Long-term application of digestate and biofuel ash to arable soil
– Effects on the solubility of Cd, Al and trace metals as evidenced by simulated scenarios

Elias Bäckström

Long-term application of digestate and biofuel ash to arable soil
– Effects on the solubility of Cd, Al and trace metals as evidenced by simulated scenarios

Elias Bäckström

Abstract

The importance of nutrient recycling could not be emphasized enough in to-day's society. Reduction of waste as well as recycling of nutrients would be the result if ash and biogas digestate could be used as fertilizer. However, the solubility of Cd, Al and micronutrients might be affected in a different way than by standard fertilizers. In this thesis, the effects of ash and biogas diges-tate on the solubility of Cd, Al, Ni, Zn and Cu were investigated on a long-term basis using the Visual MINTEQ model. As input to the model, geochem-ically active metals as determined by extraction were used. Batch experi-ments were made with the studied soils to provide data for model calibration. Values from literature were used not only for plant uptake, leaching and run-off, but also for the prediction of the long-term accumulation of soil organic matter (SOM) and exchangeable cations. Three scenarios were simulated; ap-plication of ash, digestate and a mix containing these two. The ash simulation showed an increase of the solubility for Cd, Ni, Zn, and Cu. Except for Cu this was caused mainly by an increase of exchangeable cations that led to stronger competition for sorption sites onto soil particles. The desorption of Cu was instead affected by the increase in pH following ash application. The digestate simulation showed a clear decrease in solubility for the same metals. This effect was caused by the addition of humic substances (HS) from the digestate, onto which the metals were sorbed. Aluminum behaved differently from Cd, Ni, Zn and Cu, the exception was the decreased Al solubility result-ing from the digestate application at Skedevi. The Al solubility was controlled by equilibrium with $Al(OH)_3$, which explained the different behavior. The mix simulation did not substantially change the solid-solution distribution for any metal. The competition for sorption sites resulting from the ash applica-tion was balanced with the addition of HS from the digestate. The biggest source of uncertainty was believed to be the plant uptake and leaching of cat-ions. However, the results nevertheless give an indication on the change of the soil chemical environment due to ash, digestate and mix applications. As such, it shows that a mix could be preferable over single applications of ash or digestate if the soil conditions are to be kept unchanged.

Keywords: cadmium, fertilizer, Visual MINTEQ

Populärvetenskaplig sammanfattning

Mycket är vunnet på att återanvända de näringsämnen som finns i flera av samhällets producerade avfallsprodukter. Istället för att låta näringsämnena försvinna på deponi så kan detta återvinnas som näringsrikt gödselmedel på åkrar och fält. På det sättet motverkas övergödningen samt att vi bli mer själv-försörjande av gödsel i Sverige. Till exempel; i det substrat som blir kvar vid biogastillverkning, så kallad rötrest, finns höga halter kväve (N). Från anlägg-ningar där avfallsförbränning sker kommer stora mängder aska, vilken inne-håller framförallt fosfor (P), magnesium (Mg) och kalium (K). Ett gödnings-medel bestående av både aska och rötrest ger således ett komplett näringsin-nehåll. Utöver näringsämnen innehåller rötresten mycket organiskt material (OM). Askan innehåller höga halter kalcium (Ca) samt har ett högt pH. På grund av detta kan dessa produkter vid applicering ändra den rådande miljön i jorden. Mikronäringsämnen som zink (Zn), koppar (Cu) och nickel (Ni) samt toxiska ämnen som kadmium (Cd) och aluminium (Al) finns naturligt i jorden, dessa kan då bli mer lösliga och därmed mer växttillgängliga. Detta kan vara bra vad gäller mikronäringsämnen, men inte vad gäller de toxiska. Därför är det relevant att ta reda på vad som händer i jorden om gödsling sker med dessa produkter.

Det här examensarbetet har undersökt konsekvenserna av långvarig (30 år) tillförsel av rötrest, aska och en mix av dessa båda. Undersökningen base-rades på jordprover från två brukade jordar i Östergötland, Sverige. För att kunna göra en långtidsanalys byggdes en modell i programvaran Visual MINTEQ 3.1. I modellen simulerades långtidstillförsel av vardera; aska, röt-rest och mix.

När aska applicerades så höjdes pH. Kadmium, nickel, zink, och koppar blev mer lösliga. Detta skedde på grund av den stora mängden Ca som tillför-des. Ca konkurrerar ut Cd, Ni och Zn från deras platser på partiklar i jorden. Cu blir inte lösligt på grund av Ca utan istället av det förhöjda pH-värdet. Rötrestsimuleringen resulterade i både ett minskat pH och minskad löslighet. Bidragande orsak var tillförseln av OM. OM genererar fler bindningsställen för metallerna att binda till, vilket minskade konkurrensen, alla metaller kunde binda. Generellt sett gällde annars att då Cd, Ni, Zn, och Cu blev mer lösliga blev Al mindre lösligt och tvärt om. Detta berodde på att aluminiumets löslighet påverkades starkt av utfällning av aluminiumhydroxid. Detta mine-ral bildas vid högt pH (basiskt), men löses upp vid låga pH (surt). Simulering av mixen visade på nästintill oförändrat pH samt löslighet av metaller. Den ökande konkurrensen från Ca i askan motverkades av det tillförda OM från rötresten. Resultaten ger en fingervisning om vad som kan ske i jorden vid tillförsel av aska och/eller rötrest. Tendensen är att en mix av aska och rötrest

ger minst förändring i både pH och metallernas löslighet, vilket är fördelaktigt vid förhindrande av att Cd tas upp av växten. Fördjupad forskning behövs dock, till exempel ett långtidsprojekt där applicering sker under lång tid med möjlighet till årliga analyser av förändringen i ämnenas löslighet.

Table of contents

List of tables

List of figures

1   Introduction

In the 7th Environment Action Programme (EAP) (European commission, 2016) the EU declared that in order to protect, conserve and enhance the Union´s natural capital, by 2020 the nutrient cycle (N and P) should be managed in a more sustainable and resource-effective way. There are several benefits on the aspects of nutrient recycling; mostly discussed are phosphorus (P) and nitrogen (N). Nutrient recycling reduces the need for mining and energy-demanding production processes. When the input to the nutrient cycle is smaller, accumulation of nutrients and thereby the eutrophication of streams and lakes is less.
Since cadmium (Cd) exists in close relationship with the phosphate rock recovered as fertilizer, the element normally lingers as a contaminant in the product. Since conventional P-fertilizer application onto arable land is custom, it can increase the risk of Cd contaminating of crops (Roberts, 2014).

Biofuel incineration as well as biogas production plants are two well established energy systems in Sweden. While producing car fuel, electrical power and heat they leave residues; ash and biogas digestate. Ash is by nature highly alkaline and therefore toxic to biota in high doses and should not be spread uncontrolled in nature. In Sweden 2012, 1 709 000 Mg ashes were produced from biomass incineration. Around 3 % was recycled and spread onto forests, mainly to compensate for the withdrawal of nutrients and the acidification that occurs due to harvesting (Hjerpe *et al.,* 2014). More than half of the total amount of biofuel ash is used as landfill cover, thus the nutrient content in ashes goes to waste (Svenska energi Askor, 2012).

As for the biogas production in Sweden in 2015 the residue production of digestate was 2 676 000 Mg. Much of this was used as fertilizer due to its high content of N and organic matter (OM). The recycling efficiency of the digestate at local farms (biogas production) was 100%. However, a large amount of digest from co-biogas plants and sewage treatment plants is not recycled (ES 2016:04).

Blending ash with digestate has the potential of producing a fully functioning fertilizer. Ash is normally rich in phosphorus (P), potassium (K) and magnesium (Mg), which complements the high values of N and OM. The Cd content is normally lower than for the standard P fertilizer; the same is true for other heavy metals (Bernesson *et al.,* 2008: Demirel *et al.,* 2013). The product is a slurry, a typical property of digestate, which makes the spreading of the otherwise dry and transient ash onto the fields easier. Also, the high pH of ashes could be buffered by

the digestate to keep the product from changing soil pH (Bernesson *et al.,* 2008). However, the effects of the ash/digestate mix on soil chemistry is uncertain. A rise in pH as well as the addition of OM could lead to sorption and immobilization of nutrients that decrease the phytoavailability. For toxic metals such as Cd, however, this is the desired effect. High addition of cations, on the other hand, might solubilize the metals. A beneficial effect for a certain type of amendment would be to maintain a strong sorption of Cd and other toxic heavy metals, and at the same time increase the solubility of micronutrients as Cu, Ni and Zn. This separation between cations could be possible by using their Lewis acid properties. Cadmium is a soft Lewis acid while many of the nutrients are intermediate (Welikala *et al.,* 2018).

In this thesis batch equilibrium tests were followed by multisurface modeling to simulate the soil sorption behavior for Al, Cd, Zn, Cu, and Ni. This type of model has been proved successful in explaining the soil chemistry of Cd, Cu and Zn (Linde *et al.,* 2007: Khai *et al.,* 2008). A multisurface model combines different models that describe sorption onto different types of soil particle surfaces. In this thesis three reactive surfaces are assumed: (hydr)oxides, organic matter and phyllosilicates.

2   Aim

The aim of the present thesis was to investigate how the application of bottom ash and biogas digestate as well as a mix might affect the solubility of Al, Cu, Ni, Zn and Cd. Which property will govern metal sorption the most?
This is addressed by building a model in Visual MINTEQ 3.1, which is calibrated using results from batch experiments. Three different scenarios were simulated in a long-term perspective of 30 years.
The hypotheses were the following:

- Metal solubility will decrease due to an increase of particulate organic matter as a result of the addition of digestate, which will adsorb the metals.

- The increase of pH due to ash application will decrease metal solubility due to an increase in negative surface charge of the particles.

- In the "mix" scenario, the digestate will buffer the high pH of the ash.

3   Background for metals in soil

Metals, both native and anthropogenically added, may accumulate through different retention mechanisms or leave the soil system through leaching or plant uptake. The species that are accessible to plant uptake and leaching (the mobile and easily desorbed) are the ones that pose a risk to humans and biota (Berggren Kleja *et al.,* 2006). The net balance is determined by a range of chemical mechanisms. Sorption is a commonly used term to include all reactions that remove the metal from the solution phase and that lead to accumulation in the solid phase (Essington, 2015). This includes: adsorption and absorption to particles as well as precipitation.

3.1   Speciation

Normally, the largest amount of metals in soil is in the solid phase. Retained metals are neither mobile nor phytoavailable/toxic. The solid phase thus contains both precipitates and sorption products such as surface complexes.

Metals in the solution phase are present both as the free (hydrated) ions and as soluble complexes with organic or inorganic ligands. Hydrated ion species formation is shown in Eq. 1, while the formation of a soluble complex with ligand/hydration exchange is shown in Eq. 2 (Carrillo-Gonzales *et al.,* 2006).

$$M_{(aq)}^{a+} + xH_2O \Leftrightarrow M(H_2O)_{x(aq)}^{a+} \tag{1}$$

$$M(H_2O)_{x(aq)}^{a+} + L_{(aq)}^{b-} \Leftrightarrow ML_{(aq)}^{a-b} + xH_2O \tag{2}$$
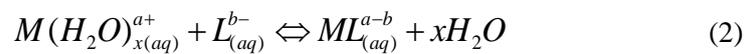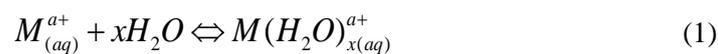
where:
M = metal
L = ligand

The hydrated ion complex is usually more phytoavailable compared to soluble complexes (Berggren Kleja *et al.,* 2006). The soluble complexes can be both inner-sphere (where the hydration sphere is replaced by other ligands) and outer-sphere (where the hydration sphere is still present between the ion and the ligand). Metal speciation in the soil is governed not only by the pH value, but also by the

redox potential (Eh), the solubility of carbonates, sulfides and (hydr)oxides, as well as the concentration of dissolved organic matter (DOM) (Carrillo-Gonzales *et al.*, 2006).

3.1.1 Partitioning coefficient

The partitioning between the desorbed soluble phase and the sorbed solid phase of the metal can be mathematically described by the *partitioning coefficient K_d*:

$$Kd = \frac{q}{C_{eq}} \qquad\qquad (3)$$

where:
K_d = Ratio describing the metal sorption in soil (L Kg^{-1})
q = Sorbed metal mass per unit mass of adsorbent (mg Kg^{-1})
C_{eq}=Soluble metal mass per unit solution volume (mg L^{-1})

The K_d depends on solution pH, soil texture, soil organic matter (SOM) content and metal concentration and is therefore unique for each metal and environmental situation (Sauvé *et al.,* 2000). A high K_d value indicates strong sorption of the metal onto particles and a low K_d value shows that a considerable amount is in the solution phase. Hence the $K_{d,}$ value is related to the mobility and phytoavailability (Loganathan *et al.,* 2012).

