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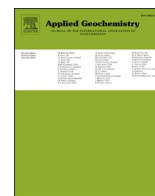
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# Cadmium accumulation in soil resulting from application of biogas digestate and wood ash – Mass balance modelling

Jon Petter Gustafsson<sup>a,\*</sup>, Marie-Cécile Affholder<sup>a,b</sup>, A. Sigrun Dahlin<sup>a,c</sup>

<sup>a</sup> Department of Soil and Environment, Swedish University of Agricultural Sciences, Box 7014, 750 07, Uppsala, Sweden

<sup>b</sup> Bordeaux University, INRAE, UMR BIOGECO INRAE 1202, Batiment B2, Allée Geoffroy St. Hilaire, CS50023, 33615, Pessac, France

<sup>c</sup> Department of Crop Production Ecology, Swedish University of Agricultural Sciences, Box 7043, 750 07, Uppsala, Sweden

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## ABSTRACT

This study investigates the impact of substituting conventional NPK fertilizer with wood ash and biogas digestates at an agricultural field site in southwest Sweden. A three-year field experiment, comprising a crop rotation cycle of spring wheat, winter wheat, and oats, was conducted. The obtained results were employed to establish a dynamic mass balance model for the A horizon of the soil at the site. The Cd leaching term in the model was estimated using the Stockholm Humic model (SHM), which was recalibrated to accommodate low Cd concentrations by incorporating Cd complexation to thiol sites. The findings indicate that treatments receiving NPK fertilizer and biogas digestates experienced a net Cd loss, whereas treatments with wood ash demonstrated net Cd accumulation, attributed to its higher Cd content. Harvest yields were highest in the NPK treatment, and lower in two of the wood ash treatments, likely due to lower nitrogen additions in the latter. Cd offtake mirrored this trend, with the highest values in the NPK treatments and the lowest in the wood ash treatments, potentially also influenced by a pH difference of 0.2 units during the last year of the experiment. Geochemical modelling showed that Cd leaching is highly dependent on pH and that geochemically active soil Cd in the A horizon may have doubled between 1950 and 2002, due to elevated atmospheric deposition and fertilizer Cd during this period. Despite significant reductions in anthropogenic Cd fluxes since 2002, soil Cd has only decreased by 4%, showing the slow response of the soil pool to flux changes. Attaining a new steady-state after alterations in input fluxes will require hundreds of years. These results carry significance for determining sustainable application rates for recycled nutrient sources and underscore the crucial role of pH-dependent Cd sorption for Cd leaching.

## 1. Introduction

Cadmium is an element that causes toxicity to humans even at low levels (Nordberg et al., 2022). During the 1900s, the levels of cadmium in agricultural soils worldwide increased significantly (Andersson, 1992; McLaughlin et al., 2021). In part, this was due to the occurrence of cadmium in the apatite ores used for mineral P fertilizer production, and because of the rapid rise in the use of mineral fertilizer after the Second World War. However, a substantial part of the increase was also due to atmospheric deposition of Cd from a wide range of anthropogenic sources, such as fossil fuel combustion, iron and steel production, cement production etc (Alloway and Steinhilber, 1999). As a result of the increase in soil Cd to levels close to those thought to cause human toxicity, several measures were introduced to decrease Cd pollution, including the introduction of improved technologies for combustion and

metal processing, as well as regulations concerning the Cd content in fertilizers. Based on the principle of zero-net accumulation, which states that the soil Cd content should not increase over time, the EU introduced the current EU-wide maximum Cd level in mineral fertilizer in 2018, set at 137 mg Cd (kg P)<sup>-1</sup>. However, some countries, such as Sweden, are allowed to keep a lower guideline; for Sweden, it is 100 mg Cd (kg P)<sup>-1</sup>.

In 2022 and 2023 the cost of N and P fertilizers increased due to international conflicts (Brownlie et al., 2023). Moreover, as much of the N fertilizer is fossil fuel-based, and P is a finite resource, the current use of fertilizers is not sustainable (e.g., Cordell and Neset, 2014). Hence, there is an interest in using recycled nutrient sources such as agricultural by-products, sewage sludge, biogas digestates, wood ash, beachcast seaweed etc., to replace part of the mineral fertilizer being applied. However, a problem is their often high cadmium (Cd) content. Historically, applied sewage sludge was regarded as a Cd input source of

\* Corresponding author.

E-mail address: [jon-petter.gustafsson@slu.se](mailto:jon-petter.gustafsson@slu.se) (J.P. Gustafsson).

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concern. For example, results from a long-term field trial at Uppsala, Sweden (Bergkvist et al., 2003) showed a much increased crop uptake as well as soil Cd content due to sewage sludge application. More recent field trials show smaller or even non-significant effects of sewage sludge on soil and crop Cd contents (e.g. Börjesson et al., 2014), reflecting upstream work to reduce Cd input into wastewater. For other recycled nutrient sources, the effects on Cd in soils and crops have been less studied. The properties and Cd content of biogas digestate vary substantially due to differences in feedstock (e.g. agricultural residues, household waste, etc.) and production methods (Dragicevic et al., 2018; Salomon et al., 2022). Similarly, the Cd content in beachcast is variable and strongly dependent on location, species composition, and season (Franzén et al., 2019). As concerns wood ash, it often contains elevated Cd levels, but it also contributes to a high pH, which, in turn, limits Cd uptake. Moreover, the bioavailability of Cd in ash is not well known (see e.g. Johansen et al., 2021). Consequently, there is a need to increase knowledge on the extent to which recycled nutrient sources can be used without causing a net accumulation of Cd in soils.

To estimate to what extent nutrient inputs through fertilizers or recycled nutrient sources causes net Cd accumulation in the soil, early Scandinavian works employed mass balances, in which inputs and outputs of Cd were quantified, although often using crude assumptions (Hovmand, 1984; Andersson, 1992; Tjell and Christensen, 1992). Over time, the mass balance methods have been developed further and used as a basis for the work to develop EU-wide guidelines, and the methods to calculate the various mass balance terms have been widely discussed (e.g. Six and Smolders, 2014; Römkens et al., 2018; Sterckeman et al., 2018; McLaughlin et al., 2021). Most mass balance methods consider inputs to, and outputs from, the A horizon of agricultural soil, i.e. in the topsoil down to the plow depth (usually at 25 cm). Although crops to some extent are able to take up Cd also from the subsoil (Imseng et al., 2018) this pathway is usually neglected in models because of the uncertainties involved in quantifying it. Another potentially important Cd flux to and from the subsoil is physical soil mixing, but again, its effect on the overall Cd balance is very poorly known.

Leaching is considered the most uncertain term of the soil Cd balance due to the complexities involved in determining it (e.g., Römkens et al., 2018; McLaughlin et al., 2021). Although Cd leaching can, in principle, be determined in the field, accurate measurements are complicated and expensive to carry out, and different methods may provide varying results (e.g., Bergen et al., 2023). Instead, empirical partition-relations, based on laboratory experiments in the literature, have often been used (Degryse et al., 2003, 2009; de Vries et al., 2011, 2013; Six and Smolders, 2014). However, the validity of such relations has sometimes been questioned based on results obtained in the field, as Cd leaching has been found to be overestimated (Römkens et al., 2018; Sterckeman et al., 2018).

