

Modeling Organic Carbon Dynamics and Cadmium Fate in Long-Term Sludge-Amended Soil

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ABSTRACT

A model is described that may help to resolve uncertainty and controversy over the long-term consequences of sludge applications to arable land, especially with regard to the effects of sludge adsorption characteristics on trace metal solubility and bioavailability (e.g., the sludge “time bomb” or sludge “protection” hypotheses). Mass balances of organic and inorganic material derived from sludge and crop residues are simulated. Each pool has a potentially different adsorption affinity for trace metals, and this leads to changes in the adsorption capacity of sludge-amended soil that influence leaching and crop uptake. Model simulations were compared with measured changes in organic carbon and ethylenediaminetetraacetic acid (EDTA)-extractable cadmium contents in a clay loam soil following 41 years of sludge applications. The model adequately reproduced the data, although discrepancies in the vertical distribution of Cd were attributed to the effects of macropore transport and root-uptake driven recirculation. A Monte Carlo sensitivity analysis demonstrated that the most important parameters affecting leaching and crop uptake were the Cd loading and parameters controlling adsorption, especially the partition coefficient for sludge-derived inorganic material and the exponent regulating the effect of pH on sorption. Scenario simulations show that no general conclusions can be drawn with respect to the validity of the sludge “time bomb” and sludge “protection” hypotheses. Either may occur, or neither, depending on three key system parameters: the ratio of sludge adsorption capacity to the initial adsorption capacity of the soil, the proportion of the sludge adsorption capacity contributed by the inorganic fraction, and the sludge Cd loading.

SEWAGE SLUDGE represents a potentially valuable source of nutrients and organic matter for arable farming, but its use may be limited due to the presence of toxic trace metals, especially the more mobile trace elements such as Cd. Thus, studies have shown that sludge application to arable soils can result in an increased bioavailability and crop uptake of Cd (McGrath et al., 2000). With regard to leaching risks, most long-term field experiments show only very slow translocation of the added Cd below the plow depth (Chang et al., 1984; McGrath, 1987; Yingming and Corey, 1993), although some studies have indicated a potential for preferential, accelerated migration of dissolved organic carbon (DOC)-complexed Cd in macropores (Cambreco et al., 1996; Richards et al., 1998). Despite intensive experimental efforts, there is still continuing controversy over the likely long-term effects of sludge applications on metal uptake and leaching, especially with regard to the effects of sludge adsorption properties

on metal solubility and bioavailability (the sludge “protection” hypothesis), and the role of organic matter decomposition following cessation of applications (the “time bomb” hypothesis). These questions remain unanswered largely due to the scant and often conflicting or equivocal nature of the experimental evidence (McBride, 1995; Chang et al., 1997; Hyun et al., 1998; Hamon et al., 1999).

Models may prove useful in helping to understand the complex and interacting processes affecting Cd fate in soil systems, and therefore the likely long-term consequences of sludge application. At best, they may help to explain apparently contradictory experimental results and also allow us to explore the likely consequences of alternative management practices by posing “what if” questions in “scenario” simulations. However, the use of models is hampered by the lack of suitable long-term datasets for model calibration and testing. Most model applications to date have therefore focused on improving our understanding of short-term transport and retention processes under controlled conditions, usually with concentrated pulse inputs of Cd²⁺ in solution (Selim et al., 1992; Buchter et al., 1996). It is not straightforward to transfer these results to sludge-amended field soils, because trace metals are applied in largely adsorbed forms and usually at much lower rates. To our knowledge, only two studies have compared model simulations of the long-term mobility of Cd with field data. Černík et al. (1994) applied analytical solutions of solute transport models to polluted industrial sites, while Streck and Richter (1997b) used the convection–dispersion equation within a stochastic framework to successfully predict the Cd distribution found in a sandy soil after 29 years of wastewater irrigation.

Soil organic carbon content strongly affects Cd adsorption (Boekhold and van der Zee, 1992; Gray et al., 1999), which implies that the fate of Cd in sludge-amended soils might be inextricably linked to organic carbon turnover (McBride, 1995). Therefore, for long-term modeling purposes, descriptions of Cd transport and retention should be linked to a submodel of organic carbon dynamics. In this paper, we describe a model of Cd fate and mobility in sludge-amended soil, linked to a model of organic carbon turnover. A key feature of the model is that it accounts for the effects of the differing adsorption affinities for Cd of inorganic and organic mass fractions, both in the added sludge and in the resulting topsoil–sludge mixture. Model simulations are compared with measurements of Cd distribution made in a clay loam soil at Ultuna (Uppsala, Sweden) that had received sewage sludge for 41 years (Bergkvist et

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Abbreviations: DOC, dissolved organic carbon; EDTA, ethylenediaminetetraacetic acid; ICBM, Introductory Carbon Balance Model.

al., 2003). The model was parameterized from a combination of site-specific measurements (Bergkvist, 2003; Bergkvist et al., 2003) and from the literature, where data was missing. A Monte Carlo sensitivity analysis is also performed to identify the key parameters controlling plant Cd concentrations and leaching from the topsoil. As an illustration of the potential use of the model as a management tool, exploratory scenario simulations are presented that show the conditions under which sludge “protection” and the sludge “time bomb” can be expected to occur.

MATERIALS AND METHODS

Model Description

Conceptual Basis, Scope, and Limitations

Figure 1 shows a schematic diagram of the conceptual basis of the model described in this paper. Two pools of Cd are recognized: free ions in solution, which are considered bio-available, and matrix-adsorbed Cd^{2+} ions in equilibrium with the soil solution concentration. It is assumed that the equilibrium partitioning for Cd^{2+} ions between soil and solution is governed by an extended Freundlich isotherm (e.g., Elzinga et al., 1999). As noted earlier, and shown schematically in Fig. 1, the long-term fate of trace metals supplied with sludge to arable land may be strongly influenced by changes in sorption capacity due to changes in soil organic carbon pools. An increased solid phase organic carbon content may increase sorption (Boekhold and van der Zee, 1992; Streck and Richter, 1997a; Gray et al., 1999) and therefore retard transport. Since carbon dynamics per se are not the central focus of our model, we chose to extend and modify the simple Introductory Carbon Balance Model (ICBM) described by Andrén and Kätterer (1997). This model recognizes two pools of organic carbon (Fig. 1), with “fast” and “slow” turnover rates, representing undecomposed fresh crop residues and recalcitrant humified

material, respectively, while the effects of temperature and moisture on decomposition are treated only implicitly through a soil climate “factor.” In our modified version, two parallel, separate pools for both fresh and humified carbon are defined, one derived from sewage sludge and one from crop residues. This is because experimental evidence suggests that humus derived from sludge may differ in quality and thus show a different affinity for metal adsorption (Bergkvist, 2003).