3.2   Sorption

Sorption sites are found on phyllosilicates, (hydr)oxides and SOM in the solid-solution interface between the solid and the bulk solution. Here electrostatic forces influence the ions (Essington, 2015). Sorption sites are usually either positively or negatively charged, attracting either cations or anions.

These sorption sites are divided into two groups: those with permanent and pH-dependent charge. pH-dependent sorption sites exist on metal (hydr)oxides, SOM and on the edges of phyllosilicates. For cations, sorption increases with increasing pH and for anions the opposite is normally true (Loganathan *et al*., 2012: Essington, 2015). This effect is due to the deprotonation of hydroxyl groups occurring on pH dependent charged sites as the pH increases. At low pH protonation occurs and the affinity for anions increase while the cations are repelled. Permanently charged surface sites are unique for phyllosilicates, most commonly with negative charges, due to isomorphic substitution (Essington, 2015). Sorption by surface complexation occurs in two ways. Similar to the soluble complexes they form inner-sphere (specific adsorption) and outer-sphere (electrostatic adsorption) complexes. Inner-sphere complexation (also referred to as specific adsorption) binds the metals strongly in direct bonds. Here the metal ions only retain part of the hydration complex obtained in solution. These ions are not easily exchanged or de-

sorbed, but at certain conditions or by specific ions it is possible. The general order for site affinity and thus the exchange capacity is explained by the Irving-Williams order:

$$Hg^{2+} > Pb^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} \approx Co^{2+}Cd^{2+} \qquad (4)$$
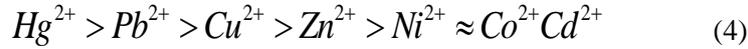
Cu^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} form inner-sphere complexes relatively easily (Essington, 2015), however, the sorption strength is strongly dependent on pH. When going below pH ≈ 6 these ions increasingly changes from specific to electrostatic complexation onto the permanent negative charged surface sites of phyllosilicates (Gu & Evans, 2008). Naidu *et al.* (1994) found that Cd solubility decreased with decreasing pH for different types of soils. They also found that the lower Cd concentrations and stronger affinity of soil (high CEC), the smaller impact did a pH change have (Naidu *et al.*, 1994)**.**

3.2.1 Lewis acids

Cd^{2+} is a soft Lewis acid while Ni^{2+}, Cu^{2+}, Zn^{2+} are all borderline Lewis acids. These properties could help explaining different effects regarding sorption in soil (Welikala *et al.,* 2018). These metals prefer to bind with different ligands according to the principle of hard and soft acids and bases (Essington, 2015). Examples of intermediate organic Lewis base ligands are: carboxylic and phenolic functional groups, while soft organic ligands are: reduced sulphur functional groups (Welikala *et al.*, 2018).

3.2.2 Soil organic matter (SOM)

SOM is considered by many as one of the most important sorbents for Cu, Cd and Zn (Khai *et al.*, 2008: Linde *et al.,* 2007: Berggren Kleja *et al.,* 2006). SOM is an array of heterogeneous organic compounds that differ in molecular weight, solubility and affinity for metals. The SOM exists either in dissolved (DOM) or as humic substances (HS) in the solid phase. SOM is in both phases mostly comprised of the high affinity fulvic (FA) and humic (HA) acids. While FA can to some extent be dissolved, HA tends to be solid in the normal pH range. Other constituents within SOM are the low affinity carbohydrates, lipids and acids (Essington, 2015: Groenenberg *et al.,* 2014). Because of their high affinity for cations, both dissolved and solid HA and FA are considered the "active" part of SOM. The ratio between active and non-active SOM can vary between 0.31 and 0.87 (Groenenberg *et al.,* 2014). At normal soil solution pH (>4) the SOM surface sites are negatively charged, mainly due to deprotonated carboxyl and phenolic groups but also due to amino and sulfhydryl groups. The humic substances (HS) can sorb metal ions from solution (Khai *et al.*, 2008). DOM (mostly FA), on the other hand function as ligands in soluble complexes with the metal; it desorbs the metal from solids into solution, i.e. the opposite to HS. The active fraction of DOM is commonly set to 65% (Groenenberg *et al.,* 2014). Thus, a detailed study from Swedish lakes

and rivers suggested a value of 82.5 % for the active part (Sjöstedt *et al.*, 2010). The HA and FA are heterogeneous and this is reflected in their metal sorption properties (Benedetti *et al.,* 1995) meaning that they bind a small amount of metal very strongly, whereas larger amounts of metals bind more weakly. The metal binding strength depends on factors such as valence, soft/hard Lewis acid and concentration. For example, the multivalent cations Ca^{+2}, Mg^{+2} and Al^{+3} are assumed to compete for the same sites (Benedetti *et al.,* 1995). Welikala *et al.* (2018) found that high CEC organic amendments, such as certain composts, sorbed Cd better than it sorbed Ni or Zn. One possible reason was the role of reduced sulphur functional groups (soft ligands) within the compost material. The binding strength for FAs are stronger by Cu^{2+} than Cd^{+2}. This is because Cu^{2+} is a borderline hard/soft acid, which gives it the properties of binding to carboxylic acids. Cd^{2+} prefer soft ligands such as S, which are not very common compared with the carboxylic acids in SOM.

3.2.3 Hydrous metal oxides and phyllosilicates

Phyllosilicates and metal oxides, hydroxides and oxyhydroxides ((hydr)oxides) are secondary minerals, most often to be found in the clay and silt fractions. The phyllosilicates are sheet silicates; 1:1 or 2:1. The 1:1-layered phyllosilicates (i.e., kaolinite) have very little permanent charge, leading to mostly specific adsorption onto the pH-dependent sites (Gu & Evans 2008). The 2:1 sheet (i.e., vermiculite and montmorillonite) can contain more permanent charge (higher CEC) which then results in electrostatic sorption of cations (ion exchange).

The (hydr)oxides in soils are mainly the ones formed from Fe and Al. They can be more or less amorphous or crystalline. Amorphous metal (hydr)oxides have larger specific surface areas than the crystalline oxides. Thus, they contain more pH-dependent sites that generate greater reactivity and specific sorption.

The complexes formed both on the edges of phyllosilicates and (hydro)oxides get stronger with increased pH, due to the increase of negative surface charge.

3.3   Fertilizers

In this chapter the products that will be used as fertilizer and hence simulated in the model are described.

3.3.1 Bottom ash from biofuels ("bio-ash")

Bio-ash originates from incineration plants and is the inorganic fraction of the organic waste that is incinerated. Bio-ash is formed from cereal crops as: wheat, oats or rapeseeds as well as from hemp. Bottom ash is formed at the bottom of the incinerator and is much coarser than the fly ash from the top; hence, it consists of only small fractions of organic matter. The high content of nutrients in the ash makes it valuable as a source for plants. Marmolin *et al.* (2008) found median values for P_{tot} and K_{tot} from oat bottom ash to be around 10% each. The heavy metal

content is normally low. For instance, ash has lower Cd concentration than the best conventional fertilizers (Bernesson *et al.,* 2008). It is an established fact that ash is alkaline. The high alkalinity is an effect mainly of hydroxides, carbonates and bi-carbonates (Etiegni & Campbell, 1991). To what extent the ash is combusted affects the alkalinity, nutrient concentrations, the metal speciation as well as the organic content (Wei *et al.,* 2011). The alkalinity increases with decreased efficiency of incineration (Etiegni & Campbell, 1991) as do the organic content and P_{tot}. The outcome of a chemical analysis of ash depends also on what product is put into the incinerator, for example hemp tend to generate lower P and K concentrations than does the cereals (Marmolin *et al.,* 2008). The alkaline properties of ash are often used to increase the pH, especially in acid forest soils. Ohno *et al.* (1990) found a linear relationship between the amount of applied ash and the rise in pH. In other words, a smaller dose of applied ash caused a smaller effect on pH (Demeyer *et al.,* 2001). According to Ring *et al.* (2006) the pH remained unaltered when using ash was used at smaller doses than 9 Mg ha^{-1}. A study by Saarsalmi *et al.* (2012) found that a one-time single application of 1 Mg ha^{-1} had caused an increase in pH of 0.1, 30 years after the dose.

3.3.2 Bio-digestate

Biogas used as car fuel, heat or energy is quite common in Sweden. More than 2 TWh is produced annually, according to the Swedish Energy Agency (ES 2017:07). The anaerobic process to generate biogas can be done on: slaughter waste, source-separated household waste, and different farm animal manures or sewage. The product is mainly methane and carbon dioxide. Bio-digestate is the residue from biogas production at local farm and co-digester plants. It is a slurry of solids and water, normally with a dry matter content of 1-5 %. The digestate from biogas production at sewage treatment plants is normally dewatered and hence has a higher dry weight. This thesis uses the bio-digestate slurry.

The composition of the digestate is governed by the parent material and by the type of digester. However, generic properties are the high contents of N and OM. The heavy metal content is normally low (Demirel *et al.,* 2013). The organic matter is comprised of materials from all stages of decomposition, hence, a variety of HS and DOM exists. Decomposed OM has a high ratio of acids (Ch. 2.2.2) and some sulfur; this gives the digestate acidic properties (Kirchmann *et al.,* 1996). In Sweden there is a certificate system to be used as a guideline if the bio-digestate is to be put on agricultural soils, the SPCR 120 (Avfall Sverige, 2018). For the digestate coming from sewage treatment plants the corresponding certificate is called Revaq (REVAQ 4.2, 2018). At local farms in Sweden, biodigestate as fertilizer is used to 100% and the co-digestate around 96%. As for the digestate coming from biogas production at sewage treatment plants, the rate is only 10% (ES 2017:07).

In soils to which only digestate was added, Bergkvist *et al.* (2005) found that despite the increase in SOM and Fe oxides in the soil the solubility of Cd was unaltered. They argued that this might be due to the initial high sorption affinity for Cd the soil and to the competing effect from Fe and Zn.

3.3.3 The mix

If bottom-ash and bio-digestate are mixed a fully functional fertilizer could be gained. It would contain a high amount of phytoavailable P, N and K as well as organic matter. To be able to successfully make a fertilizer out of ash and digestate, there are some engineering problems to overcome. Since the ash normally exhibits high alkaline properties the percentage of ash should not be over 5 % to inhibit ammonia release. Much of the content in ash contributes to grinding and attrition of pipes and machines and should thereby be added to the mix as late as possible (Bernesson *et al.,* 2008). What Bernesson *et al.* (2008) also found was that despite the alkaline properties, the pH of the soil did not necessarily increase due to the good buffering capacity of the digestate.

García-Sánchez *et al.* (2015) compared digestate and fly-ash amendments and arrived at the conclusion that, after adding digestate an increase in e.g. EC, C_{tot}, and N_{tot}, as well as the biological activity was found. For the ash application, only the EC was increased (the effect on pH was not investigated). The authors suggested that these two amendments had different roles in soil chemistry: digestate is a suitable organic amendment while the ash acts as fertilizer.

Guo *et al.* (2018) made a pot study mixing inorganic (hydrated lime or/and hydroxyapatite) with and without organic fertilizer to investigate dissolved Cd in the soil solution. They found that for acidic soils the mix of alkaline materials with organic fertilizers is both efficient and economically beneficial. The increased soil pH generated by the alkaline materials was considered the most important factor for Cd retention. The inorganic materials used in the study by Guo *et al.* (2018) could be compared with ash and the organic matter with the bio-digestate.

3.4   Multisurface models

Earlier studies have concluded that the use of an assemblage/multi-surface model to simulate the outcome of sorption behavior in soil for Cd, Zn, Cu, and Ni is applicable (Linde *et al.,* 2007: Khai *et al.,* 2008). In this thesis, to enable the prediction of the result of the application of different amendments, a multisurface model was used. A multisurface model combines thermodynamic data (inorganic speciation, equilibria, redox etc.) in a *speciation model* with separate submodels for ion sorption to reactive components (oxides, phyllosilicates and SOM). The complexity of sorption onto heterogeneous sorbents is simplified to obtain practical models. The models distinguish between electrostatic and specific binding as well as taking into account the competition between ions. These models are more complex than the traditional empirical relationships (*Kd* and Langmuir/Freundlich). Visual MINTEQ 3.1 is an example of a speciation model. Sorption submodels commonly used for humic substances are the NICA-Donnan and the Stockholm Humic model (SHM), both incorporated in Visual MINTEQ 3.1. They both use the concept of specific and electrostatic adsorption but differ in their description of the binding

characteristics and of the electrostatic contribution. SHM is a so called discrete-site model, where ions sorb to the sorption sites according to the action of the mass law. It contains eight proton-binding sites, and seven adjustable parameters to describe the dissociation reactions. The model also takes into account both mono- and bidentate complexes and uses a heterogeneity parameter to simulate the preferential sorption onto sites with high affinity.

