Modelling metal solubility in limed soil with WHAM

Solubility of major cations and trace metals (Cu, Zn and Cd) in soil extracts of some contaminated agricultural soils near a zinc smelter in Norway: modelling with a multisurface extension of WHAM

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Summary

Mechanistic modelling offers a means of simulating the speciation and solubility of trace metals in soils. The WHAM/Model VI model has previously been used to simulate pH buffering and Al solubility in acid soils, and metal partitioning in highly organic soils, but has not previously been applied to agricultural soils. Here we have extended WHAM/Model VI framework to include surface complexation to oxides and cation exchange, and applied it to batch titrations of limed agricultural soils contaminated by emissions of Cd and Zn from a metal smelter. In contrast to previous studies on forest soils, model predictions were most sensitive to the size of the geochemically ‘active’ soil Ca pool. Following optimisation of this pool the model reproduced trends in pH and major cations well. Blind predictions of soil metal (Cu, Zn, and Cd), using estimates of the active soil metal obtained by extraction with 0.22 M HNO₃, were mostly very reasonable. Where predicted metal solubility was biased the model could be fitted to the data by optimising the size of the active metal pool. In some cases the optimised metal pool was unrealistically large, indicating a possible deficiency in the way the model considers binding activity and competition. Organic matter was the dominant binding phase in these soils. These results support the contention that speciation modelling has great promise in providing a holistic description of ionic chemistry in soils for both major and trace elements.

Introduction

Metal contamination in soils may pose risks to humans and the environment by a number of pathways, from uptake of metal by crop plants to direct effects on the soil microbial biomass. Rigorously assessing such risks requires understanding of the processes controlling the mobility, bioaccumulation and toxicity of metals. In all cases, the processes
controlling the concentrations and speciation of metal in the soil solution are key.

Downward and lateral movement of metals to surface and groundwater occurs largely by transport in the soil solution. Evidence also strongly suggests that metal speciation in the soil solution controls bioavailability and toxicity to soil organisms (Sauvé 2002), although generalisations must be made with caution since metal uptake routes and regulation processes do vary among organisms. The solid–solution partitioning of metals in soils is commonly quantified by the partition coefficient \( K_d \) since this is a common parameter in many environmental fate models, or by isotherms such as the Langmuir for which parameters can be obtained in the laboratory. However, there is doubt as to whether \( K_d \) values obtained in laboratory experiments using manipulated soil can be realistically transferred to field conditions, due to variations in key parameters such as the soil:water ratio and the solution pH between the field and laboratory. Neither can \( K_d \)s or simple isotherms describe the changes in metal partitioning that might result from secondary effects such as soil acidification. Speciation models (e.g. Windermere Humic Aqueous Model, WHAM (Tipping 1994; Tipping 1998) that include descriptions of the chemistry of soil solid phases and solution ligands provide a mechanistic alternative to the use of \( K_d \)s or isotherms. Such models are parameterised on laboratory experiments with isolated or synthetic solid phases and ligands and so represent a synthesis of theoretical knowledge for testing against the behaviour of multicomponent systems such as soils. Several authors have applied speciation models to laboratory studies of soil metal solubility (e.g. (Lofts et al. 2001a; Dijkstra et al. 2004; Lumsdon 2004; Fest et al. 2005; Ponizovsky et al. 2006)) with reasonable success. A key finding, reinforced by a number of studies, is the importance of natural organic matter as a binding phase in many soils. The complex chemistry of natural organic matter has presented a significant challenge to modellers, but in recent years sophisticated models for organic matter have been developed, of which the
most prominent are the non-ideal competitive adsorption (NICA-Donnan) model
(Kinniburgh et al. 1996) and Humic Ion Binding Models V and VI (Tipping & Hurley
1992; Tipping 1998). As a component of the WHAM speciation model (Tipping 1994),
Models V and VI have previously been used to model proton solubility and Al speciation
in forest soils (deWit et al. 1999; Lofts et al. 2001a) and the speciation of radionuclides
and trace metals in upland English soils (Tipping et al. 1995; Tipping et al. 2003). All
these studies have focused on speciation and solubility in acid organic soils, where organic
matter can robustly be assumed to comprise the solid phase component controlling the
solution chemistry (including metal speciation and partitioning). Applications of the
model to soils lower in organic matter, and soils of circumneutral pH, have also been made
but on a more limited basis (e.g. (Ponizovsky et al. 2006). There is thus a need to extend
the assessment of the model to such soils.