Perhaps surprisingly, organic complexation models such as WHAM 7 (Tipping et al., 2011), NICA-Donnan (Kinniburgh et al., 1999), and the Stockholm Humic Model (SHM) (Gustafsson, 2001) have so far not been widely used to estimate Cd leaching for mass balance studies. There may be different reasons for this, although a potential problem of using these models is the fact that they were calibrated for data sets containing rather high amounts of Cd. For example, organically bound Cd ranged from 0.51 to 2160 mmol Cd kg<sup>-1</sup> OM (organic matter) in the data used to calibrate the SHM, based on data compiled by Milne et al. (2003). By contrast, the amount of organically bound Cd in typical agricultural soils is somewhere between 0.01 and 0.05 mmol Cd kg<sup>-1</sup> OM. Some results suggest a deviation between model-generated and measured dissolved Cd at naturally low soil Cd concentrations. For instance, WHAM-Model VI overestimated dissolved Cd in British upland soils by a factor of 2.8, on average (Tipping et al., 2003). Similarly, although WHAM 7 in general provided very good fits for dissolved Cd for a number of data sets from the literature, the model almost always overestimated dissolved Cd at very low (i.e., naturally occurring) solution concentrations (<10<sup>-7.5</sup> mol L<sup>-1</sup>) (Peng et al., 2018). By contrast, the NICA-Donnan model often

underestimated dissolved Cd at very low solution concentrations (Weng et al., 2001). These discrepancies may arise from the distinct approaches these models take in handling the heterogeneous binding-site affinity of organic matter (OM). Specifically, WHAM 7 and SHM assume site heterogeneity for 99.1% of the sites, while the NICA-Donnan model applies heterogeneity to all 100% of the sites. Given that organically bound Cd commonly occupies less than 0.01% of the OM sites in soils, these differences may result in contrasting model behavior.

In this study, we use previously unpublished laboratory data to recalibrate the SHM for use at low natural levels of soil Cd. We show that a low concentration of a high-affinity component of the solid organic matter pool, likely thiol-type groups, needs to be considered in the SHM to properly model Cd solid-solution partitioning in agricultural soils. The revised SHM is then integrated into a dynamic mass balance model, which is calibrated for a field study at the Rådde experimental site, south-west Sweden, and applied for scenarios to investigate whether the replacement of mineral fertilizer by biogas digestate or biofuel ash will lead to net accumulation of soil Cd. The ultimate aim is to provide additional evidence as to whether recycled nutrient sources could be a sustainable alternative, from a Cd point of view, to mineral fertilizers.

## 2. Materials and methods

### 2.1. Experimental

A field experiment was carried out at the Rådde experimental farm, W Sweden (57°36'N, 13°15'E) between 2018 and 2020 using spring wheat (*Triticum aestivum* L. cv. Alderon), winter wheat (cv. Ellvis) and oats (*Avena sativa* L. cv. Cilla) as test crops. The mean annual temperature and precipitation over the period 1981–2010 were 6.5 °C and 997 mm, respectively, while the mean annual discharge was 529 mm (SMHI, 2022). The soil was a sandy loam with 56% sand, 35% silt, and 8% clay. The pH(H<sub>2</sub>O) was 5.7 and organic C was 3.1%. Total Cd, as determined by aqua regia digestion, was 0.16 mg kg<sup>-1</sup>, while 0.1 M HNO<sub>3</sub>-extractable Cd was 0.121 mg kg<sup>-1</sup> (for additional soil chemical characteristics, see Table 1).

Two biogas digestates were used in the experiment, one from the city of Uppsala and the other from the city of Linköping. Both had been produced in biogas digesters, from mainly source-separated household waste (food waste) with additions of wastes from the food industry and commercial kitchens. Wood ash was taken from the district heating plant of Mora municipality, Sweden, fueled with waste from a sawmill, forest residues and energy wood. Prior to use, it had been hardened by breaking it into fragments smaller than approximately 10 mm and leaving it open to the atmosphere for a period of 2 months, occasionally moistening and stirring to encourage hardening. The composition of the ash and the digestates is shown in Table S2.

**Table 1**  
Soil properties of the Rådde A horizon.

pH(H <sub>2</sub> O)	5.74	Cd – Aqua regia (mg kg <sup>-1</sup> ) <sup>b</sup>	0.16
pH (1 mM CaCl <sub>2</sub> )	5.25	Cd – 0.1 M HNO <sub>3</sub> (mg kg <sup>-1</sup> ) <sup>c</sup>	0.121
Organic C (%)	3.1	Cd – 0.001 M CaCl <sub>2</sub> (μg kg <sup>-1</sup> ) <sup>d</sup>	2.89
Sand (%)	51	Oxalate-Al (mmol kg <sup>-1</sup> ) <sup>e</sup>	186
Silt (%)	41	Oxalate-Fe (mmol kg <sup>-1</sup> )	95
Clay (%)	8	Oxalate-P (mmol kg <sup>-1</sup> )	20.7
Exchangeable Ca <sup>2+</sup> (cmol <sub>c</sub> kg <sup>-1</sup> ) <sup>a</sup>	6.27	P <sub>Al</sub> (mmol kg <sup>-1</sup> ) <sup>f</sup>	1.1
Exchangeable Mg <sup>2+</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	0.46		
Exchangeable Na <sup>+</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	0.03		
Exchangeable K <sup>+</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	0.15		

<sup>a</sup> Extracted by 0.1 M BaCl<sub>2</sub> (Hendershot and Duquette, 1986).

<sup>b</sup> ISO 11466.

<sup>c</sup> Gustafsson and Kleja (2005).

<sup>d</sup> Soil-solution ratio 1:10, shaking for 2 h.

<sup>e</sup> Van Reeuwijk (2002).

<sup>f</sup> Egnér et al. (1960).

**Table 2**  
Parameter values used in the HD-MINTEQ model.

Parameter	Value	Source/method of acquisition
Soil layer thickness (m)	0.25	Plow depth given by farm
Bulk density ( $\text{kg m}^{-3}$ )	1150	Determined in this study
Annual discharge ( $\text{L m}^{-2}$ )	529	SMHI (2022)
Soil moisture ( $\text{m}^3 \text{m}^{-3}$ )	0.2	Estimated
Winter temperature ( $^{\circ}\text{C}$ )	3	Estimated
Summer temperature ( $^{\circ}\text{C}$ )	14	Estimated
DOC ( $\text{mg L}^{-1}$ )	10	Estimated (see text)
$\text{CO}_2$ pressure (atm)	0.005	Estimated
Dissolved $\text{NO}_3^-$ ( $\mu\text{mol L}^{-1}$ )	0.5	Estimated
Dissolved $\text{NH}_4^+$ ( $\mu\text{mol L}^{-1}$ )	0.5	Estimated
Dissolved $\text{Mg}^{2+}$ ( $\mu\text{mol L}^{-1}$ )	10	Estimated
Dissolved $\text{Na}^+$ ( $\mu\text{mol L}^{-1}$ )	80	Estimated
Dissolved $\text{K}^+$ ( $\mu\text{mol L}^{-1}$ )	20	Estimated
Dissolved $\text{Cl}^-$ ( $\mu\text{mol L}^{-1}$ )	80	Estimated
Dissolved $\text{SO}_4^{2-}$ ( $\mu\text{mol L}^{-1}$ )	20	Estimated
$\text{Cd}_{\text{lime}}$ ( $\text{g ha}^{-1} \text{yr}^{-1}$ )	0.6 every 10th year <sup>a</sup>	Liming intensity and frequency from farm, Cd content from supplier
$\text{Cd}_{\text{dep}}$ ( $\text{g ha}^{-1} \text{yr}^{-1}$ )	0.2 <sup>b</sup>	Ilyin et al. (2012), Klemetz et al. (2023)
$\text{Cd}_{\text{fert}}$ ( $\text{g ha}^{-1} \text{yr}^{-1}$ )	Fig. S1	See text

<sup>a</sup> Prior to 1951, liming was assumed to take place every 20th year. Liming was assumed not to take place in plots subject to ash application.