Apart from the influence on adsorption, changes in organic carbon content also influence metal translocation by altering soil physical properties. In particular, the buildup of soil organic matter resulting from sludge applications causes a reduction of soil bulk density accompanied by an increase of topsoil thickness. Since the depth of plowing is generally constant, this process will, in the long-term, result in a “transfer” into the upper subsoil of sludge-derived Cd, together with organic and inorganic material that was originally incorporated into the topsoil (Bergkvist et al., 2003). The model accounts for “translocation” of mass into the subsoil by relating long-term changes in bulk density and layer thickness to organic carbon content.

Not all features of the model have been activated in this study. For example, the complete model includes kinetic sorption, following the “two-site” model described by Altfelder et al. (2000), and a description of DOC-facilitated transport of trace metals, mostly following the concepts described by Knabner et al. (1996), but incorporating a description of DOC generation from organic matter decomposition, and allowing for the heterogeneous nature of DOC by accounting for two DOC fractions (hydrophobic and hydrophilic). However, Bergkvist (2003) showed that <6% of Cd in solution was likely to be DOC-complexed in the topsoil of the Ultuna sludge-amended plots, while no data was available to parameterize kinetic sorption.

Several other potentially important processes are not considered in the model, or are treated in simplified fashion. For example, transient water flow is not considered. Instead, the model assumes steady state water flow q and a constant water

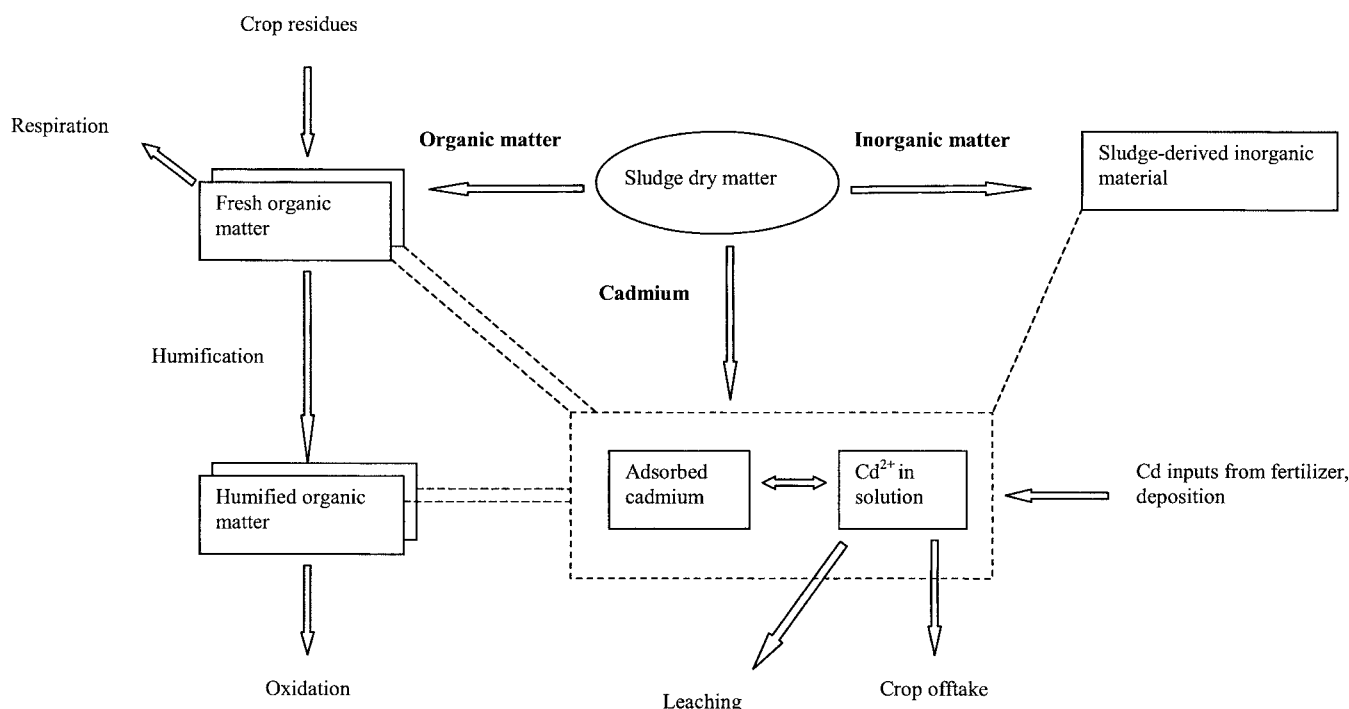


Fig. 1. Schematic diagram of the model. Boxes indicate “pools,” arrows indicate flows, and dashed lines show links or interactions between pools.

content θ with time and depth in the soil profile. This is a reasonable simplification for very strongly sorbed compounds subject to long-term, slow transport processes. In such situations, transport is not sensitive to variations in q and θ (Černík et al., 1994). Furthermore, the non-equilibrium resulting from preferential flow and transport, for example in soil macropores, is neglected.

Long-term changes in soil pH are often observed following repeated sludge applications. For example, acidification can result from the mineralization of organic nitrogen and sulfur and/or from organic acids present in the sludge (Kirchmann et al., 1996; Bergkvist et al., 2003). Soil pH is a critical soil property determining the strength of Cd adsorption (Christensen, 1984; Boekhold and van der Zee, 1992; Gray et al., 1999; Bergkvist, 2003), and so pH is included in the model as a controlling parameter for Cd adsorption. However, changes of soil pH are not explicitly modeled. For predictive applications, pH can usually be assumed constant with time (although it may vary with depth), since under normal agricultural practice, farmers usually maintain topsoil pH within an optimum range by liming. Alternatively, for applications to research sites, the user can force pH changes with time as a function of sludge dry matter input.

Cadmium Partitioning, Transport, and Uptake

The total Cd content, A , in a soil volume is given by:

$$A = c(\theta + \gamma k_{\text{soil}}^{\text{Cd}} c^{m-1}) \quad [1]$$

where c is the concentration of Cd^{2+} in solution, θ is the volumetric water content, γ is the soil bulk density, and $k_{\text{soil}}^{\text{Cd}}$ and m are the coefficient and exponent of the Freundlich adsorption isotherm, respectively. Transport of Cd is calculated with the convection–dispersion equation with a sink term for crop offtake, U_c , and a source term, I_a , for Cd inputs:

$$\frac{\partial A}{\partial t} = \frac{\partial}{\partial z} \left(D \theta \frac{\partial c}{\partial z} - qc \right) - U_c + I_a \quad [2]$$

where z is depth, t is time, q is the Darcy flow rate, and D is the dispersion coefficient. We assume that all Cd inputs are incorporated evenly by plowing within the plow depth, so that the source function, I_a , is given by:

$$I_a = \left(\frac{A_s + A_f + A_d}{z_{\text{pl}}} \right) ; z \leq z_{\text{pl}} \quad [3]$$

$$I_a = 0 ; z > z_{\text{pl}}$$

where A_s , A_f , and A_d are the areal application rates of Cd supplied by sludge, commercial fertilizer, and deposition, respectively, and z_{pl} is the plow depth. The sink term for crop offtake, U_c , in any given soil layer is calculated from the concentration of Cd in solution using Michaelis–Menten type kinetics (Murali and Aylmore, 1983):

$$U_c = c_{\text{p(max)}} B_{\text{ag}} (1 - f_{\text{ag}}) \left(\frac{c}{K_p + c} \right) \frac{r_f}{\Delta z} \quad [4]$$

where $c_{\text{p(max)}}$ is the maximum plant Cd concentration, B_{ag} is the annual aboveground biomass production, f_{ag} is the fraction of the aboveground biomass that is not harvested, K_p is the soil concentration at which the plant concentration reaches half the maximum value, and r_f is the fraction of roots in the layer of thickness Δz .

