fig 7c). During the sludge application period, the solution Cd concentration may increase or remain almost unchanged, depending on the ratio of A to k_d (eq 8), but following cessation of sludge applications, mineralization of soil organic matter results in a gradually decreased sorption capacity and thereby increased solubility of previously adsorbed Cd, leading to increased crop Cd uptake. However, even a small contribution by inorganic sludge components (e.g. 25%, fig 7c) would minimize the impact of the reduction in the sorption capacity in the soil organic matter phase due to mineralization and eliminate the “time bomb”. This is also in accordance with the outcome of the sensitivity analysis, as a small but significant correlation between the plant Cd concentration and the adsorption capacity of the sludge inorganic fraction was found.

Some of the conditions and prerequisites for sludge-“protection” and the sludge “time bomb” were identified in the scenario simulations described above: the cumulative total amount of Cd added, the partitioning coefficient of the sludge compared to the native soil and the contribution of the inorganic fraction to the sludge sorption capacity were of great importance in determining the long-term solubility of the sludge applied Cd. As both the composition and the chemical properties in sewage sludge from different sources and also the soil sorption properties may vary widely, no general statements can be made concerning the validity of either the sludge “protection” or the “time bomb” hypotheses. Either may occur, or neither, as was indicated in the Ultuna study.

Modelling Cd solubility at various soil chemical conditions using WHAM-S, a complementary study

A modeling exercise was undertaken in order to further increase understanding of the effects of soil properties on Cd solubility. This study was performed using the chemical equilibrium model WHAM-S (Tipping, 1994) using the basic model parameterisation shown in Paper II (table 5). The soil pH and the CEC of the soil, reflected by the humus and clay content, have been identified as significantly influencing the soil Cd adsorption capacity (Christensen, 1989, Eriksson, 1989). Thus, the magnitude of changes in the distribution of Cd between the solution phase and clay and organic phases of the soil matrix were modelled following stepwise changes in these soil chemical and textural properties.

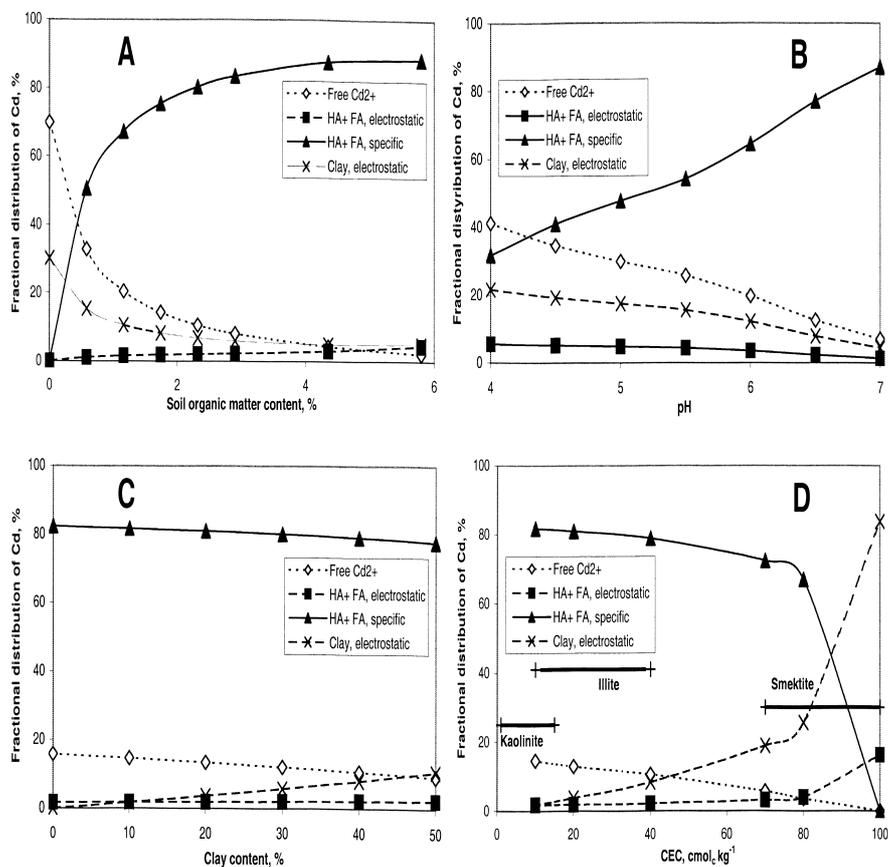


Fig 8. Fractional distribution of Cd on clay minerals, colloidal fulvic and humic acids and free solute species, according to modeling results in WHAM. A) at increasing soil organic matter content, B) at increasing solution pH, C) at increasing clay content D) at increasing clay mineral CEC. The range of CEC for kaolinite, illite and smectite clay minerals are shown in the figure.