<sup>b</sup> Set at this value from 2008 and onwards. Prior to 2008,  $\text{Cd}_{\text{dep}}$  was estimated from historical deposition estimates (see text).

Between 2008 and 2017, a five-year crop rotation scheme was used at the site. For the experimental plots, a six-year scheme was envisaged, beginning in 2018. This consisted of: spring wheat (year 1), winter wheat (sown in year 1, harvested in year 2), oats (year 3), and ley (years 4–6). The years with ley were not part of the 3-year experiment, but are included in typical crop rotations at the site. The field experiment was laid out according to a randomized block design using plots 30 m<sup>2</sup> in size (10 × 3 m). There were seven different treatments and four replicates, causing the total number of plots to be 28. The seven treatments were: (1) No PK, (2) NPK, (3) Wood ash, (4) Uppsala digestate, (5) Linköping digestate, (6) Wood ash + Uppsala digestate, (7) Wood ash + Linköping digestate, where the NPK treatment represents the current management at the site. The ash and digestates were applied once a year at different rates, depending on the recommended P application rate for the respective crop at the anticipated yield level in the area. For the wood ash the application rates were 1.04 ton ha<sup>-1</sup> in 2018, 1.36 ton ha<sup>-1</sup> in 2019, and 0.37 ton ha<sup>-1</sup> in 2020 (dry weight basis). Similarly, for the digestates the rates ranged from 0.13 ton ha<sup>-1</sup> (Uppsala ash 2020) to 1.36 ton ha<sup>-1</sup> (Linköping ash 2019). In addition, the NPK plots received annual doses of NPK or PK fertilizer (NPK 21-3-10, Yara, and PK 11–21, Yara, respectively). For all plots, the mean annual total P additions ranged from 0 (No PK) to 14 kg ha<sup>-1</sup> (PK and the combined ash + digestate treatments). In addition to the treatments, all plots received a topdressing of NS fertilizer (NS Axan 27/4, Yara; annual average 43 kg N ha<sup>-1</sup>) at straw elongation.

During harvest, the crops were cut 10 cm above the soil. Straw and grain were separated, and their elemental composition was determined by ALS Laboratories after microwave digestion with  $\text{HNO}_3/\text{H}_2\text{O}_2$ . At the site, the harvested straw was used for other purposes and not returned to the soil in any form. The winter wheat, which was sown in 2018, was strongly affected by winter stress – for this reason, the harvest in 2019 was unusually low.

The treatment effect of the digestates, ash and NPK on crop data (yield, pH, and Cd concentration in grain and straw) and soil pH was evaluated by analysis of variance using the JMP Pro 17.0.0 (SAS Institute Inc., Cary, NC, USA). Where significant effects were indicated, pairwise comparisons of means were made using Tukey's HSD test.

## 2.2. Scenarios and mass balance calculations

In the current manuscript, the following soil Cd mass balance will be used:

$$\text{Cd}_{\text{dep}} + \text{Cd}_{\text{fert}} + \text{Cd}_{\text{lime}} = \text{Cd}_{\text{harv}} + \text{Cd}_{\text{leach}} + \Delta\text{Cd}_{\text{ads}} \quad (1)$$

where all terms are expressed in  $\text{g Cd ha}^{-1} \text{yr}^{-1}$  and  $\text{Cd}_{\text{dep}}$  is the Cd input from atmospheric deposition,  $\text{Cd}_{\text{fert}}$  the input from fertilizer and recycled nutrient sources,  $\text{Cd}_{\text{lime}}$  the input from liming agents, while  $\text{Cd}_{\text{harv}}$  is the net amount of Cd harvested and removed from the system,  $\text{Cd}_{\text{leach}}$  the amount of Cd leached from the A horizon, and  $\Delta\text{Cd}_{\text{ads}}$  the change in soil Cd due to adsorption or desorption over one year. In Equation (1), some very minor terms have been neglected, such as the amounts of Cd in seed and in pesticides, given their minimal contribution to the mass balance. Additionally, crops in Sweden are rarely irrigated (Zajac et al., 2022). Thus, Cd input through irrigation water does not need to be considered. Four different scenarios were used for the mass balance calculations. The scenarios were based on four of the treatments as follows: 'NPK' (continuation of mineral fertilizer use), 'Digestate only' (replacement of mineral fertilizer with Linköping digestate), 'Ash only' (replacement with ash), and 'Ash + digestate' (replacement with both ash and Linköping digestate). The two treatments with Uppsala digestate were not used since this digestate was similar in composition to the Linköping digestate, and applied in smaller amounts. Also, the 'No PK' treatment was not considered as this management scenario is atypical for managed agricultural soils.

To conduct the mass balance calculations, several parameters had to be estimated, utilizing site-specific data where possible (see Table 2). For instance, DOC (dissolved organic carbon) was set to 10 mg L<sup>-1</sup>, which closely approximates the median value of subsurface drainage from various agricultural fields in Sweden (Norberg et al., 2022). The different terms in the Cd mass balance (Equation (1)) were estimated as follows:

First, the present-day atmospheric deposition of Cd ( $\text{Cd}_{\text{dep}}$ ) at the Rådde site was estimated to 0.2 g ha<sup>-1</sup>, based on monitoring data from the Swedish west coast (Klemetz et al., 2023) and the modelled geographical distribution (Ilyin et al., 2012). Estimates of the historical variation of  $\text{Cd}_{\text{dep}}$  were based on data and suggestions by Jones et al. (1987), Andersson (1992) and Rühling and Tyler (2001). However, these estimates are somewhat speculative, particularly for the pre-war period. The present-day estimate of 0.2 g ha<sup>-1</sup> was also used for the long-term scenarios of the future Cd mass balance.

The input through mineral fertilizer ( $\text{Cd}_{\text{fert}}$ ) during the experimental period was based on Cd concentrations given by the manufacturer, which was 8.3 mg Cd (kg P)<sup>-1</sup> for both types of fertilizer. However, due to the Ukraine war and the resulting decreased supply of low-Cd fertilizer, the Cd content increased to 12 mg Cd (kg P)<sup>-1</sup> for NPK 21-3-10 and to 30 mg Cd (kg P)<sup>-1</sup> for PK 11–21 from 2022, which is still lower than the Swedish limit of 100 mg Cd (kg P)<sup>-1</sup>. In the 'NPK' scenarios, these more recent values have been applied for the time period from 2022 and onwards, resulting in an average input of 0.54 g ha<sup>-1</sup>. Between the 1930s and 1949, the farm was not used for crop production but was a horse farm. Hence, there was no mineral fertilizer used, and Cd offtake was very low. For  $\text{Cd}_{\text{fert}}$  between 1950 and 2018, estimates were based on data on fertilization supplied by the farm, and on historical data on the Cd content of mineral fertilizer (Andersson, 1992). For the preceding period,  $\text{Cd}_{\text{fert}}$  was probably low as manure recycled within the farm was the dominating fertilizer agent, hence the input was set to 0 g ha<sup>-1</sup> in 1850, rising to 0.2 g ha<sup>-1</sup> in 1949. For the other scenarios, the Cd input was based on median values of the annual inputs between 2018 and 2020, which were 1.3 g ha<sup>-1</sup> for 'Ash only', 0.25 g ha<sup>-1</sup> for 'Digestate only', and 1.55 g ha<sup>-1</sup> for 'Ash + digestate'.

The input from liming agents ( $\text{Cd}_{\text{lime}}$ ) was calculated using the current liming frequency (3 ton ha<sup>-1</sup> of limestone once every 10 years), and the Cd concentration given by the supplier. Prior to 1950 it was assumed

that liming was made only every 20 years, due to the lower yields. The Cd inputs over time for the four scenarios are summarized in Fig. S1.