Following van der Zee and van Riemsdijk (1987), Streck and Richter (1997a), and Elzinga et al. (1999), we express the Freundlich coefficient in an extended form, which allows explicit consideration of the effects of soil components of

differing reactivity and soil pH on Cd sorption. In this study, we modify and generalize these existing approaches by recognizing that the various solid constituents found in sludge and in sludge-amended soils may have widely varying sorption affinity for Cd (Li et al., 2001). Thus, it is well known that the characteristics of sludge itself can strongly influence the extent of sorption and bioavailability of Cd in soil (e.g., Jing and Logan, 1992; Sloan et al., 1997), and that topsoil physical and chemical characteristics can be significantly altered by repeated sludge additions in the long term (e.g., Bergkvist et al., 2003). We define six adsorbing mass fractions (kg kg^{-1} soil), each with their own sorption partition coefficient: inorganic material derived from sludge (k_{ms}), fresh organic matter derived from crop residues (k_{oc}) and sludge (k_{os}), humified organic matter derived from crop residues (k_{hc}) and sludge (k_{hs}), and one indigenous inorganic fraction (k_{mi}). The Freundlich coefficient is then given by:

$$k_{\text{soil}}^{\text{Cd}} = \sum_i f_i k_i \left(\frac{10^{\text{pH}}}{10^{\text{pH}_{\text{ref}}}} \right) \quad [5]$$

where f_i is the mass fraction of a sorbing component, k_i is the partition coefficient for that component, a is an exponent accounting for the effect of soil pH on Cd sorption (Streck and Richter, 1997a; Elzinga et al., 1999), and pH_{ref} is a reference soil pH.

To solve Eq. [2], a zero flux surface boundary condition is adopted, since Cd input to the soil is treated as a source term in the model. The bottom boundary condition is given as a convective outflow (i.e., zero dispersion).

The model described by Eq. [1] through [5] requires a sub-model to calculate mass balances of the adsorbing organic and mineral components, as influenced by inputs from crop residues and sludge. This is described in the following sections.

Carbon Inputs and Turnover

The mass balances of young (C_y) and humified (C_h) organic carbon are given by:

$$\frac{dC_y}{dt} = I - rk_y C_y \quad [6]$$

$$\frac{dC_h}{dt} = hrk_y C_y - rk_h C_h \quad [7]$$

where I is the input rate of fresh organic material, r is a soil climate factor, k_y and k_h are first-order decomposition rate constants for fresh and humified organic matter, respectively, and h is a humification constant reflecting the efficiency of microbial respiration. The supply of fresh carbon from sludge is assumed to be evenly distributed throughout the plowed depth, and is given as the product of the annual sludge dry matter application rate I_s , the organic fraction of the sludge f_o , and the carbon fraction of sludge organic matter. The carbon supply from crop residues comprises two components: aboveground residues that are plowed into the soil and root decomposition. The former term is given as the product of the yearly aboveground biomass production, B_{ag} , the residue fraction of this biomass that is plowed in, f_{ag} , and the carbon content of the biomass. Root carbon input to a soil layer is calculated as the product of the annual root biomass production (in turn assumed to be a fixed fraction of the aboveground biomass), the fraction of roots in the layer, and the carbon content of the root biomass. The subsoil root distribution is given by an exponential function (Gerwitz and Page, 1974):

$$r_i = \xi \left(\frac{\Delta z}{z_{\max}} \right) \exp \left[-\xi \left(\frac{z_{\text{mid}}}{z_{\max}} \right) \right] \quad [8]$$

where ξ is a root distribution parameter, z_{mid} is the midpoint depth of the layer, and z_{\max} is the root depth.

The mass fractions of the carbon pools f_i and the total organic carbon content f_{oc} in a soil layer are given by:

$$f_i = \frac{C_i}{\gamma} \quad [9]$$

$$f_{\text{oc}} = \sum_i f_i \quad [10]$$

where C_i refers to the carbon content in one of the four pools (fresh and humified material derived from sludge or crop residues).

Sludge-Derived Inorganic Matter

Sewage sludge commonly contains 40 to 60% inorganic matter, including silicates, phosphates, carbonates, and manganese oxide, some of which may show high adsorption affinity for heavy metals such as Cd (Li et al., 2001). Therefore, in addition to the organic carbon pools described above, the model also calculates the mass balance of sludge-derived inorganic matter M_s :

$$\frac{dM_s}{dt} = (1 - f_o)I_s \quad [11]$$

The mass fraction of sludge-derived inorganic matter in soil is then defined as:

$$f_{\text{ms}} = \frac{M_s}{\gamma} \quad [12]$$

Topsoil Thickness and Soil Physical Properties

An empirical "S"-shaped function (van Genuchten, 1980) is used to describe the relationship between soil bulk density and organic carbon content in the plowed horizon:

$$\gamma = \gamma_{\min} + (\gamma_{\max} - \gamma_{\min}) [1 + (\alpha_{\text{vg}} 10^{100f_{\text{oc}}})^{n_{\text{vg}}}]^{\left(\frac{1}{n_{\text{vg}}} - 1\right)} \quad [13]$$

where γ_{\min} and γ_{\max} are the minimum and maximum bulk densities and α_{vg} and n_{vg} are shape parameters. The layer thickness is then given by:

$$\Delta z = \left[\frac{(\gamma_0 \Delta z_0) + \Delta M}{\gamma} \right] \quad [14]$$

where Δz_0 and γ_0 are the initial layer thickness and bulk density, respectively, and ΔM denotes the change in total mass (organic plus inorganic) in the soil layer since the start of the simulation. For the sake of simplicity, any changes in bulk density and (numerical) layer thicknesses due to changes in organic matter content below the topsoil are ignored. Once a year, on the day of plowing, all mass components are redistributed evenly throughout the plowed depth. As layer thicknesses increase with continued carbon inputs, this results in a gradual apparent "translocation" of incorporated material into the subsoil below plow depth.

Numerical Solution and Verification

Equation [2] is solved using an explicit finite difference solution, corrected for numerical dispersion and with a fixed time step (maximum one day). An iterative procedure is used to solve for the unknown solution concentration, c , in the case

of nonlinear adsorption ($m \neq 1$). The numerical solution was verified by comparing simulation results to analytical solutions of the convection-dispersion equation (van Genuchten and Alves, 1982; van der Zee, 1990).