In the range of 0-8 % soil organic matter content and assuming a 70 % FA + HA concentration in the soil organic phase, the model results demonstrate the dominant contribution of soil humic compounds on Cd sorption (fig 8A). Despite a relatively high clay content, 36%, the binding of Cd to the clay fraction was limited to ca 30 % in the complete absence of humic compounds. Introducing a small organic matter concentration, 1%, reduced the solubility of Cd dramatically, as a result of an increase in the overall sorption capacity, but particularly of the introduction of specific sorption sites for Cd in the humic substance. As specific sorption of Cd by chelate binding to humic reactive groups is energetically more favourable and thus more stable compared to electrostatic sorption, Cd previously bound to clay becomes instead more strongly attracted to the humus (McBride, 1994).

Increasing the solution pH in the range of 4-7 also results in a sharp decrease in Cd solubility (Fig 8B). These sorption effects are explained by the increasing specific sorption on humic compounds due to deprotonation of reactive groups, but also a reduced contribution by electrostatic binding to cation exchange sites on clay minerals.

Increasing the clay content in the range of 0-50 %, assuming a clay CEC in accordance with illite minerals, gave only a small reduction in the calculated fraction of Cd in the solution, from 18 to 10%, due to a slight increase in the electrostatic attraction of the clay minerals (Fig 8C.) Thus, electrostatic attraction of Cd to sorption sites on clay surfaces remains low even at high clay contents in the presence of humic substances in the soil at least for the CEC values of clay in the range of illitic minerals (10-40 cmol_c/kg.). The CEC of clay minerals was also changed in order to show the influence of clay types on Cd distribution in the soil-solution system. CEC was changed in the range 10- 100 cmol_c kg⁻¹, representing kaolinitic, illitic and smectitic clay minerals. The model outcome shows that smectite clay minerals might compete effectively with soil humic matter for Cd, due to its higher CEC (Fig 8D).

This modeling exercise suggests that the soil pH is a critical variable determining the Cd solubility. The presence of native soil organic matter and especially the concentration of active humic and fulvic acids also plays a crucial role in Cd sorption chemistry. The effect of clay content depends strongly on the local clay mineralogy.

Conclusions

Continuous amendment of sewage sludge led to soil acidification by mineralization of sludge-derived organic compounds and buildup of humic compounds. The sensitivity analysis in the SLAM model as well as batch studies indicate that the reduced adsorption capacity due to acidification was a critical factor in controlling both plant Cd uptake and leaching.

Long-term sewage sludge additions at this test site increased the soil organic content, but did not increase the sorption capacity for Cd. This might be explained at least partly by the Fe salts added by wastewater treatment for P precipitation that might reduce the Cd binding capacity in the sludge-organic phase by blocking access to sorption sites. Although not investigated explicitly in this study, another possible explanation is that humic compounds derived from sludge may exhibit a smaller sorption capacity for Cd compared to native humic substances. Thus, humic compounds are complex in their composition and their sorption capacity for Cd and other pollutants is determined not only by quantity but also by quality.

The affinity of Cd for soil humic compounds exceeds the affinity for clay compounds. This is explained by a dominance of chemisorption of Cd^{2+} to humic compounds and by weaker electrostatic bonding to pure clay compounds. The Cd sorption capacity is thus mainly correlated to the soil humic content in loamy and clay soils dominated by kaolinitic and illitic clay minerals, as was the case in the long-term fertility experiment test site.

The recovery of Cd in the sludge amended treatment was ca 92 % in the topsoil after 41 years of continuous sludge supply, indicating a strong sorption capacity in the soil and a low leaching rate of Cd.

The influence of complexation of Cd to dissolved organic compounds was apparently of little significance for leaching at this site. Occurrence of macropore flow was also apparently of little significance for leaching, and this was attributed to physical non-equilibrium between Cd concentrations in the matrix pores and the macropores, resulting from incorporation of the sewage sludge by digging.

The sludge applications had resulted in increased solubility of Cd by a factor 20 as a consequence of acidification and increased total Cd concentration, as well as an increased proportion of potentially bioavailable Cd. Due to the increased solubility, the Cd concentration in the straw fraction increased by a factor two but remained unchanged in the grain fraction.