For the experimental period (2018–2020), Cd offtake,  $Cd_{harv}$ , was obtained from measured Cd concentrations of grain and straw, in combination with the weight of the harvested biomass. Based on this, soil-crop transfer factors (TF) could be calculated. Similar to other studies (Six and Smolders, 2014; Sterckeman et al., 2018) these were defined as:

$$TF = \frac{Cd_{crop}}{Cd_{soil}} \quad (2)$$

Where  $Cd_{crop}$  is the weight-averaged concentration of the straw and grain, while  $Cd_{soil}$  is the 0.1 M  $HNO_3$ -extractable Cd concentration, both with the unit  $mg\ kg^{-1}$ . The resulting TFs were 0.38 for winter wheat and 0.3 for oats. Because of the poor winter wheat crop, the TF for winter wheat was not calculated based on the harvested crop but assumed equal to the one for spring wheat in 2018 (=0.38). For ley, Cd concentrations were not determined in the study, and for the purpose of modelling we assumed a transfer factor of 0.3. Further, in line with the grain yield results (Fig. 3) we assumed that replacement of NPK fertilizer led to a decrease in crop yield (resulting in lower Cd offtake), with a factor 0.9 for the 'Digestate' and 'Ash + digestate' scenarios and 0.8 for the 'Ash only' scenario. In fact, the difference in crop yield in 2020 was even greater (Fig. 3), but here we assume that in the future, beyond the time scale of the current field experiment, the same N and K application rates would be used for all treatments (the crop yield in 2020 was likely affected by differences in N application, c.f. the Results and Discussion section).

The leached Cd,  $Cd_{leach}$ , was calculated from geochemical modelling with the SHM (see next section) assuming the water volume that leaves the A horizon was equal to the annual discharge of the area, i.e., 529 mm (SMHI, 2022). This value was set constant in the scenarios. The pH value, which was an input parameter to the geochemical model, was assumed to vary during each liming cycle. Immediately after liming, the pH was set to 6.2. Then it decreased linearly until 5.6 at the time of the next liming event. However, for the 'Ash only' and 'Ash + digestate' scenario, the alkalizing effect of the ash was assumed to be sufficient to increase the pH to 6.2 over a period of 10 years, after which the pH was maintained at pH 6.2 without any lime being used.

Finally, the change in the storage of adsorbed Cd in each time step,  $\Delta Cd_{ads}$ , was calculated by difference from the other terms of the mass balance in Equation (1).

The mass balance modelling calculations were carried out using the HD-MINTEQ software (Löfgren et al., 2017), which is a scenario tool that was previously used to simulate long-term changes in forest soil chemistry (McGivney et al., 2019). The inputs to the model are summarized in Table 2.

### 2.3. Recalibration of the Stockholm Humic Model

The SHM and its application to soil has been described in earlier publications (Gustafsson, 2001; Gustafsson and Kleja, 2005; Linde et al., 2007; Gustafsson et al., 2011; Tiberger et al., 2018). In brief, the SHM is a discrete-site/electrostatic model in which the humic acid (HA) and fulvic acid (FA) are assumed to have eight proton-binding sites with

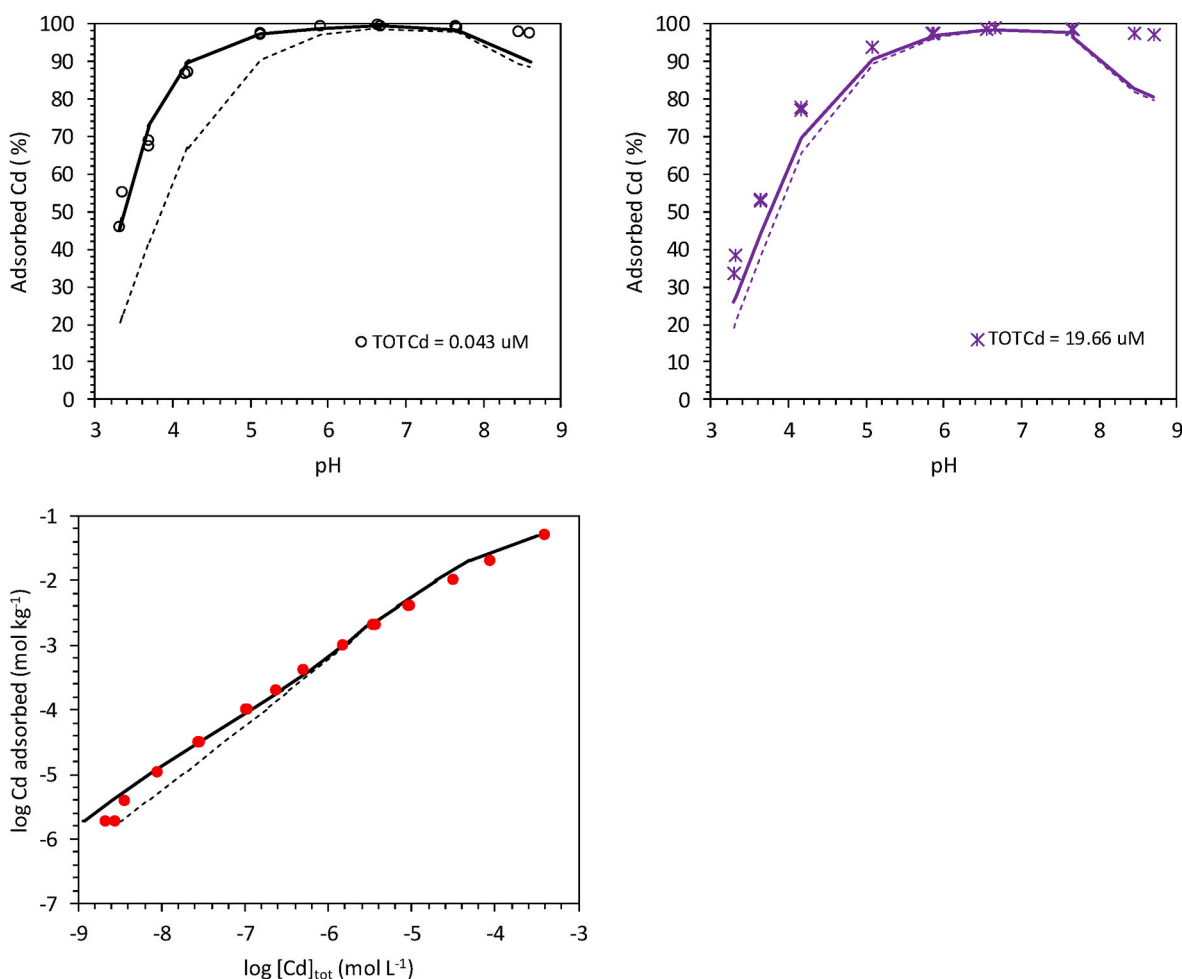


Fig. 1. Adsorbed Cd against pH (upper row) or total dissolved Cd (lower row) for the Lund A soil in suspensions with a 0.01 M  $NaNO_3$  background. Dashed lines are Stockholm Humic Model (SHM) fits using the generic parameters without high-affinity thiol sites, whereas the solid lines include the effect of high-affinity thiol sites.