Application to the Ultuna Long-Term Soil Fertility Experiment

The model described above has been tested against data obtained from a field trial at SLU, Ultuna (Uppsala), Sweden, ongoing since 1956 (Kirchmann et al., 1994). Measurements were made in 1997 in plots from a control treatment (calcium nitrate fertilizer) and a treatment that had received sewage sludge biennially for 41 years. The soil is a well-structured clay loam, slightly calcareous in the subsoil, with topsoil pH values of 6.31 and 4.98 in the control and sludged plots, respectively. The available data include vertical distributions of Cd (both HNO_3 and EDTA-extractable) and soil organic carbon, crop Cd concentrations (Bergkvist et al., 2003), and results of batch adsorption experiments performed to investigate the influence of soil properties and sludge applications on Cd adsorption (Bergkvist, 2003). Measurements were also made of soil Cd concentrations and soil physical and chemical properties in samples collected before the start of the experiment in 1956. The parameterization of the model shown in Tables 1 and 2 is based on a combination of these site-specific measurements (Bergkvist, 2003; Bergkvist et al., 2003), literature estimates, and to a limited extent, model calibration. The parameterization procedure that was adopted is now briefly described.

Annual records of sludge additions of organic matter and annual aboveground biomass production were available (Kirchmann et al., 1994; unpublished data). The inorganic fraction in the sludge constituted, on average, 41% of the total dry mass (Table 1). We assumed that carbon represented 50% of the sludge organic fraction, giving an estimate of the total carbon supply from sludge during the 41-year experimental period of 7.3 kg m^{-2} .

Parameters related to carbon turnover were mostly derived from a previous comparison of the ICBM carbon turnover model with the measured changes in topsoil organic carbon content in the control and sludge-amended plots. Details of the procedures followed can be found in Andrén and Kätterer (1997). Table 1 shows that the humification fraction for organic matter derived from sludge was much larger than from crop residues (0.47 vs. 0.12), and this is largely attributed to the fact that the sludge is already partly humified due to the treatment process. The parameters γ_{\min} , γ_{\max} , α_{vg} , and n_{vg} describing the relationship between soil bulk density and organic carbon content (Table 1) were calculated from the known values of these variables in the topsoil of the sludge-amended plots. The root distribution factor (Table 1) was derived by fitting Eq. [8] to measured barley root distributions at a nearby site on the same soil type (Andrén et al., 1993).

Cadmium concentrations in the sludge actually applied to the plots were not measured, but estimates of the annual Cd loadings were reconstructed from measurements of Cd concentrations in the source sludge material at the Uppsala municipal sewage treatment works (Bergkvist et al., 2003). Only EDTA-extractable Cd is modeled. This is because no evidence was found of any transfer of Cd from EDTA- to non-EDTA-extractable forms during the 41-year period, based on the known EDTA-extractable fractions in the topsoil of the sludge-amended plots in 1956 (approximately 56%) and in 1997 (approximately 63%), and in the sludge in 1997 (approximately 77%) (Bergkvist et al., 2003). The EDTA-extractable fraction is considered to be a good representation of "bioavail-

Table 1. Parameter values for carbon turnover.

Parameter	Value	Comments; source
Carbon supply by roots, fraction of aboveground biomass production	0.48	site-specific; Andrén et al. (1993) and Andrén and Kätterer (1997)
Carbon fraction in root biomass	0.45	assumed
Carbon fraction in aboveground biomass	0.5	assumed
Organic fraction in sludge (f_o)	0.59	site-specific; Kirchmann et al. (1994)
Fraction of crop residues (aboveground) (f_{ag})	0.05	site-specific; Andrén and Kätterer (1997)
Root depth, m	1.0	assumed
Root distribution factor (ξ)	5.0	site-specific; Andrén et al. (1993)
Humification fraction (h) for crop residues	0.12	site-specific; Andrén and Kätterer (1997)
Humification fraction (h) for sludge	0.47	site-specific; Andrén and Kätterer (1997)
Climatic factor (r)	1.0	site-specific; Andrén and Kätterer (1997)
Decomposition rate constant (k_d), 1/year	0.8	site-specific; Andrén and Kätterer (1997)
Oxidation rate constant (k_h), 1/year	0.006	site-specific; Andrén and Kätterer (1997)
Maximum bulk density, kg m ⁻³	1530	site-specific; Bergkvist et al. (2003)
Minimum bulk density, kg m ⁻³	770	site-specific; Bergkvist et al. (2003)
Shape parameter in the bulk density–organic carbon relationship (α_{vg})	0.0312	site-specific; Bergkvist et al. (2003)
Shape parameter in the bulk density–organic carbon relationship (n_{vg})	1.4064	site-specific; Bergkvist et al. (2003)

able” Cd (Roca and Pomares, 1991), and includes water-soluble and exchangeably sorbed Cd and Cd bound to organic matter and inorganic precipitates (Sims and Kline, 1991). The initial subsoil Cd concentrations were set equal to the EDTA-extractable Cd contents measured in the control plots in 1997, since the measurements from samples stored since 1956 seemed unreliable.

The generalized isotherm used in the model allows for the separate contributions of six soil constituents to Cd adsorption. However, despite batch experiments performed on soil samples taken at the site (Bergkvist, 2003), we were not able to parameterize the adsorption affinity of each constituent. The adsorption coefficients of the two fresh organic components were not measured, and have therefore been set to zero. This is perhaps reasonable since the mass fractions of these components will usually be relatively small. The batch experiments reported by Bergkvist (2003) showed that adsorption of Cd followed a linear isotherm ($m = 1$, Table 2) within the measured concentration range (0.14–35.7 $\mu\text{g L}^{-1}$) and was not statistically different between the sludge-amended and control plots, despite 90% larger organic carbon contents in the sludged plots. It was therefore concluded that the sludge-derived organic and inorganic material did not cause any in-

crease in the overall sorption capacity of the soil. Thus, assuming that inorganic and organic fractions of sludge have equal sorption affinity for Cd (Li et al., 2001), k_{hs} and k_{ms} were set to 175 L kg^{-1} , equivalent to the original K_d value of the topsoil measured at the in situ pH value (calculated using the methodology described below).

For a large number of natural soils, Elzinga et al. (1999) showed that besides pH, soil cation exchange capacity (CEC) was the most important soil property controlling Cd adsorption in batch studies, while Breeuwsma et al. (1986) explained most of the variability in CEC ($\text{mmol}_c \text{kg}^{-1}$) measured at pH 6.5 by the mass fractions of clay, f_{clay} , and organic carbon:

$$\text{CEC} = 2725f_{oc} + 500f_{\text{clay}} \quad [15]$$

Unfortunately, Bergkvist (2003) was not able to distinguish between the contributions of soil organic carbon and clay content to sorption of Cd in the control treatment plots, perhaps because these two variables were strongly correlated. Therefore, we made use of the data in Breeuwsma et al. (1986) to estimate k_{hc} and k_{mi} , the partitioning coefficients for indigenous soil inorganic matter and humified organic matter derived from crop residues (Table 2), assuming that adsorption

Table 2. Parameter values for Cd fate and mobility.