The purpose of this study was to extend the current soil version of WHAM (Tipping et al.
2003) to consider soil solid phases other than organic matter when modelling major ion
and trace metal partitioning, and to apply the model to agricultural soils collected in an
area in Norway influenced by a local zinc smelter. The aquatic version of the model has
been previously extended to consider solid phases in aquatic suspended particulate matter
(Lofts & Tipping 1998; Lofts & Tipping 2000). The soils version of the model developed
here is rather similar but also includes precipitation reactions for aluminium and iron(III),
both of which elements are important influences on trace metal speciation (Tipping et al.
2002). Following on from previous studies we firstly seek a description of pH and the
major ion concentrations in the soil solutions prior to modelling the solubility of the trace
metals.
Materials and methods

Site description

The sampling area is along the “Sørkjorden” fjord near Odda, western Norway (370 km west of Oslo). Due to the topography (Figure 1) local deposition from industry, including the zinc smelter, occurs largely to the valley floor. The zinc smelter was established in 1924 and is the main source of Cd and Zn contamination of local soils (Steinnes et al. 2001). The locations of the sampling sites are shown in Figure 1 and soil properties are given in Table 1. Samples were collected at 2-5 cm depth and subsequently stored moist and cold (at 4°C). Site #1 is an old orchard located 12.3 km north of the zinc smelter, whereas sites #3 and #8 are within a 1 km radius from the smelter. Site #4, located about 5 km south of the smelter and partly hidden from it by mountains, has intensive grass production for domestic animals. Site #3 is an actively managed orchard site, whereas site #8 is a garden lawn. Sites #4 and 8 are frequently limed (every 5-7 yr) to maintain favourable soil pH for grass.

Soil analysis

Soils were subjected to two extractions for trace metals, using aqua regia and 0.22 M HNO₃, respectively. Subsamples were pulverized by an agate mortar and digested with aqua regia (3:1 concentrated HCl: concentrated HNO₃) in “Erlenmeyer” flasks. Digestion comprised an initial short parboiling, cooling and resting for about 16 hours, boiling for 2 hours, evaporation to dryness, and dissolution in 10% HNO₃ (reagent grade). The extract concentrations of Cd were determined using a Perkin-Elmer graphite furnace atomic absorption spectrophotometer (AAS, Perkin-Elmer, Norwalk, CT), whereas for the determination of Cu and Zn, a Thermo Jarrell Ash inductive coupled plasma (ICP, Thermo
Jarrell Ash, Franklin, MA) was used. Two grams of field moist soil were shaken in 35 ml 0.22 M HNO₃ overnight and the solutions filtered through Whatman glass fibre filters, GF/C (1.2µm). Filtrate metal concentrations were determined using a Quadropole Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Perkin Elmer Elan 6000). Soil pH was measured in deionised water at a solid:solution ratio of 1:2.5. Acid oxalate and pyrophosphate extractable Fe and Al were determined, after the methods of Saunders (1965) and Bascomb (1968) respectively. Copper chloride–extractable Al was determined after (Juo & Kamprath 1979). Aluminium and Fe concentrations were determined using an atomic absorption spectrophotometer (AAS, Perkin-Elmer, Norwalk, CT). Exchangeable base cations and exchangeable acidity (extracted by 1.0 M NH₄NO₃) were also measured. Base cation concentrations were determined using an ICP (Thermo Jarrell Ash, Franklin, MA). Exchangeable acidity was determined by titration with NaOH to pH 7.00. Cation Exchange Capacity (CEC) was computed as the sum of exchangeable base cations and acidity. The inorganic carbon was determined as the difference between total carbon in soil and total organic carbon. Parallel soil samples were repeatedly washed with 2 M HCl to remove inorganic carbon, before total organic carbon was determined using a LECO CHN 1000 analyser. (Leco, St. Joseph, MI). The particle size distribution was measured using the pipette method of Elonen (1971).

Batch titration

Between four and six subsamples (20 g) of each field moist soil were suspended in <50 ml 0.01 M NaCl to which small volumes of NaOH (0.1 M) or HCl (1.0 M or 0.1 M) were added to adjust pH. The final total solution volume was 50.0 ml, including the soil water, 0.01 M NaCl extract and acid/base added to adjust pH. The volumes of acid and base were chosen, based on range–finding tests, to achieve a final pH range of 1–2 units above and below that
pH obtained without addition of acid or base (the ambient pH). Soil–solution mixtures were shaken continuously (100 strokes min\(^{-1}\)) for 55 hours, and the supernatants removed and filtered through Whatman glass fibre filters, GF/C, 1.2 µm). No attempt was made to exclude the atmosphere from the samples during the experiments. The pH and concentrations of dissolved organic carbon (DOC), Mg, Al, K, Ca, Cu, Zn, and Cd were measured in the supernatants. Metal concentrations were determined using a Quadrupole Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Perkin Elmer Elan 6000). A Shimadzu TOC-5000 analyser (Shimadzu Scientific, Columbia, MD) was used to determine supernatant DOC. pH was measured using a combination electrode.