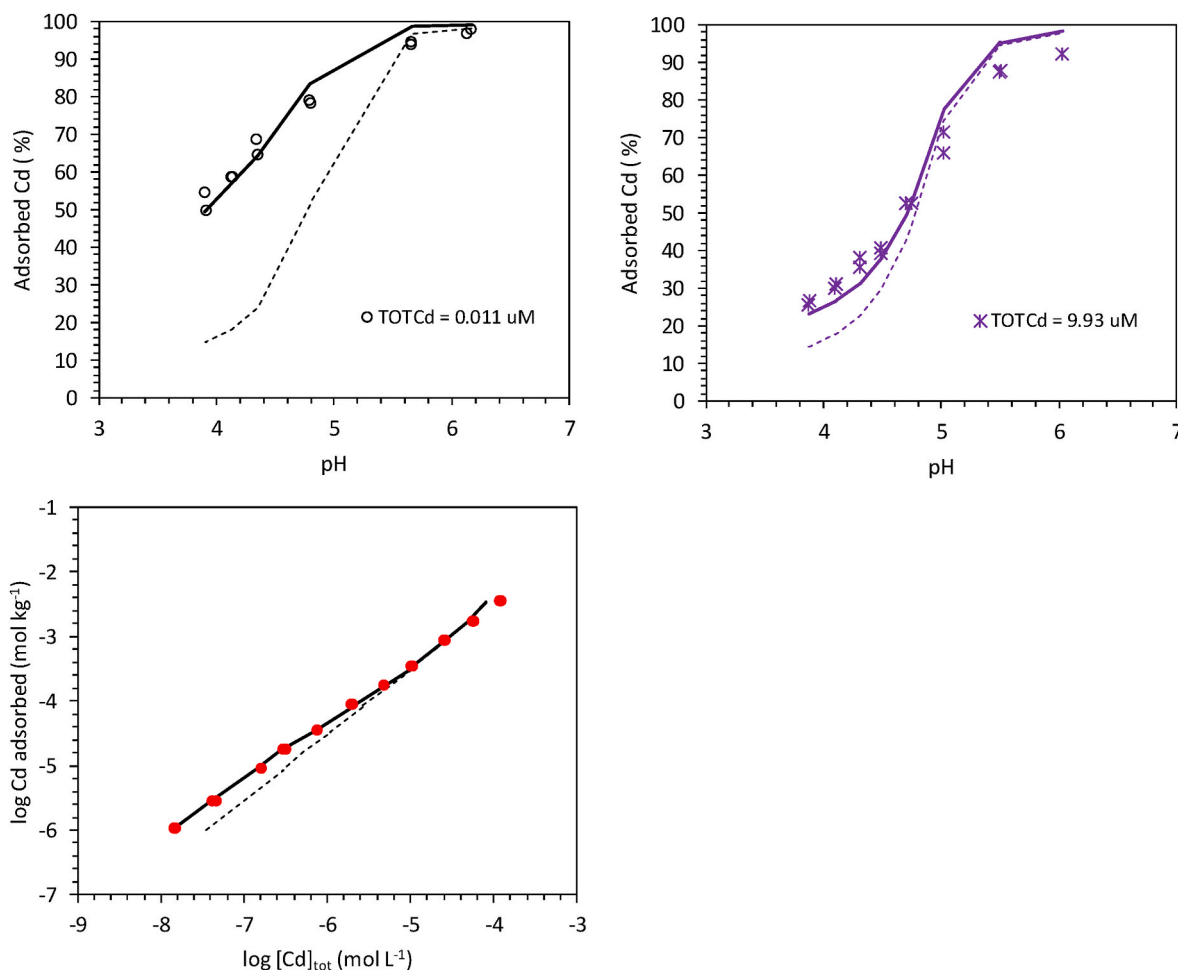


Fig. 2. Adsorbed Cd against pH (upper row) or total dissolved Cd (lower row) for the Romfartuna Bhs soil in suspensions with a 0.01 M NaNO<sub>3</sub> background. Dashed lines are Stockholm Humic Model (SHM) fits using the generic parameters without high-affinity thiol sites, whereas the solid lines include the effect of high-affinity thiol sites, using log  $K_{CdSH} = -0.85$ .

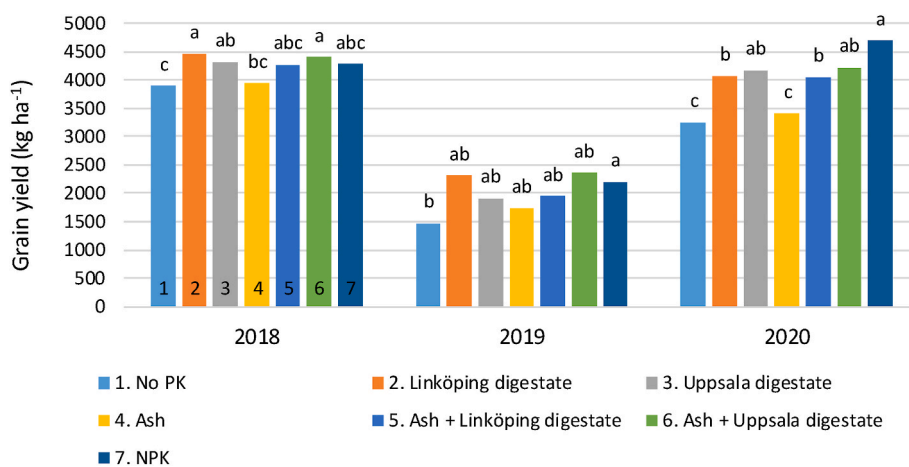


Fig. 3. Mean grain yields in the 7 different treatments of the Rådde field experiment. Bars not sharing a letter differ significantly within each year ( $n = 4$ ).

different acid-base characteristics. Metals are allowed to bind to HA or FA by forming monodentate and bidentate complexes, or by electrostatic attractions. Generic Cd-binding parameters for the SHM were calculated using datasets given by Milne et al. (2003). Equilibrium constants for the complexation of Cd<sup>2+</sup> and major cations are given in Table S1. In earlier studies for Pb<sup>2+</sup>, it was found that the generic parameters underestimated Pb<sup>2+</sup> binding to SOM (solid-phase organic matter) at low Pb

concentrations in soils, probably because of the importance of a high-affinity site within this fraction (Gustafsson et al., 2011; Tiberg et al., 2018). Hence an extra site was defined having a concentration equal to 0.01 % of the total organic C content of the soil, and by adding two reactions associated with it, one acid-base reaction, and one Pb complexation reaction (Tiberg et al., 2018). In the current paper we use a similar approach to describe Cd binding.

For this we use two studies of Cd binding data to soils, in which the solubility of Cd as a function of pH was determined in batch experiments (Jansson, 2002; Gustafsson et al., 2003). General properties of the five soils being studied are shown in Table S3. In the study of Gustafsson et al. (2003), 2 g of field-moist soil was suspended in 30 mL of solutions with variable composition, with 0.01 M NaNO<sub>3</sub> as background. In one set of samples, 10 or 20 μmol L<sup>-1</sup> of Cd<sup>2+</sup> as Cd(NO<sub>3</sub>)<sub>2</sub> (for Romfartuna Bhs and Lund A, respectively) was added together with varying additions of HNO<sub>3</sub> and NaOH to produce a range of pH values. In a second set of samples, conditions were identical as in the first set, except that no Cd was added to the suspensions. In the third set of samples, different concentrations of Cd<sup>2+</sup> ranging from 0.06 to 2500 μmol L<sup>-1</sup> of Cd<sup>2+</sup> were added, with final equilibrium pH values ranging from 5.8 to 6.6 (Lund A) and from 4.7 to 4.9 (Romfartuna Bhs). The samples were shaken for 7 d at 8 °C. Further details on procedures are given in Gustafsson et al. (2003).