Parameter	Value	Comments; source
Freundlich exponent (m)	1.0	site-specific; Bergkvist (2003)
Reference pH (pH_{ref})	6.5	assumed
Exponent for pH sorption effect (a)	0.497	site-specific; Bergkvist (2003)
Partition coefficient for humified sludge carbon (k_{hs}), $\text{m}^3 \text{kg}^{-1}$	0.175	site-specific; Bergkvist (2003)
Partition coefficient for humified crop residue carbon (k_{hc}), $\text{m}^3 \text{kg}^{-1}$	3.875	literature/site-specific; Breeuwsma et al. (1986), Bergkvist (2003)
Partition coefficient for fresh sludge carbon (k_{os}), $\text{m}^3 \text{kg}^{-1}$	0.0	assumed
Partition coefficient for fresh crop residue carbon (k_{oc}), $\text{m}^3 \text{kg}^{-1}$	0.0	assumed
Partition coefficient for inorganic sludge residue (k_{ms}), $\text{m}^3 \text{kg}^{-1}$	0.175	site-specific; Bergkvist (2003)
Partition coefficient for indigenous soil mineral fraction (k_{mi}), $\text{m}^3 \text{kg}^{-1}$	0.711	literature/site-specific; Breeuwsma et al. (1986), Bergkvist (2003)
Adsorbing indigenous mineral fraction (f_{mi})	clay content	site-specific; Bergkvist (2003)
Half-maximum soil concentration for Cd uptake (K_p), mg m^{-3}	120	assumed (large value ensures that first-order uptake is simulated)
Maximum plant concentration [$c_{p(\text{max})}$], mg kg^{-1}	8.8	calibrated
Fraction of EDTA-extractable Cd in sludge	0.77	site-specific; Bergkvist et al. (2003)
Dispersion coefficient (D), $\text{m}^2 \text{d}^{-1}$	3.6×10^{-5}	estimated from 175 mm annual recharge and a dispersivity of 3 cm
Annual recharge (q), m yr^{-1}	0.175	site-specific average precipitation of 575 mm yr^{-1} minus estimated evaporation of 400 mm yr^{-1}
Soil water content (θ), $\text{m}^3 \text{m}^{-3}$	0.4	site-specific, profile-averaged water content at field capacity; Johansson et al. (1985)

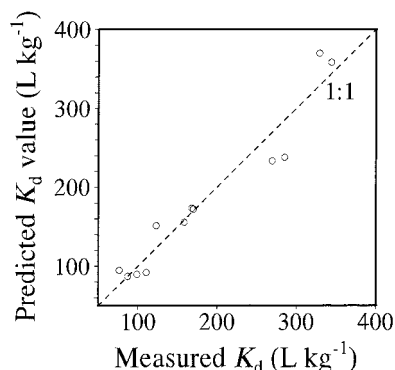


Fig. 2. Comparison of measured adsorption K_d values for the Ultuna control plots with values predicted from Eq. [16] where $\beta = 1.422 \text{ L mmol}_c^{-1}$, $\text{pH}_{\text{ref}} = 6.5$, and $a = 0.497$. The r^2 value of the regression is 0.93.

is linearly dependent on CEC, with a proportionality constant β (L mmol_c^{-1}). Neglecting k_{oc} , k_{os} , k_{hs} , and k_{ms} , substituting $\beta \times \text{CEC}$ for the remaining two adsorbing constituents k_{hc} and k_{mi} in Eq. [5], re-arranging, and taking logarithms, gives:

$$\log\left(\frac{K_d}{\text{CEC}}\right) = \log\beta + a(\text{pH} - \text{pH}_{\text{ref}}) \quad [16]$$

where CEC is the cation exchange capacity ($\text{mmol}_c \text{ kg}^{-1}$) measured on samples from the control plots and K_d (L kg^{-1}) is the linear adsorption coefficient at different soil pH values derived from batch experiments on soil samples taken from the control plots (Bergkvist, 2003). By setting pH_{ref} to 6.5 (Breeuwsma et al., 1986), a linear regression of $\log(K_d/\text{CEC})$ against pH minus 6.5 gave a as the slope (0.497; Table 2) and β as the antilog of the intercept ($1.422 \text{ L mmol}_c^{-1}$). Finally, the two partitioning coefficients k_{hc} and k_{mi} were estimated from β , making use of Eq. [15] and [16] (Table 2). Figure 2 shows that this approach gives acceptable predictions of the measured K_d values. Changes of topsoil pH were simulated making use of measured pH values at the start of the experiment in 1956 and in 1997 (Bergkvist et al., 2003) and assuming that pH changes were proportional to the input of sludge dry matter.

The available data were insufficient to allow independent estimation of the two parameters, $c_{p(\text{max})}$ and K_p , controlling the Michaelis–Menten uptake kinetics described by Eq. [4]. However, we considered that soil concentrations inducing a “plateau effect” in plant concentrations were unlikely to have been reached in this study, so that Eq. [4] was reduced to the first-order uptake response often found in experiments (Eriksson, 1989; Chang et al., 1997; McGrath et al., 2000) by setting K_p to an arbitrary large value (120 mg m^{-3} ; Table 2) compared with the expected soil concentrations, and treating $c_{p(\text{max})}$ as an empirical parameter, calibrating it against the total offtake of Cd from the sludge-amended plots. This was estimated to be 4.2 mg m^{-2} based on harvest yields and measurements of Cd concentration in grain and straw, sampled occasionally during the experimental period (Bergkvist et al., 2003).

Sensitivity Analysis

The simulation of the sludge-amended plots at Ultuna described above served as the basis for a simple sensitivity analysis of the 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 (Janssen et al., 1992). Since too little

Table 3. Parameters and ranges tested in the sensitivity analysis.

Parameter	Range
Carbon supply by roots, fraction of aboveground biomass production	0.4–0.6
Carbon content in aboveground biomass	0.4–0.6
Carbon content in root biomass	0.4–0.6
Fraction of crop residues (aboveground) (f_{ag})	0.01–0.1
Root distribution factor (ξ)	4.5–5.5
Root depth (z_{max}), m	0.4–0.8
Humification fraction (h) for crop residues	0.08–0.16
Decomposition rate constant (k_d), 1/year	0.6–1.0
Oxidation rate constant (k_h), 1/year	0.004–0.008
Freundlich exponent (m)	0.8–1.0
Exponent for pH sorption effect (a)	0.3–0.5
Partition coefficient for humified sludge carbon (k_{hs}), $\text{m}^3 \text{ kg}^{-1}$	0.1–10.0
Partition coefficient for sludge inorganic fraction (k_{ms}), $\text{m}^3 \text{ kg}^{-1}$	0.1–10.0
Maximum plant Cd concentration [$c_{p(\text{max})}$], mg kg^{-1}	0.5–10.0
Half-maximum soil Cd concentration (K_p), $\mu\text{g L}^{-1}$	1.0–20.0
Inorganic fraction in sludge ($1 - f_o$)	0.3–0.7
Soil water content, $\text{m}^3 \text{ m}^{-3}$	0.1–0.5
Soil water recharge, m yr^{-1}	0.1–0.3
Dispersivity, cm	1.0–6.0
Cd concentration in sludge, mg kg^{-1}	1–39

is known concerning the kinds of distributions to be expected for most of the parameters (i.e., normal or log-normal), we decided in this initial analysis to assume uniform distributions for all parameters. In total, 150 Monte Carlo simulations were run, with the parameters assumed to be uncorrelated with one another. Table 3 shows the parameters and ranges tested. Two target output quantities were investigated, the total crop offtake and the amount of Cd displaced below 28 cm depth after 30 years. Multiple linear regression between input parameters (independent variables) and output target variables (dependent variable) was used to identify the most important sources of variation (i.e., the most sensitive parameters; Janssen et al., 1992). Both partial rank correlation coefficients and standardized and normalized rank regression coefficients were calculated.