4 Materials and methods

4.1 Study area

The soil samples used in this thesis were collected from two arable soils in Östergötland, Sweden: Öjebro (58°23'6.25"N; 15°11'21.21"O) and Skedevi (58°31'01.5"N 15°14'33.0"E). Only one depth was examined, 0-25 cm, e.g. the plough layer. Three different fertilization treatments were used one year ahead of sampling: (1) unfertilized (2) ash-fertilized and (3) digestate-fertilized. Fertilizers were applied prior to seeding (the same day) 2017-05-02 at Skedevi and 2017-04-11 at Öjebro. For all systems 150 kg NS 27-4 Axan (nitrogen fertilizer with sulfur content) (Lantmannen, 2018) was also applied, even to the "unfertilized" treatment. This corresponds to 54 kg N ha^{-1} and 8 kg S ha^{-1}. In the previous year potatoes were cultivated while wheat was grown during the year of sampling. The soil characteristics for each area are summarized in Table 1, indicating clay soils with high CEC for both Skedevi and Öjebro.

4.2 Basic soil characterization

Basic preparation of the soil samples was conducted. The samples were homogenized and sieved with 4 mm sieve. While one part was air-dried at ≈ 38°C the other part was left as natural field-moist samples, stored in a cold room at +5ºC. The water content of both the air-dried and wet samples was determined. Data used for the model setup were obtained by different extraction methods. All extractions were performed in duplicate on air-dried soil samples (38°C) if not stated otherwise. The soil texture as well as the element concentrations regarding ash and digestate were not analyzed within the frame of this thesis, though, the analyzed matter was the same as used in the fertilization of the soils as mentioned earlier (ch. 3.1.). (The digestate were analyzed using influx where the filters are digested with HNO_3/H_2O_2 (M-4) at ALS and the ash was analyzed with ICP-MS after digestion in aqua regia according to SS-EN 13657 (Swedish standard institute, 2003) (MAR3)).

Table 1. *The unfertilized soil characterization for Skedevi and Öjebro as well as selected values from the ash and digestate used in this thesis.*

Parameter	Unit	Ash	Digestate		Soil	
			Uppsala	Linköping	Öjebro	Skedevi
Dry weight	%	95.3	3.1	3.7	86	81
pH_{H2O}	-	12.7	8.1	8.1	6.3	6.3
pH_{CaCl2}	-	12.6	7.9	7.9	5.8	5.7
N-tot	%	0.1	6	5.5	0.12	0.17
C-tot	%	24.1	38.7	38	1.3	2.0
DOC	mg L^{-1}	-	-	-	5.45	5.8
Inorg-C	%	2.5	-	-	<0.0005	<0.0005
Al^H	mg kg^{-1} TS	18350	70	60	1184	1615
B (lll)^H	mg kg^{-1} TS	-	-	-	0.9	0.7
Ca^b	mg kg^{-1} TS	186000	45100	43900	1632	1713
Cd^H	mg kg^{-1} TS	13.3	0.36	0.49	0.13	0.12
Cu^H	mg kg^{-1} TS	122	42	46.6	3.9	2.3
K^b	mg kg^{-1} TS	31700	40900	27900	86	122
Mg^b	mg kg^{-1} TS	19100	4410	3240	101	106
Na^b	mg kg^{-1} TS	-	-	-	9.9	6.4
Ni^H	mg kg^{-1} TS	17.8	9	12.3	1.7	2.1
P (PO_4)^o	mg kg^{-1} TS	13300	14500	14100	342	330
Zn^H	mg kg^{-1} TS	3150	163	266	9.4	8.9
Si (H_4SiO_4)^o	mg kg^{-1} TS	-	-	-	141	239
HFO	mg kg^{-1} TS	-	-	-	1073	2919
CEC	$cmol_c$ kg^{-1}	-	-	-	157	167
Clay	%	-	-	-	12	22
Silt	%	-	-	-	34	54
Sand	%	-	-	-	55	24

^{o} oxalate-extracted from soil

^{b} BaCl$_2$ extracted from soil

^{H} 0.1 M HNO$_3$ extracted from soil

4.2.1 Oxalate

Reactive amorphous (hydr)oxides of Al, Fe, P and Si (including organically bound Al) were determined by oxalate extraction. It is one of the most common methods regarding these species (Groenenberg *et al.,* 2014). This was done by shaking 1.00 g soil with 100 mL of a 0.2 M ammonium oxalate/oxalic acid buffer at pH 3 in 250 mL bottles. The samples were equilibrated for 4 h on a horizontal shaker (Reax 2 Heidolph) in the dark, and afterwards centrifuged at 4000 rpm for 20 min. Filtration was done with a Sartorius filter (0.2 µm), and diluted 5 times before ICP-OES measurement using a Thermo iCap 6000 instrument. Measured values can be found in A4.

4.2.2 Pyrophosphate

Pyrophosphate extracts organically bound Al and Fe, but also a limited amount of Al (hydr)oxides (Kaiser & Zech, 1996) as well as Fe oxides (Parfitt & Childs, 1988). Therefore, it should only be considered indicative as regards the concentration of organically bound Al and Fe. In the extraction, 1.00 g soil sample was mixed in a 250 mL bottle with 100 mL 0.1 M $Na_4P_2O_7$ in a horizontal shaker for 18 h afterwards the samples were centrifuged at 4000 rpm for 25 min. They were filtrated with Sartorius filter (0.2 µm) and diluted 5 times before ICP-OES measurement as above. Measured values can be found in A5.

4.2.3 BaCl$_2$

Exchangeable cations (Al, Ca, Mg, K and Na) were determined by extraction with 0.1 M $BaCl_2$, according to the method of Olofsson (2016). 10.0 g of soil was mixed with 50 mL 0.1 M $BaCl_2$ and equilibrated for 1 h on a horizontal shaker. The suspension was centrifuged for 10 min at 2500 rpm and filtered with Munktell OOH filter paper. A similar second extraction of the samples was done in which another 50 mL 0.1 M $BaCl_2$ was added, followed by 1 h equilibration. The same procedure with respect to centrifugation and filtration was then performed, and the second supernatant was mixed with the first in an E-flask. 20 mL of each extract was collected in 20 mL bottles and stored in the cold room. The extracts were diluted 5 times before measurement using ICP-OES, as above. Measured values can be found in A6.

4.2.4 HNO$_3$

The amount of geochemically active trace elements was determined by 0.1 M HNO_3 extraction. 2.00 g field-moist soil sample was mixed with 35 mL 0.1 M HNO_3 in a bottle, equilibrated for 16 h in an end-over-end shaker, then centrifuged at 3000 rpm for 20 min, and finally filtered with a Sartorius filter (0.2 µm). Measured values can be found in A7.

4.2.5 pH measurement

The pH value in both deionized water, pH_{H2O}, and $CaCl_2$, pH_{CaCl2}, was determined for all samples. 6.0 g of soil was mixed with 15 mL of either deionized water or with 0.01 M $CaCl_2$. The samples were shaken for about 1 min and then left over night (ca 8 h). On the next day the pH was measured with a PHM 93 reference pH meter, carefully in the supernatant without steering up the soil.

4.3   Batch equilibrations

Batch equilibrations were made for the two unfertilized soil samples from Öjebro and Skedevi. These were performed at different pH values to determine dissolved

metals at different pH for each soil. The results were then used to calibrate the model. In order to get the amount acid or base needed to reach a certain pH for the different soil samples, centrifuge tubes were filled with 6 g of wet soil. To each tube 10 mL of 0.03 M $NaNO_3$ was added. Thereafter, 20 mL HNO_3 in different concentrations (0.5, 1, 2, 3, 4, 6, 8 mM and 0) was added to seven tubes. Another 3 tubes were provided with different concentrations of NaOH (0.5, 1, and 2 mM). The suspensions were equilibrated for 3 days, centrifuged at 2000 rpm, and then the pH was measured in the supernatant.

Based on the pH found for each concentration, the batch equilibrium series were determined (Table A2). The batch experiments were conducted on unfertilized wet samples in duplicates from both Skedevi and Öjebro. The samples were equilibrated for 3 days, centrifuged at 2000 rpm for 20 min and filtered using an Acrodisc 0.2 µm filter.

4.3.1 Analysis

ALS Scandinavia AB
- Batch series extracts
- 0.1 M HNO_3 extracts

  These were analyzed with their E-2a method on ICP-SFMS. A high resolution analyzing technique done on samples with high interference, able to detect low concentrations (ALS, 2018).

Swedish university of agricultural sciences (SLU), Uppsala
- DOC

  Analyzed with a TOC-VCPH Shimadzu, on filtered (0.45 µm) supernatant from centrifuged soil according to TOC SS-EN 1484 (Swedish standard institute, 1997) standard method. This analyze was done in the accredited geochemical laboratory.

- Tot-C and tot-N

  Analyzed at the soil chemistry laboratory using a LECO Truemac CN, following the SS-ISO 10694 (Swedish standard institute, 1996) standard method.

4.4 Modelling

4.4.1 Model optimization

To build a model that fitted the dissolved metal concentrations in the extracts, the results from the batch experiments were compared to those predicted using Visual MINTEQ 3.1. In VM 3.1 the parameters from the values from DOC measurements, HNO_3 (geochemically active trace elements), $BaCl_2$ (base cations), oxalate

extractions (P and Si) as well as the HFO were used found in A2-A3. Also used were the pH and the added amount of NO_3 and Na for each pH. The concentrations of dissolved metals from batch experiments as a function of pH were compared to those simulated by the software. To improve the fit, the values for the trace elements; Cd, Ni, Zn and Al as well as f_{HS} were adjusted, the new values are within brackets in Table A2-A3. To find the best fit, all HNO_3 metal concentrations had to be reduced; this was likely due to the HNO_3 ability to dissolve small amounts of the non-geochemically active trace elements e.g. minerals.

For model setup of organic complexation, the Stockholm Humic Model (SHM) mostly with default assumptions to simulate soil organic matter (SOM), was used. Here, the ratio of active dissolved organic matter (DOM) to DOC is 2 whereas 100% of the active DOM was FA and none of the HA is considered to be dissolved. Particulate HA and FA (HS) are by default assumed to be present in equal proportions in the active part of the SOM. The particulate active OM is assumed to be twice the amount of C_{tot}. The active fraction of the particulate organic matter (f_{HS}) was, however, adjusted from the default value of 0.50 to 0.80 to obtain the optimal model fit.

Sorption onto (hydr)oxides was estimated by using the diffuse layer model (DLM) of Dzomback & Morel (1990) using the default value for specific surface areas of ferrihydrite of 600 m^2/g. To provide input to the required concentrations of these (hydr)oxides, the oxalate- and pyrophosphate extractable Al and Fe values were used, assuming that oxalate-extractable Fe was a good representation of ferrihydrite, and that oxalate-extractable Al – pyrophosphate-extractable Al represented $Al(OH)_3$ with the same adsorption properties as those of ferrihydrite (Table 2). Solid phases of ferrihydrite and $Al(OH)_3$(s) were assumed to govern the activities of Fe^{3+} and Al^{3+} in the soil solution. Model parameter values and equilibrium constants are shown in Table 2. Input concentrations of trace metals are taken from the HNO_3 extraction and the cations from $BaCl_2$ extractions found in Table A4-A7.