In the study of Jansson (2002), 1 g of field-moist soil was suspended in 30 mL of solutions to which 0.1 M NaNO<sub>3</sub> had been added as a background electrolyte. In addition, varying additions of HNO<sub>3</sub> and NaOH were made to produce a range of pH values, and no Cd was added. The samples were shaken for 4 d at 12 °C. Further details on analytical procedures are provided by Jansson (2002). Four soils were used by Jansson (2002); however, only three of them could be used as the fourth one (Kövlinge A) contained calcite, which would interfere with the model calibration method used, c.f. below.

To set up the SHM, we assumed that the geochemically active Cd<sup>2+</sup> (i.e. the sum of adsorbed and dissolved Cd) was adequately represented by extraction by 0.016 M EDTA, buffered at pH 4.65 ("AAAc-EDTA"; Lakanen and Erviö, 1971), which was determined in both studies (Table S3). Further, geochemically active Ca<sup>2+</sup> and Mg<sup>2+</sup>, Na<sup>+</sup> and K<sup>+</sup> were obtained from extraction with 0.1 M BaCl<sub>2</sub> (Gustafsson et al., 2003) or 1 M NH<sub>4</sub>NO<sub>3</sub> (Jansson, 2002). The effect of Fe<sup>3+</sup> competition was accounted for by assuming equilibrium with ferrihydrite, using a log \*K<sub>s</sub> of 3.8 at 8 °C and 3.5 at 12 °C. For Al<sup>3+</sup>, a value of 'geochemically active' Al was constrained by observed values of dissolved Al at low pH (Gustafsson et al., 2003) allowing Al(OH)<sub>3</sub>(s) precipitation at high pH, using a log \*K<sub>s</sub> of 9.4 at 8 °C and log \*K<sub>s</sub> of 9.1 at 12 °C. Measured values of DOC (dissolved organic carbon) were used in the modelling, assuming all of it to be fulvic acid that was active with respect to cation binding.

The fraction of active soil organic matter (ASOM) was set at 0.55 for Romfartuna Bhs (Tiberg et al., 2018; Table S3). For the other soils, ASOM was estimated using a step-by-step procedure. In the first step, the fraction of active soil organic matter (ASOM) of each soil was optimized by applying the model to the batch experiment data and calculating the pH from the mass and charge balances, assuming organic matter to be the only important phase that buffered against acid and base additions. For the Eckerud A, Östuna A, and Nättraby A soils, this procedure failed, probably because of their relatively high clay content leading to additional cation exchange. For this reason, an ion-exchange site was added to the model until a satisfactory fit was obtained. Cation binding onto the ion exchange sites were considered using the Gaines-Thomas equation, c.f. Gustafsson et al. (2003). For all soils, it was assumed that ASOM consisted of 54.5% humic acid and 45.5% fulvic acid (Linde et al., 2007).

After the above model calibration, the model was run with the pH fixed at the measured value to provide predictions of dissolved Cd in the batch experiment suspensions. As seen in the next section, dissolved Cd was consistently overestimated. A possible reason is that thiol sites, which are known to complex Cd in plant materials (Pons et al., 2021) and also often believed to be important for soil sorption at low Cd concentrations (e.g., Karlsson et al., 2007), are not specifically considered in the 'standard' version of SHM. In an effort to improve the model, we added the following two reactions to occur on a subset of "high-affinity" thiol sites comprising 0.002 % of the total soil organic C content:



As these reactions take place in the same electrostatic field as SOM, the equilibrium constants contain electrostatic correction terms (Gustafsson and Kleja, 2005). The modelling calculations were done using Visual MINTEQ, version 4.0 (Gustafsson, 2023). To consider inorganic acid-base and complexation reactions, the standard thermodynamic database of Visual MINTEQ was used.

### 3. Results and Discussion

#### 3.1. Uptake of Cd in the field experiment

The harvested grain yields were impacted by the different treatments, despite the short time frame (3 years) of the experiment. In the third year (2020), yields were highest in the NPK treatment, and significantly lower in two of the treatments with wood ash (Fig. 3). The 'Ash only' treatment and the 'No PK' treatment exhibited yields less than 80% of those in the NPK treatment, likely reflecting the lower total application of N, as these treatments only received N through topdressing. Winter stress affecting the winter wheat resulted in yields less than half of those expected in 2019 (Table 3).

Concerning Cd uptake by crops, Cd concentrations were highest in the straw, reaching a factor of 2 or more compared to the grain, consistent with earlier findings (Andersson, 1992; Öborn et al., 1995). This pattern is similar to that of Ca and Cu, but dissimilar to P and Zn, which are both higher in the grain (Table 3). Although the translocation processes of Cd and Zn within the crop are similar in many respects, the avoidance of Cd accumulation in the grain has been hypothesized to be caused by strong chelation of Cd by thiol-containing peptides in roots and straw (Wiggenhauser et al., 2016). Moreover, there were statistically significant differences in the Cd concentration depending on treatment, with the highest in the NPK treatment and the lowest in the 'Ash only' treatment, particularly pronounced in 2018 and 2019 (Fig. S2). These differences may be partially explained by variations in pH (c.f. below), known to influence Cd uptake (Eriksson et al., 1996).

For the mass balance model, we chose to use the average harvest and Cd concentrations of 2018 and 2020, as the poor harvest of 2019 represents a significant outlier compared to Swedish historical records (Swedish Board of Agriculture, 2020).

The treatments also affected the pH(H<sub>2</sub>O) and pH(CaCl<sub>2</sub>) values ( $p < 0.05$ ), with the highest values in the 'Ash only' treatment (pH(H<sub>2</sub>O) = 5.73 in 2020) and lowest in the NPK treatment (pH(H<sub>2</sub>O) = 5.51 in 2020). For more details on the pH results, see Fig. S3.

#### 3.2. Addition of high-affinity thiols to the Stockholm Humic Model

When using the original SHM to predict Cd sorption in the soils, the model performed well at high Cd concentrations, as evidenced by the Cd sorption isotherms for the Lund A and Romfartuna Bhs soils (bottom part of Figs. 1 and 2). However, at low Cd concentrations (typical for normal Cd concentrations in soils), the model underestimated Cd sorption for all five soils, most significantly for Romfartuna Bhs. Assuming that this underestimation was caused by the omission of high-affinity thiol sites from the model, a thiol site was added onto SOM, with log  $K_{SH}$  set to -3. In the model setup that resulted in the best fits, thiols were absent from DOM (dissolved organic matter), possibly reflecting the presence of membrane-thiol functionalities on bacteria with particularly high affinity for trace metals (Song et al., 2018). Using a combination of log  $K_{CdSH} = -0.85$  and a thiol site concentration of 1/50000 (or 0.002%) of the total organic C content, much improved fits were obtained for the Lund A and Romfartuna Bhs soils, as well as for the Eckerud and Nättraby soils (Fig. S4). However, for the Östuna soil, the new

**Table 3**  
Content of selected elements in harvested biomass at the Rådde experimental farm.<sup>a</sup>

Year	Sample <sup>b</sup>	n	Cd mg kg <sup>-1</sup>	Ca	Cu	P	Zn	Biomass <sup>c</sup> kg ha <sup>-1</sup>
2018	SW Grain	28	0.028 (5)	376 (53)	5.18 (46)	3350 (181)	34.9 (8)	4220 (264)
	SW Straw	28	0.062 (13)	1760 (197)	2.29 (24)	621 (168)	12.6 (33)	4280
2019	WW Grain	28	0.014 (2)	261 (23)	3.33 (27)	2820 (248)	22.3 (16)	1990 (470)
	WW Straw	28	0.045 (12)	1400 (228)	2.30 (22)	554 (108)	10.0 (14)	1950
2020	Oats Grain	28	0.029 (4)	485 (26)	5.71 (20)	5830 (190)	45.7 (20)	3980 (540)
	Oats Straw	28	0.058 (11)	3410 (360)	3.00 (23)	1600 (270)	24.8 (27)	5790

<sup>a</sup> Standard deviations are shown within parenthesis.