Scenario Simulations

Scenario simulations, in the form of a “one-at-a-time” sensitivity analysis, were performed to demonstrate the conditions under which sludge “protection” and sludge “time bombs” can be expected. Values of three critical system parameters (the Cd concentration in sludge, the ratio of sludge K_d to initial soil K_d , and the proportion of sludge K_d contributed by the inorganic sludge material) were varied around baseline values to show their influence on plant Cd concentrations.

The basic scenario was defined by a number of fixed parameters: we simulated a sludge dry matter loading of $1 \text{ kg m}^{-2} \text{ yr}^{-1}$ for 50 years. The organic fraction of the sludge, f_o , was assumed to be 0.5. Any effects of sludge application on crop production, and thus carbon turnover, were ignored, while the soil pH was assumed to be maintained at a constant value. A soil profile 80 cm deep was simulated, with a ground water recharge of 100 mm yr^{-1} . The initial Cd contents in the soil profile were set to relatively small values: 30 and 20 mg m^{-3} in the topsoil and subsoil, respectively. Linear adsorption of Cd was assumed, with an initial soil K_d value of 100 L kg^{-1} . For the sake of simplicity, first-order crop uptake was ensured by the parameterization shown in Table 2. To further ease interpretation of the simulation results, we decided to parameterize the model such that the mass balance for carbon from crop residues remained at steady state. This is because we are primarily interested in the effects of sludge-derived carbon on Cd uptake. It follows from Eq. [6] and [7] that if the carbon pools derived from crop residues are to remain at steady state,

then the initial store of carbon $C_{\text{tot}(\text{ini})}$ (equal to $C_y + C_h$) in each layer should be given by (Andrén and Kätterer, 1997):

$$C_{\text{tot}(\text{ini})} = \frac{I}{r} \left(\frac{1}{k_y} + \frac{h}{k_h} \right) \quad [17]$$

while the sizes of the fresh organic carbon and humus pools are given by their ratio:

$$\frac{C_y}{C_h} = \frac{k_h}{k_y} \quad [18]$$

The initial organic carbon content in the topsoil was set to 1%, while k_y , h , and k_h were set to the values given in Table 1. Subsoil organic carbon contents were calculated in proportion to the topsoil values, based on the known root fractions in each layer. Equations [17] and [18] were then used to determine the value of I/r that maintains steady state and the sizes of the initial carbon pools for each layer in the soil profile.

The tested ranges for the three system parameters investigated were (i) a sludge K_d value between 1 and 100 times the original K_d value of the soil, (ii) the inorganic fraction of sludge contributing between 0 and 100% of the sludge K_d , and (iii) sludge Cd concentration varying from 2 to 39 mg kg⁻¹ (the maximum value allowed for "exceptional quality" sludge under USEPA Part 503 regulations). In the case of (ii) above, the 50-year simulation was extended for an additional 100 years following cessation of sludge applications to illustrate the potential effects of organic matter decomposition on Cd bioavailability. Each parameter was varied "one-at-a-time" through these ranges, while the remaining two parameters were fixed at "baseline" values defined as follows: a ratio of sludge K_d to initial soil K_d of 100, an equal contribution of sludge inorganic and organic material to sludge K_d (Li et al., 2001), which implies an identical sorption affinity since $f_o = 0.5$, and a Cd concentration in sludge of 15 mg kg⁻¹. For the assumed dry matter loading of 1 kg m⁻² yr⁻¹, this gave a Cd loading of 150 g ha⁻¹ yr⁻¹, equal to the EU limit allowed under Directive 86/278/EEC.

RESULTS AND DISCUSSION

Ultuna Long-Term Experiment

Figure 3 shows a comparison of simulated and measured organic carbon contents in the soil profile in 1997. After 41 years of continuous sludge applications, the topsoil organic carbon content had increased by approximately 90% and this was well matched by the model. Andrén and Kätterer (1997) showed that the ICBM model could also accurately predict the time-course of changes in topsoil organic carbon content throughout the experiment. In the subsoil, organic carbon contents actually decreased during the experiment (Fig. 3), and this has been attributed to the installation of field drainage at the start of the experiment in 1956 (Bergkvist et al., 2003). The model, which was parameterized making use of only topsoil data, also accurately predicted this decrease in subsoil organic carbon contents.

Figure 4 shows a comparison of measured and simulated changes in EDTA-extractable Cd contents in the soil profile between 1956 and 1997. Very little leaching of sludge-derived Cd into the subsoil had occurred during the experiment. The mass balance reported by Bergkvist et al. (2003) suggested that only 7% of the applied Cd had moved into the upper subsoil and that

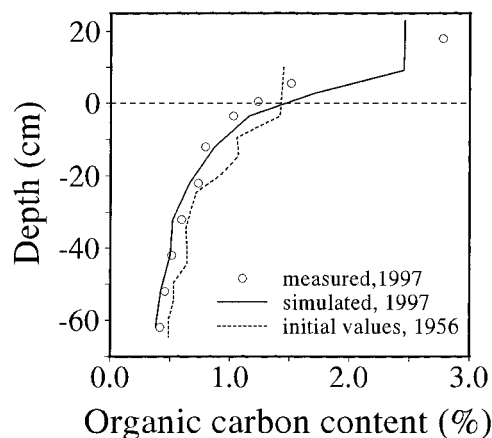


Fig. 3. Comparison of measured and simulated organic carbon content in sludge-amended soil, Ultuna, 1956-1997. The zero depth in the soil profile (marked by a dashed line) is given as the base of the topsoil in 1956, since the topsoil thickness changes with time.

no leaching out of the investigated profile had occurred. The model also predicts insignificant leaching, but does seem to overestimate the movement of Cd into the upper subsoil (Fig. 4). There are two possible explanations for this discrepancy. The first is a recirculation of Cd driven by uptake from the subsoil and subsequent remineralization of crop residues in the topsoil. The second explanation is the effects of non-equilibrium macropore flow on the solute displacement pattern in this structured clay loam soil, whereby a small fraction of the Cd is transported into the deeper subsoil (Fig. 4), while the bulk of the Cd in the matrix moves more slowly, being physically "protected" from the bypass water flow (Larsson and Jarvis, 1999). Neither of these processes is included in the model, but both appear to be significant at this site. It is difficult to explain the small increases in Cd contents observed in the deeper subsoil of the sludged plots without invoking macropore transport. Bergkvist et al. (2003) also showed that Cd contents had decreased in the upper subsoil of the control treatment during the experiment, which is strong