Table 2. *Parameters used in the Visual MINTEQ model setup with description of assumptions done.*

Parameter		Assumption
Active SOM	(solid)	Tot-C·2/(s/w)
S/W		Dry soil/soil water
Active FA and HA (HS)	(solid)	SOM·f_{HS}/2
f_{HS}		0.8
HFO		$(Al_o+Fe_o) - (Al_P+Fe_P)$
Infinite solid phase		Ferrihydrite (aged) K_s = 2.69
Possible solid phase		$Al(OH)_3$ (soil) K_s = 8.29
Atmospheric CO_2 pressure		0.005 atm
Ion strength		0.002

4.5   Simulation

Long-term scenarios were designed using the optimized model from the batch experiment results (see A2-3). Na and NO_3 concentrations from the model setup batch equilibrations (see Ch 3.3) were changed to closer match reality. The measured concentration of Na from the $BaCl_2$ extractions of unfertilized soil (Table 1: Table A6) was used as the "real" concentration. The assumption was done that the ion strength was 0.002 and atmospheric pressure 0.005 atm (Table 2). The initial (year 0) values of DOC was based on the batch series at pH 6.2 (Öjebro) and 6.0 (Skedevi) (see Table A2-A3). By varying parameter values for metals, HS and DOC, different scenario simulations were performed. The three scenarios were: ash, digestate and a combination of ash and digestate ("mix"). The input values are shown in Table 3. All 3 scenarios were based upon a similar P fertilization level of 20 kg ha^{-1}yr^{-1} to assure comparability. The amount of P applied was set to be below the Swedish environmental protection agency`s regulations about use of sewage sludge in agriculture (SNFS 1994:2) of 35 kg ha^{-1} yr^{-1}. The annual rates for all fertilizers can be seen in Table 3. None of the limits in SNFS (1994:2) for allowed metal inflow from digestate or ash to soil was exceeded with this rate. The atmospheric deposition load has not been taken into concern in this thesis when calculating the mass balances for the input variables. However, for Ca, Mg, Cu, Zn and Ni the atmospheric deposition is much smaller than the leaching (Eriksson *et al*., 2013). The annual deposition of Cd was between 0.095 and 0.14 kg ha^{-1} during 2015 within the region of Östergötland, according to the Meterological Synthesizing Centre-East (MSC-E, 2017). The deposition load varies throughout the country with a range from 0.024 to 0.25 kg ha^{-1} yr^{-1} (MSC-E, 2017). The load can be compared to the applied amount from ash and digestate as well as to the losses in Table 3.

4.5.1   Ash input data

Cations present in the bottom ash (Mg, K, Ca and Al, as well as the trace metals examined in this thesis, Cd, Cu, Ni, and Zn) were assumed to affect soil chemistry. Since the concentrations of cations in ash were much higher than the other metals

they were used in the simulation. P was not used as a variable in the model, due to assumption of complete plant uptake. In order to make assumptions of the metal accumulation rate in soil, consideration of presumptive leaching and plant uptake has been taken into concern. Based on several studies and reports on metal leaching, plant uptake and plant tissue concentrations, estimates were made, which are shown in Table 3 together with the source references. In line with the total concentrations in the materials considered, Cd, Mg, Zn, Cu, Ca and Al are accumulated at much higher rates by application of ash than of digestate. The mass of ash applied annually was 1.5 Mg ha^{-1} (Table 3). Overall 45 000 Mg ash (on a dry weight basis) was applied over 30 years.

Table 3. *Mass balances for all metals in kg ha^{-1} yr^{-1}. Soil organic matter variables DOC and HS are in mg L^{-1}yr^{-1}. "Simulation variables yr^{-1}" were used in the simulation model. Annual rate of ash, mix and digestate are in kg ha^{-1}.*

Variable	Input [+]			Outtake [−]		Simulation variables yr^{-1}		
	Ash	Dig.	Mix	Plant up-take	Leaching & Runoff	Ash	Dig.	Mix
Ca	278	61	134	12[a]	99[h]	167	-50	23
Mg	29	5	19.3	6[a]	17[h]	6	-18	-3.7
K	159	160	153	134[b]	1.8[h]	23	24	17
Al[i]	27.2	10.9	9.5	0.2[c]	10[f]	17	-0.07	-0.7
Cd	0.02	$2.2 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$	$1.8 \cdot 10^{-5}$[d]	$2.1 \cdot 10^{-4}$[g]	0.02	0	0
Zn$_{ash}$	4.72	-	-	0.16[e]	0,1[e]	4.46	-	-
Zn$_{dig}$	-	0.12	1.66	0.04[e]	0.03[e]	-	0.05	1.59
Cu$_{ash}$	0.14	-	-	0.04[e]	$7 \cdot 10^{-4}$[e]	0.14	-	-
Cu$_{dig}$	-	0.01	0.1	0.01[e]	$2 \cdot 10^{-4}$[e]	-	-	0.09
Ni$_{ash}$	0.027	-	-	0,016[e]	0,01[e]	$6 \cdot 10^{-4}$	-	-
Ni$_{dig}$	-	0.09	0.03	$4 \cdot 10^{-4}$[e]	$3 \cdot 10^{-4}$[e]	-	0.09	0.03
DOC[b]	-	-	-	-	-	-	≤0.006	≤0.005
HS	-	-	-	-	-	-	≤0.006	≤0.001
Dig.	-	$1398 \cdot 10^{9}$	$930 \cdot 10^{9}$	-	-	-	-	-
Ash	$1500 \cdot 10^{9}$	-	$500 \cdot 10^{9}$	-	-	-	-	-

[a]Hervik & Rahbek Pedersen, 2004
[b]Kirchmann *et al.,* 1994
[c]Kabat-Pendias, 2001
[d]Dipendra, 2013
[e]Adjusted from Bengtsson *et al.,* 2006
[i]Etiegni *et al.,* 1991 & Huang *et al.,* 1992

[f]Zhang *et al.,* 2016: Linefur *et al.,* 2017
[g]Öborn *et al.*, 2005
[h]Eriksson *et al.*, 2013

4.5.2 Digestate input data

The digestate has a high fraction of organic matter. For the simulation of application of digestate onto arable land an increase of SOM and thus HS and DOC was therefore assumed (Table 3). Measured data for % C from "The Ultuna long-term soil organic matter experiment between 1956-1991" (Kirchmann *et al*., 1994) was used as a basis for the expected increase in the soil organic matter content. Firstly, due to a lower amount of C applied in this simulation model (C_{tot}) compared with the amount applied in the Ultuna experiment (C_U), a C_{tot}/C_U ratio was calculated. This ratio was multiplied onto the C_U before further calculations. Secondly, a polynomial 3rd order trend line was found for best fit to C_U values against time (year) (see Figure A1). The equation for the trend line was transferred to Öjebro and Skedevi as visualized with the example of eq. 5:

$$y = 2^{-5}x^3 - 0.0008x^2 + 0.0181x + m \qquad (5)$$

where:
x = year
m = measured C_{tot} for unfertilized soil (Table 1) $\cdot 2/(s/w)$
y = SOM

Same relationship between SOM and HS was then used as described in Table 2. In this way new values for HS were given for each year in the simulation scenarios with digestate and the mix which were used in the simulations. The increase of SOM was assumed to be continuous throughout the simulated 30 years (Kirchmann *et al.,* 1994).

The increase of SOM was also assumed to lead to an increase in DOC. This was based on a linear relationship between the amount of added digestate and DOC found by Antoniadis & Alloway, (2002). This relationship was mimicked using this equation:

$$DOC_n = SOM_n \cdot \frac{DOC_m}{SOM_m} \qquad (6)$$

where:
DOC_n = the calculated new value for DOC increased by the addition of digestate
SOM_n = the calculated values of SOM from eq 5
DOC_m = measured value of DOC for unfertilized soil (Table 1)
SOM_m = measured C_{tot} for unfertilized soil (Table 1) $\cdot 2/(s/w)$

The added amount of digestate was based on the P_{tot} content and the application rate of 20 kg P TS ha^{-1}, which resulted in 1500 kg digestate yr^{-1} (dry weight) (Table 3). During 30 years of application this summed up to 236 400 Mg digestate.

4.5.3 Mix input data

The mix was created by 2/3 digestate and 1/3 ash. This blend incorporates 930 kg ha^{-1} yr^{-1} digestate (dry weight) and 500 kg ha^{-1} yr^{-1} ash (dry weight) (Table 3), based on a fertilization level of 20 kg P ha^{-1} yr^{-1}. All input data from ash and digestate were adjusted accordingly to kg ha^{-1} (dry weight). The input parameters for DOC, HS, Ca, Mg, K and Al of this scenario can be seen in Table 3.

5 Results and discussion

5.1 Model fit to batch experiment data

The model did not match the dissolved metal concentrations from the batch experiment, when only default assumptions were being made. Adjustments were made by reducing the concentrations of geochemically active metals. Moreover, the active organic matter fraction of the particulate organic matter was changed from the default value of 0.50 to 0.80 to arrive at the best fit. This is still within the range suggested by Groenenberg *et al.* (2014) and by Sjöstedt *et al.* (2010). Despite these changes, the model did not provide a perfect fit to the data, as can be seen in Figure 1. Either the simulated metal concentrations decreased too much or too little with increased pH. As for Cu, the measured vales did never really decrease to 0, which should be the case at increasing pH values. These problems can be since very low background concentrations of metals were dealt with in this work. The measured values were therefore close to the detection limits of the method. Moreover, contamination of Cu from the conservation acids used in the laboratory cannot be entirely excluded. This would give rise to a higher concentration than actually present in the soil. This would also explain why Cu did not decrease to zero and hence the difficulty to get the model to fit properly. For Cd the extracted values gave lower concentrations than the model simulation suggested. This could be caused by stronger Cd binding onto solids than the model predicts. For Zn, Ni and Al the simulation indicated a lower concentration in solution at high pH than the observed values. Again, it is not clear what caused these differences.
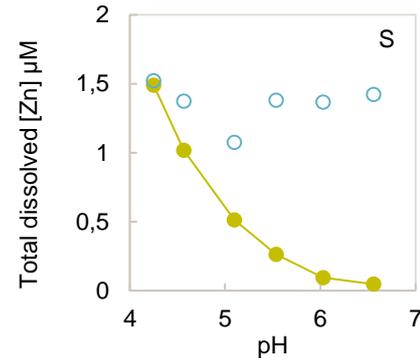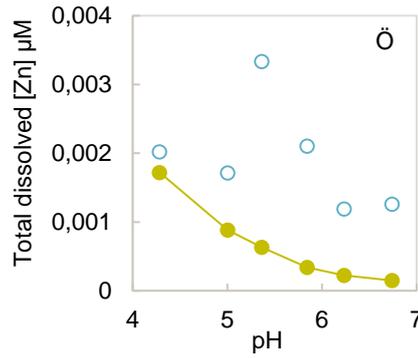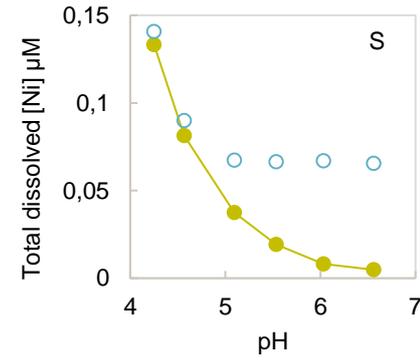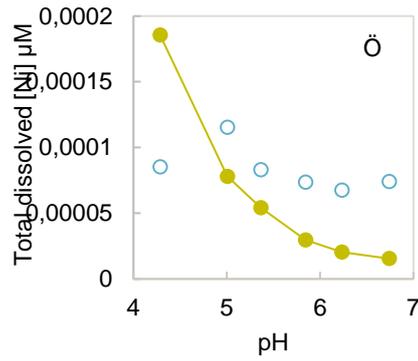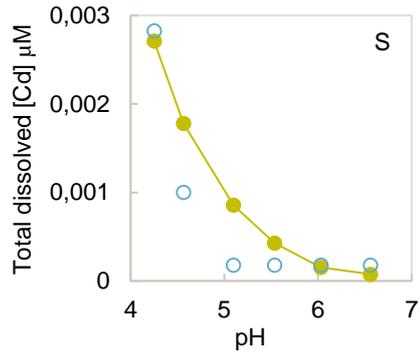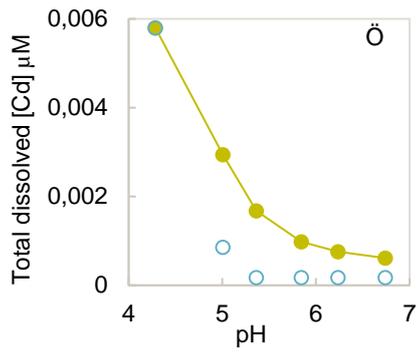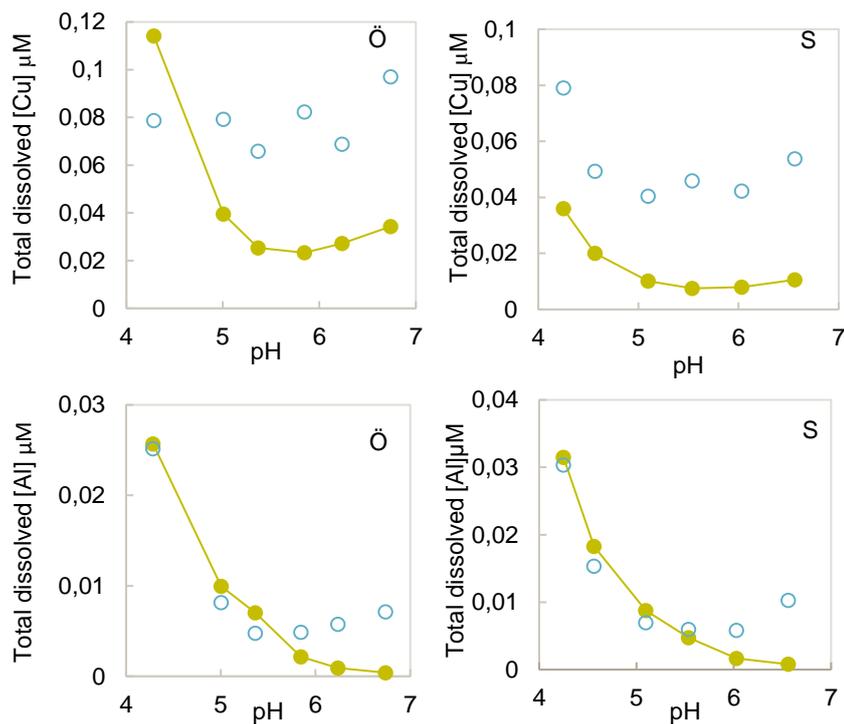
Figure 1. Modelfits to dissolved metals from the batch experiments. Simulated values are in yellow (dots and line) and measured values are in blue (circles). Left column: Öjebro soils, denoted with (Ö); right column: Skedevi soil (S).