<sup>b</sup> SW = spring wheat; WW = winter wheat.

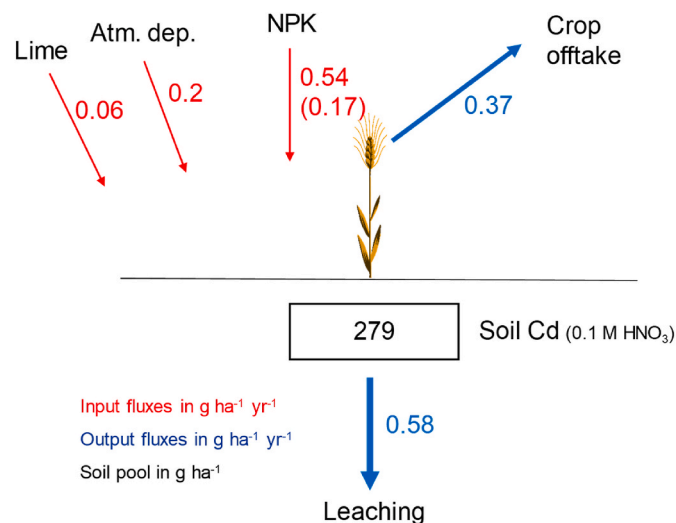
<sup>c</sup> Mean values for straw were estimated from the harvest index (i.e. ratio of grain to straw weight), which was determined using a subset of samples. For this reason, standard deviations are not available.

parameters resulted in an overestimation of Cd sorption (Fig. S4), for unclear reasons. Possibly, in reality, the concentration of high-affinity thiols is not a constant fraction of soil organic C, as assumed in the model, but site-dependent. Nevertheless, the thiol site concentration used here provided good model descriptions for 4 out of 5 soils.

To test the optimized model for the Rådde site, we used the results from the 0.001 M CaCl<sub>2</sub> extraction of the Rådde A horizon soil (Table 1). To predict dissolved Cd in the extract, the first step was to adjust ASOM in the model by matching the predicted pH with the observed one (5.25), assuming equilibrium with Al(OH)<sub>3</sub>(s) and ferrihydrite. The obtained ASOM value was 0.47. In the next step, the total dissolved Cd was predicted to be 2.8 µg kg<sup>-1</sup>, i.e. very close to the determined value (2.9 µg kg<sup>-1</sup>, Table 1). Therefore, we decided to use the newly parameterized model (with Cd high-affinity thiol sites) in the mass balance model.

### 3.3. Mass balance modelling

The current annual average Cd mass balance, applicable to the crop rotation sequence in the field experiment, could be established using measured or estimated values for Cd offtake, fertilizer and liming additions, and calculated leaching utilizing the SHM (Fig. 4, Fig. S5). As shown in Fig. 4, the exact value of Cd<sub>fert</sub> in the NPK plots depends on whether the Cd content in mineral fertilizer was based on the fertilizer used between 2018 and 2021 (which was quite low), or if the higher value for 2022 and 2023 is utilized. In both cases, however, Cd outputs



**Fig. 4.** Current Cd mass balance for the Rådde field experiment: the NPK scenario (for the other scenarios see Fig. S5). For the NPK input flux, the first value is based on fertilizer Cd contents in 2022 and 2023, while the value within parenthesis is based on fertilizer contents at the time of the field experiment (2018–2020).

exceeded inputs, indicating a net Cd loss at the Rådde site, albeit narrowly so if Cd<sub>fert</sub> is based on the fertilizer used in 2022 and 2023. Similarly, for the ‘Digestate only’ scenario, Cd outputs surpass inputs. However, in the ‘Ash only’ and ‘Ash + digestate’ scenarios, the higher inputs from the wood ash result in net Cd accumulation (Fig. S5). Nevertheless, given that annual fluxes are considerably smaller than the soil pool, substantial changes in soil Cd are likely to occur very slowly.

Investigating time scales in more detail using the HD-MINTEQ scenario tool, wherein the reformulated SHM for Cd was integrated, revealed strong temporal variations in the modelled outputs (Cd<sub>leach</sub> and Cd<sub>harv</sub>) (Fig. 5). The pattern of Cd<sub>leach</sub> aligns with the liming frequency, with the highest leaching predicted when the pH is lowest, immediately before liming. In the ‘NPK’ treatment scenario the modelled soil solution concentration of Cd ranged from 0.04 to 0.2 µg L<sup>-1</sup> depending on the pH and on the soil pool of Cd (Fig. S6). Notably, the model predicted dissolved Cd to be 0.1 µg L<sup>-1</sup> at pH ≈ 6 in the 2010s, which is equal to the result in porewater from a pot experiment in untreated soil from the same site, as found previously (Dahlin et al., 2016).

The variations in Cd<sub>harv</sub> from 2018 result from the assumed crop rotation, implying different Cd offtakes depending on the crop. Between 1850 and 2017, with identical Cd inputs for the four scenarios, the effects of peaks in Cd<sub>dep</sub> and Cd<sub>fert</sub> during the postwar period are clearly visible (Fig. S1). From 1950 to 2002, Cd outputs through leaching (Cd<sub>leach</sub>) and offtake (Cd<sub>harv</sub>) increased significantly (Fig. 5), owing to changed management practices (i.e., higher fertilizer inputs) and high inputs from atmospheric deposition. The ‘dip’ in Cd<sub>harv</sub> between 1997 and 2008 is attributed to organic farming during this period, as straw was returned to the soil. Despite the increase in Cd outputs, the adsorbed Cd level approximately doubled between 1950 and 2002 (Fig. 6). After 2002 until today, adsorbed Cd has decreased, but not by more than 4% according to the model.

From 2018 the four different scenarios resulted in divergent results for the Cd outputs. In agreement with the current mass balance (Fig. 4), the Cd outputs, as well as the concentration of adsorbed Cd, slowly decreased in the ‘NPK’ and ‘Digestate only’ scenarios, while for the scenarios that involve ash, the levels of Cd<sub>leach</sub> and Cd<sub>harv</sub> were relatively low (although increasing during the simulation), while adsorbed Cd increased, leading to net Cd accumulation (Figs. 5 and 6). However, the response times were quite long, meaning it takes centuries to reach a new steady-state. Again, this is due simply to the fact that the annual fluxes are much smaller than the soil pool.