According to the SLAM model, the most critical factors controlling plant uptake and leaching of Cd in a biosolids-amended soil are the accumulated total cadmium load, together with properties controlling the overall sorption capacity such as pH and the partitioning coefficients of the inorganic fraction of the sewage sludge. The outcome of the SLAM model stressed also that the genetically determined properties of the cultivated crops regarding Cd uptake kinetics from soils are of great importance besides the soil factors.

The scenario simulations indicated some prerequisites for a sludge “time bomb” effect to occur: the sludge should be characterized by a high initial sorption capacity compared to the native soil and the organic compounds of the sludge should contribute most to the adsorption capacity. Sludge- “protection” might occur when applying sludge of very low Cd concentration and a higher k_d value compared to the k_d -value of native soil. A third scenario is possible, which was found in the Ultuna soil, characterized by an equal partitioning coefficient in the

soil and sludge fractions, yielding no change in the k_d value of the soil/sludge mixture but gradual increase in the soil Cd concentration.

The inorganic compounds in sewage sludge that may contribute to increased sorption capacity for Cd, *i.e.* the carbonates, sulphides, phosphates and hydroxides, are also not to be regarded as chemically inert and persistent as changes in pH, redox potential and weathering processes may increase their solubility in the soil environment. Therefore, in working out regulatory criteria for sustainable farming systems, care must be taken not to rely on sludge “protection” (e.g. US EPA Part 503) either in a short or long term perspective.

Recommendations

- Sludge additions to soils of low initial adsorption capacity, *i.e.* silty and sandy soils of low inherent organic content (< 1 %) should be avoided, as we cannot rely on permanent increases in the sorption capacity of the soil-sludge mixture.
- Sludge should be incorporated into the soil soon after application in order to avoid macropore leaching of Cd.
- Soils of inherently low pH values should be avoided for sewage sludge additions. The soil pH should not fall below ca 5.5 in sludge-amended mineral soils, and regular liming, being the usual agricultural practice, is therefore recommended.
- Only cultivars of low uptake propensity should be cropped in soils of high Cd concentration or low pH in order to avoid Cd concentrations approaching potentially toxic levels in the edible parts of the crops.
- Efforts should be continued to reduce the Cd concentration in sewage sludge as well as other Cd sources, such as farmyard manure, aerial deposition, phosphorus fertilizer, and lime in order to reach a balance between Cd supply to arable soils and the crop offtake.

Future applications and research needs

The SLAM model singles out one sludge fraction as being of largest significance for the sorption capacity in the soil-sludge mixture, and thereby also leaching and crop uptake; namely the sludge inorganic precipitates. As this fraction is very heterogenous, there is a great need to define the sorption mechanisms for Cd to the various inorganic phases and to estimate the stability of these compounds under different environmental conditions.

Cd complexation to soluble organic compounds probably did not pose a risk for enhanced solubility of Cd in this study. However, other results obtained in other sludge-amended soils are quite different (Józefaciuk et al, 1996). To improve our understanding of these complex processes and how they influence Cd leaching, the mineralization processes leading to release of DOC and the sorption processes of DOC-Cd complexes in the soil matrix should be combined in a transport model that includes macroporous flow as well as matrix flow.

The Cd sorption capacity in the sludge organic phase has until now been implicitly regarded as being equal to the native soil organic phase. As the outcome of this study indicates a lower sorption capacity than expected, the underlying reasons should be further studied, where the suggestions from this work would serve as trigger questions; *i. e.* is there a competition for sorption sites on soil humic compounds between sewage sludge derived Fe and Al hydrous oxides on the one hand and Cd²⁺ ions on the other hand? Does humic matter derived from sewage sludge have a smaller number of binding sites for metal ions than native humic matter?

As evidence of root driven re-circulation of Cd from subsoil layers into the topsoil layer was found in this and previous experiments, further studies are needed to gain increased insight into the Cd uptake distribution in arable soils with different vertical distribution patterns of Cd and also with different possibilities for deep rooting in the soil profile.

The long-term effects of sorption hysteresis of Cd and other trace metals in soils on Cd migration velocity are still poorly understood. It is therefore important to conduct more studies on soils that have been contaminated for long times, as short-medium term laboratory studies may not accurately predict the sorption-desorption pattern of Cd and other pollutants, and may therefore give incorrect estimations of migration velocities in soils.

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