5.2   The simulations

5.2.1   The simulaton set-up

Extracted metals, C_{tot}, and pH for the different soil samples at Skedevi and Öjebro did not reveal any clear trends between treatments (ash, digestate and unfertilized) (Table A1). Therefore, the optimized model parameter values for the *unfertilized* soils were used to represent *year 0* for all scenarios. An alternative could have been to use the extracted values for the ash- and digestate-fertilized soil samples, hence starting with the simulations at year 1. The initial pH of the scenarios was determined by the model using the "calculated from mass and charge balance" mode and is shown in Figure 2.

5.2.2   pH changes

In the simulations the calculated pH value was influenced by the assumed change of the parameter values each year. This resulted in different outcomes for the two soils as seen in Figure 2. At Öjebro a relatively large pH increase was calculated

as a result of applying ash, from the initial pH of 6.3 to 6.7 during 30 years of application. When compared to the increase generated by ash at Skedevi (from 6.1 to 6.2) the difference is noticeable. At both sites, the same number of cations was added. As for the application of digestate, a decrease in pH was generated. Again, this trend was stronger for Öjebro than for Skedevi. The pH value at Öjebro decreased from 6.3 to 5.8 while for Skedevi the pH decreased from 6.1 to 5.8. The 'mix' simulations resulted in a stable pH throughout the period for both soils, with changes < 0.1 pH unit.

As for the long-term experiment at Ultuna, application of digestate lowered the pH of the soil (Kirchmann *et al.*, 1994). The pH decrease observed in that experiment was 0.2 pH units over a period of 35 years. The decrease was claimed to be generated due to the high sulfur content and the organic acids within the digestate (Kirchmann *et al.,* 1994). The pH decrease of 0.5 and 0.3 units of the simulations in this study is consistent with long-term results from Ultuna. However, the model of this study only considered the increase in organic matter brought about by the digestate and did not consider pH differences due to the sulfur content.

The pH increases of 0.4 and 0.1 units of the Öjebro and Skedevi soils, respectively, is also within a realistic range (Saarsalmi *et al.,* 2012). The Skedevi soil acid-base buffering capacity was stronger than the soil of Öjebro. This correlate and can be explained by the higher clay and silt content as well as the higher CEC. The differences in pH change can explain some of the differences in metal solubility between the soils. The model was simplified in regard of anion-content; an assumption of an ion strength of 0.002 was generalizing the existence of Cl^-, CO_3^{2-} and SO_4^{2-}. These are anions normally occurring in clay soils in Sweden (Eriksson *et al.,* 2013). The lack of these anions might affect the pH change regarding the slopes steepness but probably not the general trends.
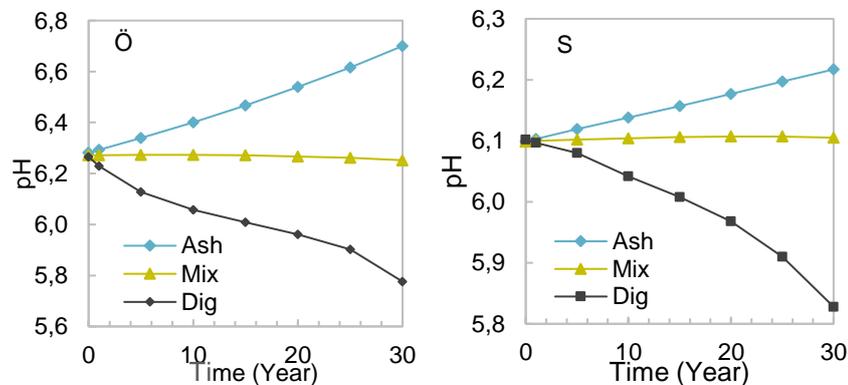
Figure 2*.* Simulated pH changes for the different scenarios and soils.

5.2.3 Solubility trends

The model-simulated distribution of geochemically active species (sorbed, dissolved and precipitated) at year 0 showed that less than 3 % of the examined elements at both Skedevi and Öjebro were dissolved. The elements with the highest

percentages of dissolved species were Zn followed by Cd, while Al showed the lowest of <0.3%. Dissolved species consisted mostly of free hydrated ions and soluble complexes with fulvic acids (M-FA), but $M-HPO_4$ and $M-PO_4$ complexes also occurred. The dissolved part of Cd, Ni and Zn preferred to exist as free hydrated ions (see Eq. 1), while Cu and Al had a very low activity as such. Instead, the latter two preferred the M-FA complexation (see Eq. 2).

Most common phase for all metals was the solid, formed by complexation to organic matter. Here, the HA part of the organic matter was the most important part forming specific binding. Besides the specifically sorbed solid M-HA species, Al was found to be precipitated as Al-hydroxides. Cd, Ni and Zn were also to be found as small amounts of electrostatically bound in the diffuse layer as well as sorbed onto Fe-oxides. The phase distribution differed between metals and the two soils.

The changes from the initial phase distribution to after the addition for 30 years of ash, mix or digestate after are shown in Figure 3. There were some major general trends (with Al excluded): (a) ash gives rise to an increase of dissolved species, (b) digestate generates a solubility decrease and (c) the mix fertilizer kept the solubility almost steady.
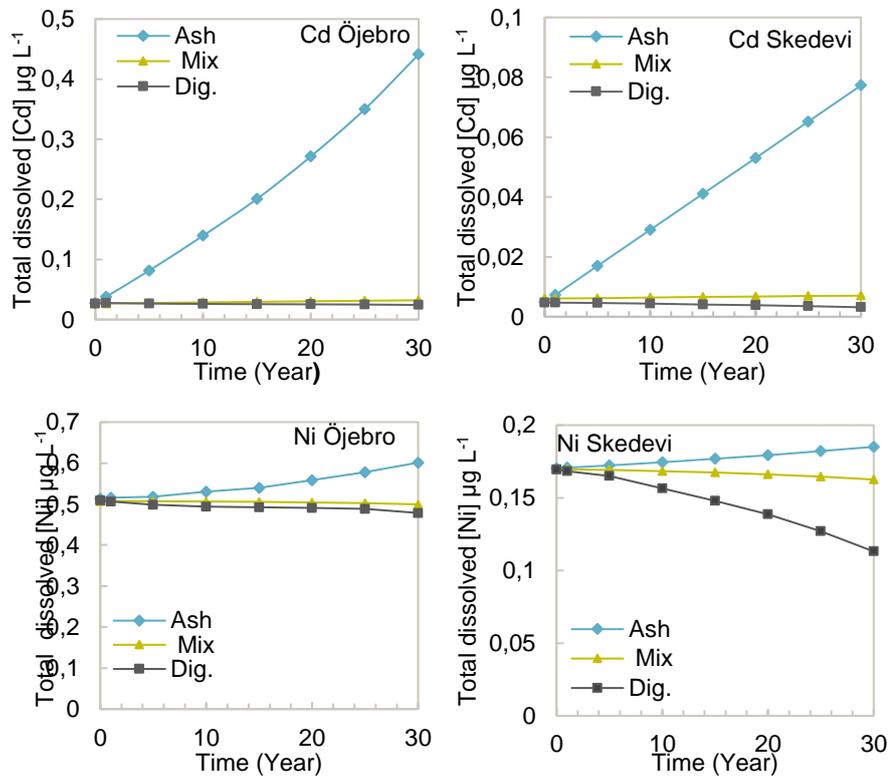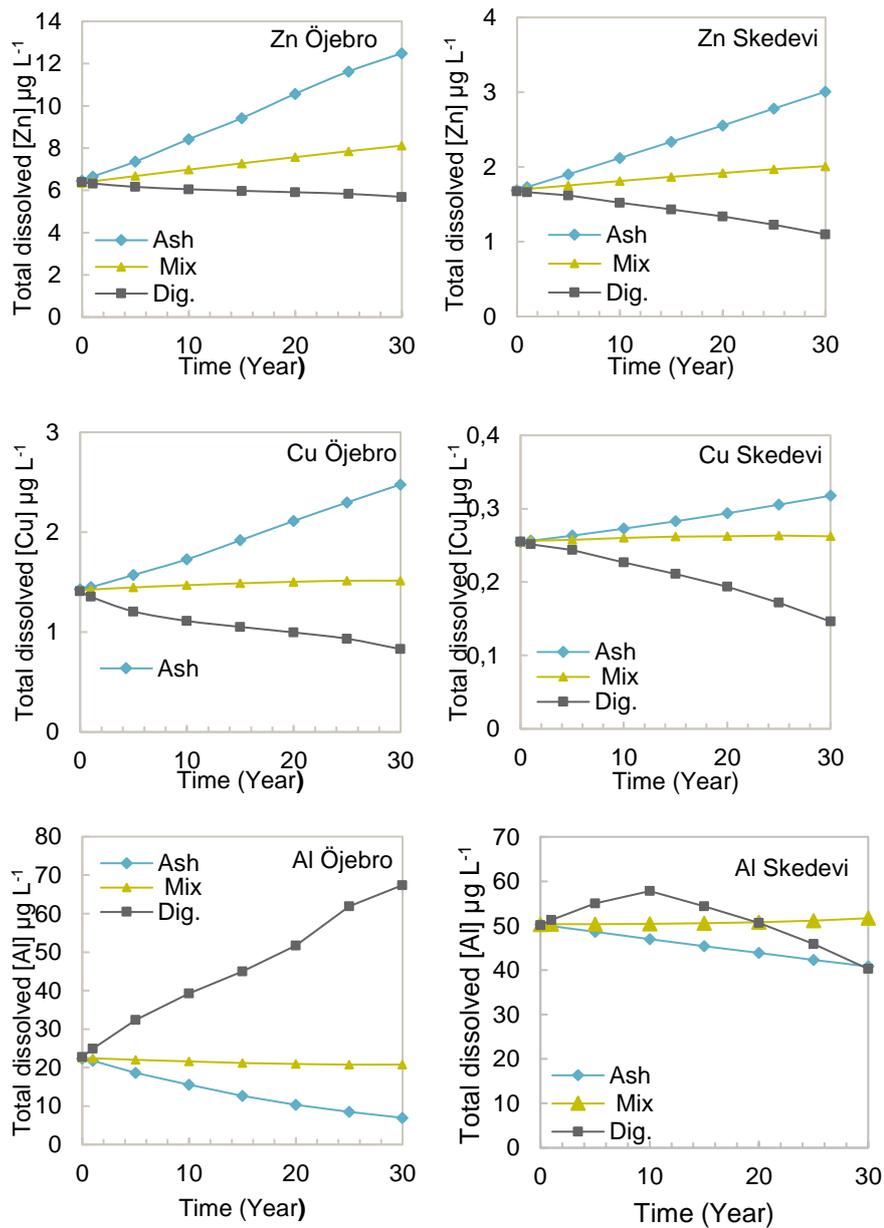
Figure 3. Total dissolved metal concentrations at Öjebro and Skedevi in µg L^{-1}. Observe the different value magnitudes between Skedevi and Öjebro for same metal, also between metals.