### 3.4. Implications and model uncertainties

The results indicate that substituting P fertilizer with wood ash led to increased Cd accumulation in the soil, consistent with several earlier studies (Mortensen et al., 2018; Kindtler et al., 2019). However, Kindtler et al. (2019) also demonstrated that ash application increased crop productivity and decreased Cd uptake, apparently due to a higher pH. In our current field study, Cd offtake instead decreased (at least initially) due to lower harvest yields in the ash treatments. The contrasting effects



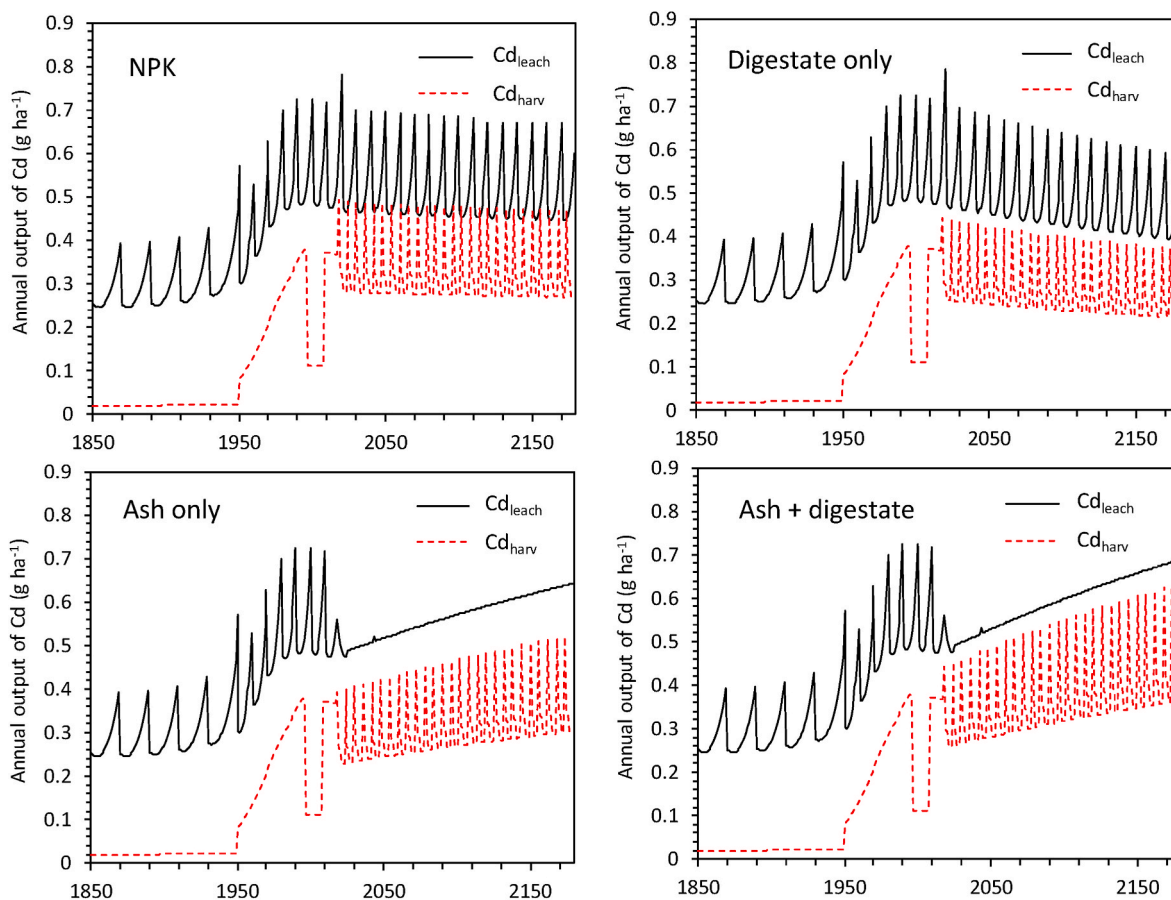


Fig. 5. Modelled annual output fluxes of Cd; Cd<sub>leach</sub> = Cd lost by leaching, Cd<sub>harv</sub> = Cd offtake.

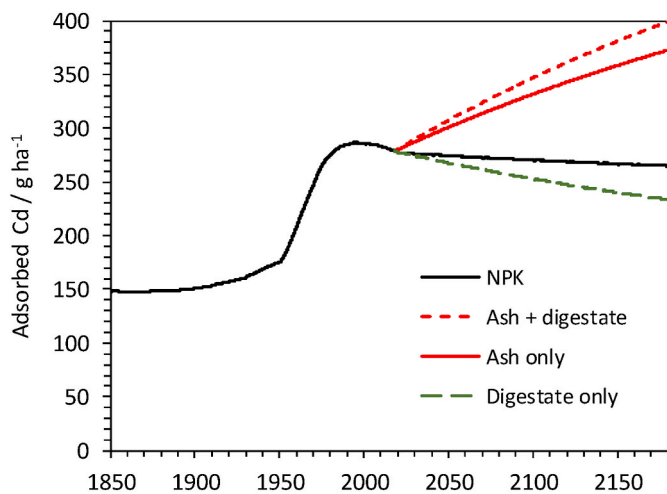


Fig. 6. The change of adsorbed Cd with time, according to HD-MINTEQ scenario calculations. In the NPK scenario for 2022 and onwards, the Cd content of fertilizer was set at the values valid for 2022 and 2023.

on yield between the two studies can likely be attributed to differences in experimental setups; here, wood ash replaced NPK fertilizer, while Kindtler et al. (2019) added mineral fertilizer to all treatments. However, the latter study suggests that TF (Equation (2)) would decrease with increasing pH, a factor not considered in our model. Therefore, the extent to which increased Cd accumulation in ash-treated soil influences Cd offtake remains uncertain. This likely depends on how TF may change with pH and the magnitude of pH increase following ash

application. Regardless, adopting the principle of zero-net Cd accumulation when evaluating different fertilizer sources suggests that wood ash, especially as the sole replacement for conventional mineral fertilizer, cannot be recommended. Moreover, this would be impractical given that wood ash has a very low nitrogen content. In contrast, the biogas digestates used in this investigation meet the criterion, as they result in a net Cd loss over time.

Another uncertainty of the model approach is related to the assumption regarding DOC. Although the revised SHM was found to describe Cd sorption data in laboratory studies very well, the predictions of Cd leaching depends also on assumptions on the DOC concentration – higher DOC would lead to increased Cd leaching, both because of a higher concentration of dissolved Cd-DOM complexes and because of a higher concentration of counterions such as Ca<sup>2+</sup>, which compete with Cd<sup>2+</sup> for soil sorption. Here, we set the DOC value using environmental monitoring data on subsurface drainage. A previous study from a site in northern Sweden using soil lysimeters suggested higher DOC (Bengtsson et al., 2006). However, as the modelled value of dissolved Cd was the same as the one found in the previous pot experiment of Dahlin et al. (2016), we believe that the assumption regarding DOC may be reasonable.

#### 4. Conclusions

The study is consistent with earlier assessments that the current Cd mass balances in agricultural soils are likely to be negative in many agricultural soils (i.e., leading to net Cd loss) due to the much reduced input fluxes from atmospheric deposition and fertilizer (e.g. Six and Smolders, 2014; Römkens et al., 2018). Despite the increased Cd input in 2022 and 2023 through mineral fertilizer, as a result of international conflicts, the mass balance of the Råde soil remained negative although

not by a large margin. The biogas digestates used in this study were low in Cd and thus they could be used to replace all of P in mineral fertilizer without any risk for net Cd accumulation. The studied wood ash, however, would cause net Cd accumulation if used, alone or in combination with digestates, as the only replacement of fertilizer P. In principle, the approach taken in this paper can be used to calculate 'safe' or 'sustainable' application rates of recycled nutrient sources, which does not lead to net Cd accumulation in the soil. However, uncertainties remain concerning e.g. the role of pH for crop uptake of Cd, and the DOC concentrations that actually occur at the interface between the A horizon and deeper mineral soil horizons.

### CRedit authorship contribution statement

**Jon Petter Gustafsson:** Conceptualization, Formal analysis, Investigation, Methodology, Software, Visualization, Writing – original draft, Writing – review & editing. **Marie-Cécile Affholder:** Data curation, Formal analysis, Investigation, Methodology, Writing – original draft, Writing – review & editing. **A. Sigrun Dahlin:** Conceptualization, Formal analysis, Funding acquisition, Methodology, Project administration, Resources, Writing – original draft, Writing – review & editing.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.apgeochem.2024.105951>.

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