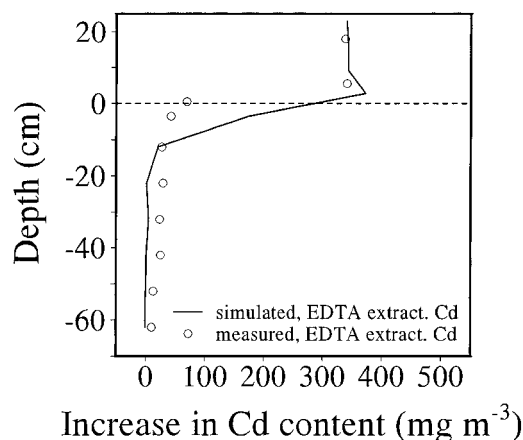


Fig. 4. Comparison of measured and simulated increases in ethylenediaminetetraacetic acid (EDTA)-extractable Cd contents in sludge-amended soil, Ultuna, 1956-1997. The zero depth (marked by a dashed line) is given as the base of the topsoil in 1956, since the topsoil thickness changes with time.

Table 4. Partial rank correlation coefficients (PRCCs) between model input parameters and total simulated leaching below a depth of 28 cm, including all variables significant at $p < 0.05$.

Parameter	PRCC
Cd concentration in sludge	0.963***
Soil water recharge	0.885***
Dispersivity	0.700***
Partition coefficient for sludge inorganic fraction (k_{ms})	-0.653***
Freundlich exponent (m)	-0.403***
Exponent for pH sorption effect (a)	0.375***
Partition coefficient for sludge organic fraction (k_{hs})	-0.371***
Humification constant (h)	-0.255**
Inorganic fraction in sludge ($1 - f_o$)	-0.254**
Half-maximum soil Cd concentration (K_p)	0.222*

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

*** Significant at the 0.001 probability level.

evidence for the recirculation of Cd by subsoil root uptake and remineralization of crop residues. Johnsson et al. (2002) showed, using the isotope Cd^{109} , that 15 to 45% of the Cd uptake by wheat plants grown in lysimeters originated from the subsoil.

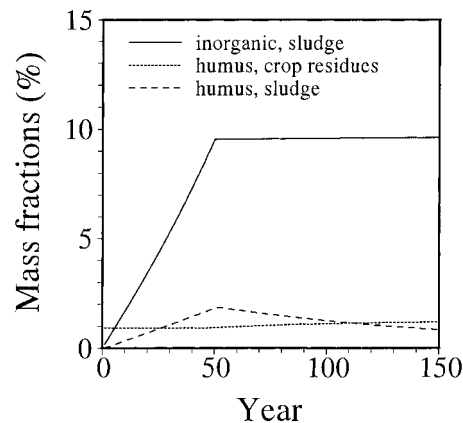
Monte Carlo Sensitivity Analysis

Tables 4 and 5 show the results of the Monte Carlo sensitivity analysis for crop offtake and leaching, respectively. Only those input parameters demonstrating a significant correlation with the selected target output quantities are shown. The overall r^2 values for the multiple linear regression on ranked variables were 91 and 94% for offtake and leaching, respectively, values that are considered sufficiently large to allow unequivocal interpretation of the results (Janssen et al., 1992). Identical results were obtained for partial rank correlation coefficients and standardized and normalized rank regression coefficients, and so only the former are presented in Tables 4 and 5. The results show that a number of key parameters appear critical for both offtake and leaching. These include the Cd concentration in the applied sludge, which is also equivalent to the Cd loading since sludge rates were kept constant, and two parameters related to adsorption, namely the exponent a controlling the effects of pH on adsorption and the partition coefficient for sludge-derived inorganic material k_{ms} . The partition coefficient for the organic fraction of the sludge k_{hs} is less sensitive (although still significant for leaching) and this can be attributed to the continuous oxidation of the supplied organic matter, while the inorganic fraction simply accumulates. For the same reason, an increasing proportion of inorganic matter in the sludge ($1 - f_o$) significantly reduces both leaching and offtake. Even though the sludge-derived inorganic frac-

Table 5. Partial rank correlation coefficients (PRCCs) between model input parameters and total crop offtake of Cd, including all variables significant at $p < 0.05$.

Parameter	PRCC
Maximum plant Cd concentration [$c_{p(max)}$]	0.927***
Half-maximum soil Cd concentration (K_p)	-0.863***
Cd concentration in sludge	0.819***
Inorganic fraction in sludge ($1 - f_o$)	-0.401***
Partition coefficient for sludge inorganic fraction (k_{ms})	-0.327***
Exponent for pH sorption effect (a)	0.284***

*** Significant at the 0.001 probability level.

**Fig. 5. Simulated mass fractions in the topsoil.**

tion appears most critical, the importance of also accounting for soil organic carbon turnover is illustrated by the fact that the humification constant, h , was also a significant parameter for leaching. The Freundlich exponent, m , exerted a significant control on leaching, but apparently not on crop offtake. Not surprisingly, leaching was also highly sensitive to soil water recharge and the dispersivity (Table 4), while offtake was very strongly influenced by the two Michaelis–Menten parameters, $c_{p(max)}$ and K_p .

Scenario Simulations

Figure 5 shows the changes in topsoil mass fractions simulated by the model. It illustrates the fact that although the organic fraction was set to 50% of the sludge dry matter, the inorganic fraction dominates in the soil, reaching nearly 10% of the topsoil mass after 50 years of sludge application. As noted earlier, this is because the inorganic material simply accumulates, while the added organic matter is subject to decomposition. The total mass of organic carbon derived from crop residues remains at steady state, although slight changes in the mass fraction are simulated, since the total soil mass changes. In contrast, the sludge-derived organic carbon at first increases to approximately 2% after 50 years, and then decreases again. However, the total soil organic carbon content has not returned to its initial value, even 100 years after cessation of applications (Fig. 5).