5.2.4 Ash

According to the model simulation, application of ash caused an increase of dissolved Cd, Cu, Ni and Zn. Hence the K_d decreased for these metals over the time-period examined. Cadmium had the highest increase in solubility. This trend could be explained by the Irving- Williams series (ch 2.2 eq 4). Thus, Ca is added to the

bulk solution in much higher concentrations than the existing concentrations of Ca and also Cd, Cu, Ni and Zn (see Table 1). Because of the increased concentration, Ca^{2+} was able to compete with these ions primarily on ion exchange positions, but also (to a minor extent) on the inner-sphere complexation sites of soil organic matter (Eriksson *et al.,* 2013). Cd, Cu, Ni and Zn was thereby desorbed as free ions in solution. According to Shi *et al.* (1998), Cu tends to desorb in spite of its strong binding to soil particles. This is due to its high affinity for DOC and to a minor extent also the formation of hydroxide complexes at high pH. This seemed to be the case also in this simulation in which the increase of Cu solubility was found to be due to the formation of $FA_2Cu_{(aq)}$ and $FA_2CuOH_{(aq)}$. Because of its strong affinity for organic matter, Cu is not easily desorbed by Ca. This strong affinity for OM might also explain why Cu was less soluble at Skedevi than at Öjebro; at Skedevi the OM content (C_{tot}) was higher than at Öjebro (Table 1).

At Öjebro, the stronger pH increase created a lower K_d value for Cd, Cu, Ni and Zn than at Skedevi. For Cd, Ni and Zn the ash caused a lower K_d value than for Cu, due (at least in part) to Ca competition.

For Al, the scenario was more complicated; Al was the only metal becoming less soluble with applied ash, hence the increase in K_d. The decrease of Al in solution was due to the precipitation of Al hydroxides. The equilibrium between the solid and dissolved phases is strongly pH-dependent (Essington, 2015) as can be seen in Eq. 8. For inorganic soils at pH > 4.2 the precipitation of $Al(OH)_3$ may govern the Al^{3+} activity and at pH > 6 dissolved inorganic Al is found at very low levels (Gustafsson *et al.*, 2001: Essington, 2015):

$$Al(OH)_3 + 3H^+ \Leftrightarrow Al^{3+} + 3H_2O \qquad (8)$$

Even though the pH increased in both soils (to a rather large extent at Öjebro) this did not decrease the metal solubility. For Zn, Cd and Ni the added Ca was in a sufficiently high amount to cause an increase in the dissolved concentration. Hence, Ca was one of the most important variables controlling the K_d value of these metals. However, Ca was also the most uncertain input parameter in the simulations. Cation additions were based on several literature sources. The losses through plant uptake were based on a Swedish source Hervik & Rahbek Pedersen (2004), while the leaching losses are based on Eriksson *et al.* (2013) and Kirchmann *et al.* (1994). All these sources were the best that could be found at the time of writing this thesis. No effort was made to consider in detail the different application rates for different metals with different fertilizers. When applying more Ca as in the ash scenario, a greater loss of Ca per dry weight could be expected. However, the uncertainties may be too big anyway to make it necessary to account for this detail. Besides, the plant uptake is correlated with the type of plant, soil pH and growth rates (Dipendra, 2013), whereas the leaching and runoff losses depend on the application as well as precipitation rates, geographic location, soil type and soil management among other parameters.

5.2.5 Digestate

The trends of the digestate simulation scenario showed a decrease of dissolved Cd, Cu, Ni and Zn with time, hence an increase of the K_d value. This scenario led to an increase in particulate HA and FA (HS) as well as dissolved FA. The digestate also contributed with competing cations to the soil, however, in much lower doses (Table 3). The sorption affinity was less affected by the decreasing pH of digestate application than of the added organic matter. Thus, the applied surface sites due to the OM counteract the effect of pH. There was a strong relationship between the decrease in Cd, Cu, Ni and Zn solubility and the increase in organically bound metals which can be seen in Figure 4. This result agrees with other literature, where HS is described as having a strong affinity towards cations (Shi *et al*., 1998: Khai *et al*., 2008: Linde *et al.,* 2007: Berggren Kleja *et al.,* 2006). Thus, the K_d value of Cd was changed to a smaller extent compared to the K_d values of Ni and Zn. Possible reasons include: a high initial sorption affinity within the soil, as well as the competing effect from the other cations on Cd solubility as suggested by Bergkvist *et al*. (2005) and Naidu *et al*. (1994)**.**
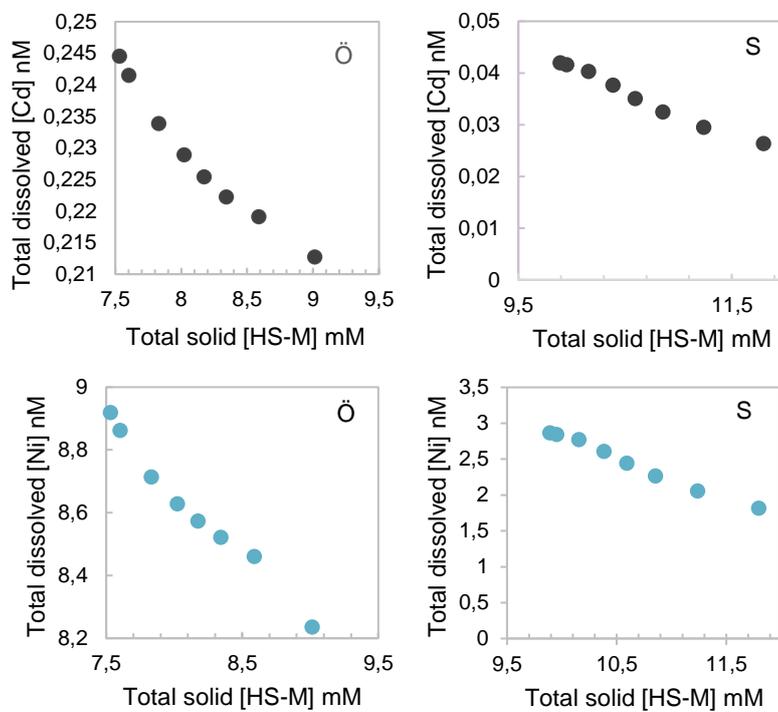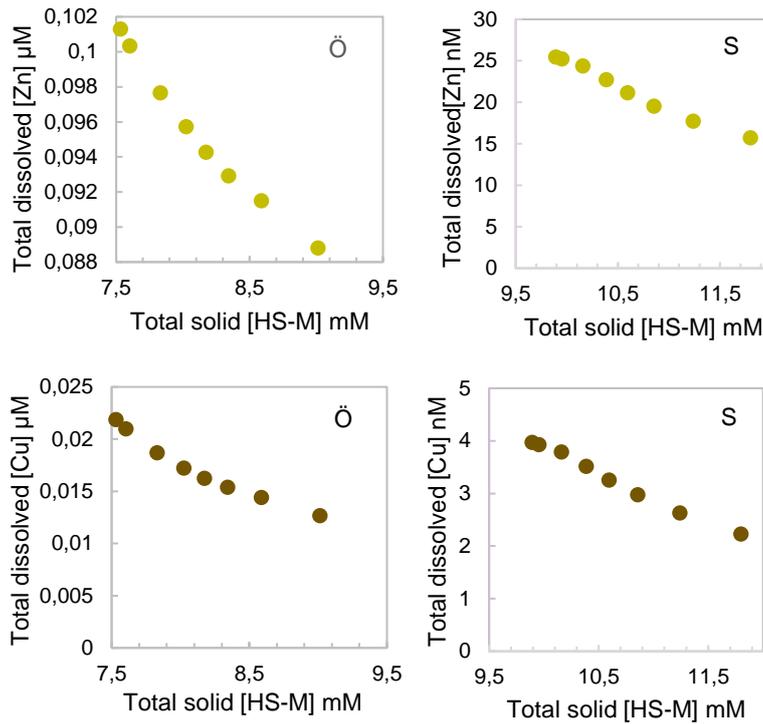
Figure 4. Total dissolved Cd, Ni, Zn and Cu concentration changes in relationship with the increase of humic substance complex formations with metals (HS-M) at Öjebro (Ö) and Skedevi.

An increase in DOC was introduced as well in this scenario. Hence, the formation of dissolved FA species did not affect the solubility sufficiently to cause an increase in in dissolved metals through soluble FA complexes. This suggests that the increased binding of metals on solid-phase HA brought about by the increase in soil organic matter from the digestate was the most influencing factor behind the observed results.

By contrast, aluminum was rendered more soluble with time in the digestate scenario. Again, as for the ash, this was due to the importance of Al hydroxide as a solubility control and to the fact that the stability of this mineral phase is very pH-dependent. With lower pH Al^{3+} dissolves (Eq. 8). The application of digestate is simulated as creating an annual loss of Al from the agricultural soil (Table 3). This loss was generated due to the small addition from the digester combined with the low suggested value for plant uptake, both which in comparison with the suggested loss from leaching and runoff are negligible.

As mentioned above, the addition of HS from digestate was a crucial parameter for the simulated metal solubility. This variable was the single most important one controlling sorption, which caused a decreased K_d value for all metals. Therefore, the assumed input values of this parameter (Table 3) was of importance. The annual input used was based on the long-term experiment at Ultuna by Kirchmann *et al.* (1994). Other studies were found that showed a similar trend of increased C_{tot} due to digestate applications over time (Kätterer *et al.,* 2014: Sharma *et al.,* 2017).

The study of Kirchmann *et al.* (1994) had the longest sampling record of the studies found and as the soil type and climate was similar to the ones of the soils in the present thesis, this reference was chosen as the source of the input value for HS. A number of factors governs the accumulation of organic matter in soil, which lead to differences between soils and years. At some point a steady state should be reached for C_{tot} if organic matter is added to an arable soil during several years. Such a steady state had not been reached after 35 years in the experiment by Kirchmann *et al.* (1994), leading the authors to suggest that it would take between 50 and 150 years to reach steady state, depending on the application. Based on this assumption a continuous increase of HS during the whole 30-year time-period was assumed.

The increase in DOC assumed in the digestate scenario seemed of little importance for metal solubility. However, it is more likely to be of interest if elevated rates of digestate are applied (>10 Mg ha^{-1} yr^{-1}; Antoniadis & Alloway, 2002).

5.2.6 Mix

Finally, the mix, consisting of 2/3 digestate and 1/3 ash, made a low impact on metal solubility compared with the other two scenarios (Figure 3).

The effect of a mixture between ash and digestate would be much dependent on the mixing ratio, and the proportions used in the model were about right to cause a negligible effect on dissolved metals. However, even if other mixing proportions were used, the effect on metal solubility would still be smaller compared to the other scenarios.

5.3   Future use

In a long term perspective, the single use of either ash or digestate will alter the pH as well as the solubility of cations including metals. When a change leads to an increase of Cd solubility it would probably lead to an increased plant uptake of Cd, thus entering the food chain to a larger extent. Also, when becoming more mobile increased amounts of Cd could enter groundwater, lakes and streams. On the other hand, in case of a decrease in metal solubility, micronutrients such as Zn will be less phytoavailable, which may be problematic in certain soils. In agricultural soils the pH value should be stable to support a good environment, both for the microgranisms as well as for the plants to function. In other words, the most beneficial scenario of the three considered, for most agricultural purposes, would be to use a mix of ash and digestate. This study showed that, because of the small impact the mix had on metal solubility, it may be a better fertilizer product than the single use of digistate. The mix of digestate and ash would be useful in two ways: by recycling of nutrients from the ash, and to limit undesirable effects of soil chemistry as caused by the fertilizer product of digestate.

A factor not considered in this study is how digestate and ash affect the N chemistry. Bernesson *et al.* (2008) observed that if more than 10% of ash is added

to the mix with digestate, the pH of the mix rose and NH_3 was favoured resulting in N losses. In our case 33% ash was used, which, if the results of Bernesson et al. (2008) could be generalized to the soils used in this study, most likely would lead to N losses. Therefore, further investigations are needed on how different proportions of ash affect N and other soil chemical variables. Furthermore, this study only included 2 soils that were quite similar in terms of soil chemical characteristics. The study could be widened to also include other soil types. Moreover, as mentioned earlier (section 2.3), there were differences between different digestates and ashes. In this study only one ash and two digestates were investigated.

6 Conclusion

The model simulations performed in this study illustrated, in least in a qualitative sense, how metal solubility is likely to be impacted by long-term application of ash, digestate and by a mixture of the two.

- Ash alone generated an increase in solubility for Cd, Cu, Ni and Zn as well as an increase in pH. For Al the solubility decreased. These results did not agree with the hypothesis that ash would decrease metal solubility due to pH rise. Other cations added with the ash (in particular Ca^{2+}) were affecting metal solubility to a larger extent than the decrease in pH.
- Digestate alone decreased the solubility of the metals through the addition of organic matter. An increased formation of metals bound to solid-phase organic matter was the most important change brought about by the digestate application. The exception was Al in the soil of Öjebro.
- When applying the mix of ash and digestate, a relatively unaltered change in the solubility was observed for all metals. This scenario indicates that the increased solubility caused by ash was counterbalanced by the addition of digestate.
- The benefit of adding ash to digestate before being used as fertilizer is not only due to the recycling of its nurients, but also to the long term benefits of keeping the agricultural soil at a stable pH.

References

Antoniadis, V. Alloway, B.J. 2002. The role of dissolved organic carbon in the mobility of Cd, Ni and Zn in sewage sludge-amended soils. *Environment pollution* 117:515-521.

Benedetti, F.M. Milne, J.C. Kinniburgh, G. D. Van Riemsdijk, H. W. Koopal, K.L. 1995. Metal ion binding to humic substances: Application of the non.ideal competitive adsorption model. *Environ. Sci. Technol.* 29:446-457. doi:10.1021/es00002a022.

Berggren, D. Elert, M. Gustafsson, J.P. Jarvis, N. Norrström, A. 2006. *Metallers mobilitet I mark.* Rapport 5536. Naturvårdsverket.

Bergkvist, P. Berggren, D. Jarvis, N. 2005*.* Cadmium solubility and sorption in a long-term sludge-amended arable soil*. Journal of Environmental Quality* 34 (5):1530-1538.doi:10.2134/jeq2004.0385

Bernesson, S. Olsson, J. Rodhe, L. Salomon, E. Hansson, P. E. 2008. *Admixture of biofuel ash into liquid biogas digestate.* SLU Rapport 002 Uppsala. ISSN 1654-9406.

Cao, Y. Conklin, M. Betterton, E. 1993. Competitive complexation of trace metals with dissolved humic acid. *Environment health perspectives* 103:29-32.

Carrillo-González, R. Šimůnek, J. Sauve, S. Adriano, D. 2006. Mechanisms and pathways of trace element mobility in soils. *Advances in agronomy* vol. 91. doi:10.1016/S0065-2113(06)91003-7.

Christensen, T. H. 1984. Cadmium soil sorption at low concentrations: l. Effect of time, Cadmium load, pH, and Calcium*. Water, air and soil pollution* 21 (1):105-114. doi.10.1007/BF00163616.

Demeyer, A. Voundinkana, J. C. Verloo, M. G. 2001. Characteristics of wood ash and influence on soil properties and nutrient uptake: an overview. *Bioresource Technology* 77 (3): 287-295.

Demirel, B. Göl, N.P. Onay, T.T. 2012. Evaluation of heavy metal content in digestate from batch anaerobic co-digestion of sunflower hulls and poultry manure*. J mater cycles waste manag.* 15:242-246 doi 10.1007/s10163-012-0107-4.

Dzombak, D.A. & Morel, F.M.M. 1990. Surface complexation modeling: Hydrous Ferric Oxide, John Wiley & Sons, New York.

Eriksson, J. 2001. *Halter av 61 spårelement i avloppsslam, stallgödsel, handelsgödsel, nederbörd samt i jord och gröda.* SLU Rapport 5148 Naturvårdsverket Stockholm.

Essington, M. E. 2015. *Soil and water chemistry: an integrative approach*. 2:ed CRC Press.

Etiegni, L. ´Campbell, A.G. 1990. Physical and chemical characteristics of wood ash. *Bioresource technology* 37: 173-178.

European commission 2016. *Environment action programme to 2020.* Available at: http://ec.europa.eu/environment/action-programme/ [2018-08-28].

García-Sánchez, M. Siles, J. A. Cajthaml, T. García-Romera, I. Tlustoš , P. Száková J. 2015. Effect of digestate and fly ash applications on soil functional properties and microbial communities. *European journal of Soil Biology* 71: 1-12. doi.org/10.1016/j.ejsobi.2015.08.004.

Groenenberg, J. E. Lofts, S. 2014. The use of assemblage models to describe trace element partitioning, speciation and fate: a Review. *Environmental toxicology and Chemistry* 33 (10): 2181-2196. doi.org/10.1002/etc.2642.

Gu, X. Evans, L. J. 2008*.* Surface complexation modeling of Cd(ll), Cu(ll), Pb(ll) and Zn(ll) adsorption onto kaolinite. *Geochimica et Cosmochimica Acta*, 72: 267-276. doi:10.1016/j.gca.2007.09.032.

Guo, F. Ding, C. Zhou, Z. Huang, G. Wang, X. 2018. Effects of combined amendments on crop yield and cadmium uptake in two cadmium contaminated soils under rice-wheat rotation*. Ecotoxicology and environmental Safety* 148: 303-310. doi.org/10.1016/j.ecoenv.2017.10.043.

Gustafsson, J.P. Berggren, D. Simonsson, M. Zysset, M. Mulder, J. 2001. Alumnum solubility mechanisms in moderately acid Bs horizons of podzolized soils. *European journal of soil science*:52, 655-665.

Gustafsson, J.P. 2018. Visual MINTEQ version 3.1. A free equilibrium speciation model. Available at: https://vminteq.lwr.kth.se/download/ [2018-09-09].

Hervik, H & Rahbek Pedersen, T. 2004. *Svavel, natrium, magnesium, calcium och mikronäringsäm nen I det ekologiska lantbruket.* Ekologisk växtodling. Jordbruksverket Jönköping.

Hjerpe, K. Andersson, S. Stendahl, J. 2014. *Återför aska till skogen*. Information från Skogsstyrelsen.

Kabat-Pendias, A. 2001. *Trace elements in soil and plants*. 3rd ed. CRC Press LLC USA.

Kaiser, K. & Zech, W. 1996. Defects in estimation of aluminum in humus complexes of podzolic soils by pyrophosphate extractions. *Soil science* 161 (7), 452-458.

Khai, N. M. Öborn, I. Hiller, S. Gustafsson, J. P. 2008. Modeling of metal binding in tropical Fluvisols and Acrisols treated with biosolids and wastewater. *Chemosphere* 70 (8): 1338-1346. doi.org/10.1016/j.chemosphere.2007.09.046.

Kirchmann, H. Persson, J. Carlgren, K. 2004. *The Ultuna long-term soil organic matter experiment, 1956-1991*. Department of soil sciences Reports and Dissertations 17. Uppsala.

Kätterer, T. Börjesson, G. Kirchmann, H. 2014. Changes in organic carbon in topsoil and subsoil and microbial community composition caused by repeated addition of organic amendments and N fertilisation in a long-term field experiment in Sweden. *Agriculture, Ecosystems and Environment* 189: 110-118. doi:.org/10.1016/j.agee.2014.03.025.

Lantmännen. 2018. *Produktkatalog*. Available at: https://c4prodiktkatalog.lantmannen.se [2018-09-04].

Linde, M. Öborn, I. Gustafsson, J. P. 2007. Effects of changed soil conditions on the mobility of trace metals in moderately contaminated urban soils. *Water, air and soil pollution* 183 (1-4):69-83. doi.org/10.1007/s11270-007-9357-5.

Linefur, H. Stjernman Forsberg, L. Forsberg, K. Andersson, S. Johansson, G. Blomberg, M.2017. *Växtnäringsförluster i små jordbruksdominerade avrinningsområden 2015/2016*. Årsredovisning för miljöövervakningsprogrammet. Typområden på jordbruksmark. Sveriges lantbruksuniversitet Naturvårdsverket. Ekohydrologi 146. Uppsala.

Loganathan, P. Vigneswaran, S. Kandasamy, J. Naidu, R. 2012. Cadmium sorption and desorption in soils: A review. *Critical reviews in Environmental Science and Technology*, 42 (5): 489-533. doi:10.1080/10643389.2010.520234.

Marmolin, C. Ugander, J. Gruvaeus, I. Lundin, G. 2008. *Aska från halm och spannmål - Kemisk sammansättning, fysikaliska egenskaper och spridningsteknik*. JTI-rapport 362 Lantbruk och industri.

MSC-E 2018. Data of HMs and POPs for the EMEP region. Sweden, Cd, all years, Deposition. Available at: http://www.msceast.org/database/map_database.php4?country=Sweden&polltant=Cd&year=2015&type=Deposition&file=http://msceast.org/database/Sweden/cd_dep_2015.txt [2018-05-18].

Naidu, R. Bolan, N.S. Kookana, R.S. Tiller, K.G. (1994). Ionic-strength and pH effects on the sorption of cadmium and the surface charge of soils. *European journal of soil science;* 45, 419-429.

Ohno, T. Erich, M. S. 1990. Effect of wood ash application on soil pH and soil test nutrient levels. *Agriculture, Ecosystem and Environment*, 32: 223-239.

Olofsson, J. 2016. *Base cations in forest soils. A pilot project to evaluate different extraction methods*. Ms. Thesis SLU.

Parfitt, R. L. & Childs, C. W. 1988. Estimation of forms of Fe and Al: A review, and analysis of contrasting soils by dissolution and Moessbauer methods. *Australian Journal of Soil Research*26 (1):121-144. doi:10.1071/SR9880121.

Ring, E. Jacobson, S. Nohrstedt, H. 2006. Soil-solution chemistry in a coniferous stand adding wood ash and nitrogen. *Can. J. For. Res*. 36:153-163

Roberts, L. T. 2014. Cadmium and Phosphorous Fertilizers: The issue and the Science. *Science direct* 83, 52-59. doi:10.1016/j.proeng.2014.09.012.

Saarsalmi, A. Smolander, A. Kukkola, M. Moilainen, M. Saramäki, J. 2012. 30-Year effect of wood ash and nitrogen fertilization on soil chemical properties, soil microbial processes and stand growth in a scots pine stand. *Forest ecology and management* 228: 63-70.

Sauvé´, S. Hendershot, W. Allen, H. E. 2000. Solid-solution partitioning of metals in contaminated soils: Dependence on pH, total metal and organic matter. *Environ. Sci.Technol*. 34:1125–1131.

Shi, B. Allen, H. Grassi, T. M. Ma, H. 1998. Model copper partitioning in surface waters. *Water r search* 32:3756-3764.

Sharma, P. Laor, Y. Medina, S. Saadi, I. Krasnovsky, A. Vager, M. Levy, J. G. Borisover, M. 2017. Compositional characteristics of organic matter and its water-extractable components across a profile of organically managed soil. *Geoderma* 286: 73-82. Doi:org/10.1016/j.geoderma.2016.10.014.

Sjöstedt, S. C. Gustafsson, J.P. Köhler, S. 2010. Chemical equilibrium of organic acids, pH, Aluminum, and iron in Swedish surface waters. *Environmental Science Technologie 44: 8587-8593*.

Statens energimyndighet 2017. *Produktion och användning av biogas och rötrester år 2016*. ES 2017:07 Statens energimyndighet & Energigas Sverige ISSN 1654-7543.

Statistiska centralbyrån 2012. Svenska EnergiAskor AB *Askor i Sverige 2012*.

Swedish standard institute, 2003. Characterization of waste-Digestion for subsequent determination of aqua regia soluble portion of elements.

Swedish standard institute, 1997. Water analysis-Guidelines for the determination of total oranic carbon (TOC) and dissolved organic carbon (DOC).

Swedish standard institute, 1996. Soil quality-Determination of organic and total carbon after dry combustion (elementary analysis).

Swedish Environmental protection Agency, 1994. Kungörelse med föreskrifter om skydd för miljön, särskilt marken, när avloppsslam används I jordbruket: SNFS 1994:2 MS:72. ISSN 0347-53001, Stockholm.

Tiberg, C. & Gustafsson, J. P. 2016. Phosphate effects on Cadmium (ll) sorption to ferrihydrite. *Journal of Colloids and interface Science* 471:103-111. doi.org/10.1016/j.jcis.2016.03.016.