Figures 6, 7, and 8 show the results of the scenario simulations for the three system properties tested. The ratio of sludge K_d to initial soil K_d exerts a strong influence on the time course of simulated plant concentrations (Fig. 6). If identical K_d values are assumed in soil and sludge, then the K_d value of the soil–sludge mixture remains unchanged during the period of sludge amendment (and even after cessation of applications). As already noted above, this kind of response was indicated by the results of the batch experiments reported by Bergkvist (2003) for the Ultuna experiment. In this case, simulated soil solution concentrations continuously increase as a result of the Cd loadings to the soil (see Eq. [1]). Assuming a constant sludge input rate and first-order plant uptake, this results in a continuous and approximately linear increase of simulated plant concen-

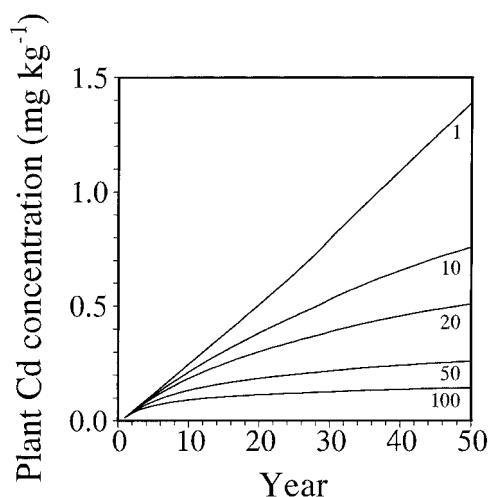


Fig. 6. Simulated plant Cd concentrations. Figures on the curves denote the ratio of sludge K_d to the initial soil K_d value.

tration (Fig. 6). As the sludge K_d value increases above the initial value found in the soil, then increasing degrees of sludge “protection” are simulated and plant Cd concentrations asymptotically approach a “plateau.” Although no sludge “protection” was found at Ultuna, ratios of sludge K_d to initial soil K_d of at least 20 have been reported (Li et al., 2001).

Similar responses are found with respect to the Cd concentration in the applied sludge (Fig. 7). With very “clean” sludge (or strictly, low loadings of Cd), a strong “plateau” is induced in plant concentrations. In the extreme case, amendment with biosolids of very low Cd concentration could in principle reduce soil solution and plant concentrations. As indicated by Eq. [1], this will happen when the metal loading rate is proportionally smaller than the increase in adsorption capacity resulting from addition of sludge. Figure 7 shows that conversely, as Cd concentrations in the sludge increase, the plateau effect becomes weaker.

Figure 8 shows the effects of varying the proportion of the sludge adsorption capacity contributed by the inorganic components for a highly adsorptive sludge ($K_d = 100$ times the initial soil value). Here, the simulations have been extended to 150 years to show the effects of organic matter decomposition during the 100-year period following cessation of applications. It shows that a sludge time bomb can only be simulated if the organic fraction in the sludge contributes most of the adsorptive capacity. In the case where the inorganic components are assumed to be entirely unreactive, the plant concentration continues to increase beyond the cessation of sludge application and is still increasing after 150 years, since organic carbon contents have still not reverted to the initial value (Fig. 5). However, even a modest contribution of sludge inorganic components to the sludge adsorptive capacity (e.g., 25%) eliminates the “time-bomb” (Fig. 8). It can also be noted that simulation of a convincing “time-bomb” also requires a high degree of initial sludge protection (i.e., a large ratio between sludge and soil K_d values). Although not shown here, in the case without any sludge “protection” at all

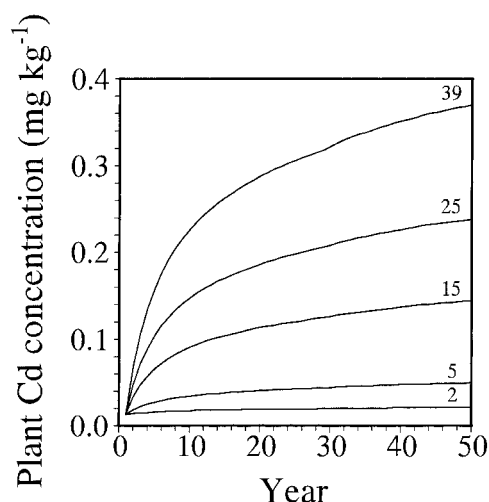


Fig. 7. Simulated plant Cd concentrations. Figures on the curves denote the Cd concentration in sludge in mg kg^{-1} .

(i.e., K_d in sludge = initial K_d in soil), soil and plant Cd concentrations will also immediately “plateau” on cessation of sludge application, and will in the long term decrease slowly as loss terms (uptake, leaching) exhaust the Cd supply. This demonstrates that a plateau observed in plant concentrations following cessation of sludge applications (Hyun et al., 1998) is not, in itself, evidence that any “protection” from sludge inorganic components has occurred.

CONCLUSIONS

The model presented here is designed to help improve understanding of the long-term effects of soil amendments such as sludge on leaching and plant uptake of trace metals from soil. It is sufficiently comprehensive to allow application to a wide range of agroenvironmental situations, but at the same time is simple and flexible enough for potential use in risk assessment. The results of a Monte Carlo sensitivity analysis show that the Cd load, together with the partition coefficient for sludge

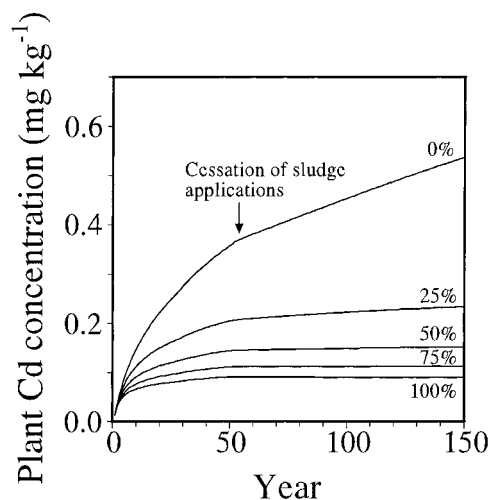


Fig. 8. Simulated plant Cd concentrations. Figures on the curves denote the proportion of sludge K_d contributed by the inorganic components. The arrow denotes cessation of sludge applications.

inorganic matter, the proportion of sludge dry matter comprising inorganic material, and the pH effect on adsorption appeared to be critical in controlling both plant uptake and leaching. Application of the model to the long-term sludge experiment at Ultuna suggests that two processes not currently included in the model, namely recirculation of Cd by root uptake and remineralization of crop residues, and macropore transport, might also be important to consider in the future.

This study has, in itself, not resolved the controversy concerning long-term effects of sludge on trace metal uptake by plants. However, the scenario simulations presented here have identified the critical factors that influence the outcome, namely the Cd concentration in the sludge, the adsorption capacity of the sludge in relation to the original adsorption capacity of the soil, and the proportion of the sludge adsorption capacity contributed by the inorganic fraction. It is quite likely that these key properties will vary from site to site and between sludge and biosolids materials from different sources. Therefore, it is not surprising that experimental evidence is conflicting or equivocal regarding the likelihood of sludge "protection" and sludge "time bombs" (McBride, 1995; Chang et al., 1997; Hamon et al., 1999). We conclude that it would be of great importance to invest much more experimental effort in determining the adsorption properties of sewage sludges applied on arable land and also the adsorption properties of the resulting soil-sludge mixtures (Bergkvist, 2003), including the characterization of adsorption affinities of organic and inorganic components (e.g., Li et al., 2001). Thus, no general statements can yet be made concerning the validity of either the sludge "time bomb" or the sludge "protection" hypotheses. Depending on the prevailing conditions either may occur, or neither (Bergkvist, 2003). Indeed, the "constant partitioning" model (McBride, 1995), which would arise if the K_d values of sludge and soil are similar (Bergkvist, 2003), also has important implications for regulatory procedures that, in principle, rely on sludge "protection" (e.g., USEPA Part 503).

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