Wei, Y. Shimaoka, T. Saffarzadeh, A. Fumitake, T. 2011. Mineralogical characterization of municipal solid waste incineration bottom ash with an emphasis on heavy metal-bearing phases. *Journal of hazardous material* 187:534-543.

Welikala, D. Hucker, C. Hartland, A. Robinson, H. B. Lehto, J. N. 2018. Trace metal mobilization by organic soil amendments: insight gained from analyses of soil and solution phase complexation of cadmium, nickel and zink. *Chemosphere* 199: 684-693. doi.org/10.1016/j.chemosphere.2018.02.069.

Zhang, W. Yin, C. Chen, C. Chen, A. Xie, X. Fu, X. Hou, H. Wei, W. 2016. Estimation of long-term Ca^{2+} loss through outlet flow from an agricultural watershed and the influencing factors. *Environmental science and pollution research* 23 (11): 10911-10921.doi.org/10.1007/s11356-016-6145-z.

Acknowledgements

I would like to give thanks to my supervisor Jon Petter Gustafsson for providing me with the necessary and most important knowledge for this thesis and also my examiner Dan Bergren Kleja for excellent inputs. When spending time in the lab at Soil and Environment the crew there were helping me out and answering my questions when not knowing how things work or where they are, thank you. Thanks also to Sigrun Dahlin for taking time to answering questions.

I also would like to give thanks to: Christina Karlsson for keeping me alive during the winter; providing me with; gas, water and wood when my car did not start (VW GOLF II 1.8 i KAT 1990 90Hk) which was very often, Emil and Christian; for being there during the semester supporting with positive energy, Gabriel Dupaul, my opponent; for doing such a furrow reading of my thesis and giving good feedback, Katarina Schorling; for the excellent grammar check, my cat; for being so cute.

Appendices

Table A1. *pH measured from soil samples with different amendments applied.*

Amendment	Skedevi pH H_2O	Öjebro pH H_2O	Skedevi pH $CaCl_2$	Öjebro pH $CaCl_2$
Digest Uppsala	6.1	6.9	5.7	6.4
Digest Uppsala	6.2	5.7	5.7	5.3
Digest Uppsala	6.1	6.2	5.6	5.5
Digest Uppsala	6.1	5.7	5.6	5.1
Digest Uppsala	-	6.8	-	6.5
Digest Linköping	6.3	6.0	5.8	5.4
Digest Linköping	6.0	6.6	5.6	6.2
Digest Linköping	6.2	6.0	5.6	5.5
Digest Linköping	6.2	6.4	5.6	6.4
Digest Linköping	-	6.5	-	6.3
Ash	7.0	6.1	6.7	5.4
Ash	6.9	5.9	6.4	5.3
Ash	6.6	6.0	6.0	5.4
Ash	6.8	7.0	6.5	6.7
Digest Upp+Ash	6.8	5.4	6.3	5.0
Digest Upp+Ash	6.9	6.6	6.5	6.3
Digest Upp+Ash	6.7	5.9	6.1	5.5
Digest Upp+Ash	6.6	6.0	6.3	5.4
Digest Lin+Ash	6.9	6.8	6.5	6.5
Digest Lin+Ash	6.8	6.5	6.4	6.1
Digest Lin+Ash	6.9	5.9	6.5	5.4
Digest Lin+Ash	6.6	6.7	6.2	6.4
Unfertilized	6.3	5.6	5.7	5.1
Unfertilized	6.3	6.1	5.6	5.5
Unfertilized	6.2	6.4	5.6	6.1
Unfertilized	6.2	6.9	5.7	6.6
NPK	5.8	5.9	5.4	5.5
NPK	5.9	5.4	5.4	5.1
NPK	5.9	5.4	5.5	5.5
NPK	5.9	6.1	5.4	5.5
NPK	-	6.5	-	6.5
NPK	-	6.8	-	6.5
Total mean	6.4	6.2	6.0	5.8
Unfertilized mean	6.3	6.3	5.7	5.8

Table A2. *Input parameters in Visual MINTEQ 3.1 for Öjebro. Values without brackets are measured values, the ones within brackets are adjusted values from model fitting and hence used in the model simulation scenarios.*

			HNO$_3$ extraction μmol kg^{-1}						BaCl$_2$ extraction mmol kg^{-1}			Acid/Base addition mg L^{-1}		Ox.-Pyr. Ext. g L^{-1}	Oxalate extraction mg L^{-1}	
pH	DOC	HS	B	Cd	Cu	Ni	Zn	Al	Ca	Mg	K	NO$_3$	Na	HFO	P$_O$	Si$_O$
4.3	6.3	610	81.5	1.14 (0.3)	61.4	29.2 (19.1)	145 (76.4)	43900 (7383)	40.7	4.15	2.16	738	230	0.10	19.7	8.12
5.0	5.65	610	81.5	1.14 (0.3)	61.4	29.2 (19.1)	145 (76.4)	43900 (7383)	40.7	4.15	2.16	698	230	0.10	19.7	8.12
5.4	4.95	610	81.5	1.14 (0.3)	61.4	29.2 (19.1)	145 (76.4)	43900 (7383)	40.7	4.15	2.16	659	230	0.10	19.7	8.12
5.8	5.2	610	81.5	1.14 (0.3)	61.4	29.2 (19.1)	145 (76.4)	43900 (7383)	40.7	4.15	2.16	640	230	0.10	19.7	8.12
6.2	5.45	610	81.5	1.14 (0.3)	61.4	29.2 (19.1)	145 (76.4)	43900 (7383)	40.7	4.15	2.16	620	230	0.10	19.7	8.12
6.7	7.55	610	81.5	1.14 (0.3)	61.4	29.2 (19.1)	145 (76,4)	43900 (7383)	40.7	4.15	2.16	620	237	0.10	19.7	8.12

Table A3. *Input parameters in Visual MINTEQ 3.1 for Skedevi. Values without brackets are measured values, the ones within brackets are adjusted values from model fitting and hence used in the model simulation scenarios.*

			HNO$_3$ extraction μmol kg^{-1}						BaCl$_2$ extraction mmol kg^{-1}			Acid/Base addition mg L^{-1}		Ox.-Pyr. g L^{-1}	Oxalate extraction mg L^{-1}	
pH	DOC	HS	B	Cd	Cu	Ni	Zn	Al	Ca	Mg	K	NO$_3$	Na	HFO	P$_O$	Si$_O$
4.3	6.35	844	68.2	1.05 (0.18)	36.3	36.0 (18.8)	137 (86.5)	59800 (13913)	42.7	4.35	3.13	741	230	0.24	17.6	12.7
4.6	5.9	844	68.2	1.05 (0.18)	36.3	36.0 (18.8)	137 (86.5)	59800 (13913)	42.7	4.35	3.13	701	230	0.24	17.6	12.7
5.1	5.55	844	68.2	1.05 (0.18)	36.3	36.0 (18.8)	137 (86.5)	59800 (13913)	42.7	4.35	3.13	660	230	0.24	17.6	12.7
5.5	5.2	844	68.2	1.05 (0.18)	36.3	36.0 (18.8)	137 (86.5)	59800 (13913)	42.7	4.35	3.13	640	230	0.24	17.6	12.7
6.0	5.8	844	68.2	1.05 (0.18)	36.3	36.0 (18.8)	137 (86.5)	59800 (13913)	42.7	4.35	3.13	620	230	0.24	17.6	12.7
6.6	6.4	844	68.2	1.05 (0.18)	36.3	36.0 (18.8)	137 (86.5)	59800 (13913)	42.7	4.35	3.13	620	237	0.24	17.6	12.7

Table A4. Oxalate extracted element where: U= unfertilized, D=digestate, A= ash.

Soil	mmol kg^{-1}			
	Al	Fe	P	Si
Öjebro U	35.3	36.3	11.1	5.0
Öjebro D	35.8	32.2	11.5	5.0
Öjebro A	35.0	37.7	10.7	4.2
Skedevi U	42.7	72.9	10.7	8.5
Skedevi D	41.9	72.3	11.1	8.6
Skedevi A	42.0	74.5	11.0	9.9

Table A5. Pyrophosphate extracted element where U= unfertilized, D=digestate, A= ash.

Soil	mmol kg^{-1}	
	Al	Fe
Öjebro U	15.6	28.2
Öjebro D	15.3	26.9
Öjebro A	14.7	27.1
Skedevi U	13.3	16.4
Skedevi D	17.9	16.4
Skedevi A	15.1	17.0

Table A6. BaCl$_2$ extracted base cations and the charge in cmol kg^{-1} with calculated CEC for each sample. Where: U= unfertilized, D=digestate, A= ash.

Soil	cmol(+) kg^{-1}					
	Al	Ca	Mg	K	Na	CEC
Öjebro U	0.155	136	13.8	7.2	1.43	158
Öjebro D	0.155	141	14.0	6.6	2.41	165
Öjebro A	0.155	120	11.3	7.1	4.28	143
Skedevi U	0.156	142	14.5	10.4	0.92	168
Skedevi D	0.156	145	14.7	10.3	3.88	174
Skedevi A	0.156	148	16.7	11.2	1.26	177

Table A7. HNO₃ extracted elements where U= unfertilized, D=digestate, A= ash.

| Soil	μmol kg⁻¹					mmol /kg⁻¹
	Cd	Cu	Ni	Zn	Al	Ca
Öjebro U	1.14	61	29	145	43901	54
Öjebro D	1.12	61	31	146	45816	60
Öjebro A	1.00	57	23	121	41347	47
Skedevi U	1.05	36	36	137	59860	72
Skedevi D	1.08	39	35	139	59415	72
Skedevi A	1.24	40	35	190	59091	77
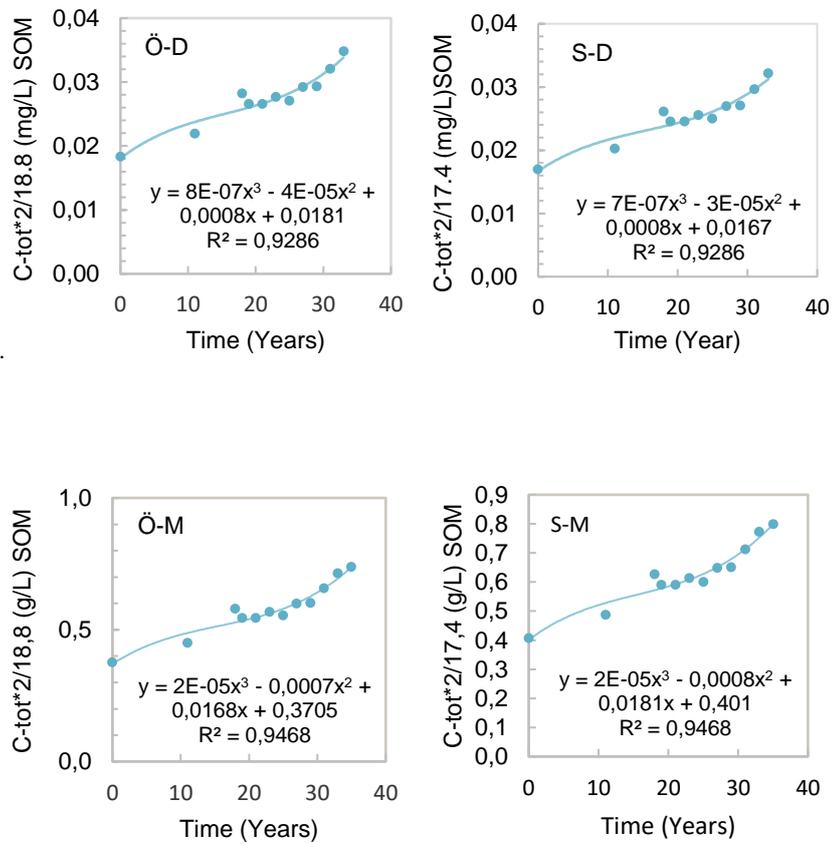
Figure A2. *Variables of DOC used in the simulation at for digestate (D) and mix (M), Öjebro (Ö) left and Skedevi (S) right.*

Table A8. DOC measured at different pH for the batch series.

Sample	DOC mg L^{-1}
Öjebro S-12	6.30
Öjebro S-8	5.65
Öjebro S-4	4.95
Öjebro S-2	5.20
Öjebro S-0	5.45
Öjebro B-2	7.55
Skedevi S-12	6.35
Skedevi S-8	5.90
Skedevi S-4	5.55
Skedevi S-2	5.20
Skedevi S-0	5.80
Skedevi B-2	6.40