**Modelling**

*Humic Ion Binding Model VI*

A full description of Humic Ion Binding Model VI (hereafter referred to as Model VI) is given by Tipping (1998). Briefly, Model VI is a discrete site/electrostatic model for simulating cation binding to humic substances. Binding of cations can occur either at discrete binding sites (specific binding) or electrostatic accumulation adjacent to the molecular surface. Heterogeneity of binding is provided for by having a number of distinct site types each with its own binding strength. The range of metal binding strengths is extended by allowing multidentate binding at specific combinations of two and three sites, and further by empirically increasing the binding strengths of subsets of these sites. Binding strengths are further modified by the (electrostatic) effect of charge development at the molecular surface resulting from ion binding and release. Electrostatic accumulation of ions adjacent to the molecular surfaces (non–specific binding) is simulated using Donnan type expressions. The relative affinity of ions for accumulation may be adjusted
using selectivity coefficients. Here we have set the selectivity coefficients for the ions 
$\mathrm{Na}^+$, $\mathrm{Mg}^{2+}$, $\mathrm{Al}^{3+}$, $\mathrm{Al(OH)}^{2+}$ and $\mathrm{Al(OH)}_2^+$ to 0.25, 0.75, 0.5, 0.5 and 0.5 respectively, after Tipping et al., (1995). All other ions have selectivity coefficients of unity. 

For the purposes of modelling, humic substances are conceptually divided into humic and fulvic acids, each having their own distinct parameter sets. The metal binding equilibrium constants have been derived by calibrating to the available literature data (Tipping 1998). These constants are regarded as “best average” values.

**Mineral surfaces**

We have chosen three mineral surfaces for modelling: iron oxide, aluminium oxide and an idealised clay cation-exchanger. Iron and aluminium oxide surface chemistry are simulated by a surface complexation model originally used by Lofts and Tipping (1998) as a component of the SCAMP (Surface Chemistry Assemblage Model for Particles) model for aquatic suspended particulate matter. In this model the oxide surfaces possess amphoteric hydroxyl groups. These groups are homogenous with respect to the strengths of proton binding and release. Metals can bind monodentately to any surface group. Metal binding is heterogeneous, with three metal binding strengths: strong, medium and weak, applying to 0.9%, 9% and 90.1% of the surface groups respectively. We assume the oxides to be in large surface area, amorphous forms; surface areas were set to the default values of 0.6 m$^2$ kg$^{-1}$ and 0.4 m$^2$ kg$^{-1}$ for iron and aluminium oxides respectively. Electrostatic effects on ion binding, and electrostatic accumulation of ions adjacent to the surface, are handled by submodels similar to those found in Model VI. Parameters for proton and metal binding are those calculated by Lofts and Tipping (1998).
Cation binding to the idealised cation-exchanger is calculated using the model introduced by Tipping (1994). Binding is by electrostatic accumulation only, using Donnan type expressions. Selectivity of binding is possible, but is not invoked here. Binding capacity is expressed by a surface charge density (in cmol$_c$ kg$^{-1}$) and a specific surface area (in m$^2$ kg$^{-1}$).

Modelling system

Model VI, the surface complexation model, cation exchanger model and a solution speciation submodel were combined as shown in Figure 2. Organic matter, comprising humic and fulvic acids, can be present in the solid phase as soil organic matter (SOM) or in the solution phase as dissolved organic matter (DOM). The default binding parameters in all the models were not adjusted in this study. The relationship between the measured amounts of organic matter on the soil solids, and the amounts of humic and fulvic acid input to the model to represent these phases, can be set a priori or input as fitting parameters. Input Al and Fe(III) can be specified as a mixture of ‘fixed’ hydroxides that have chemically active surfaces but cannot dissolve, and of ‘active’ element that can participate in solution and surface equilibria. The latter if desired can precipitate as hydroxides, and if desired the precipitates can possess chemically active surfaces. Hydroxide precipitation is simulated by conventional solubility products ($K_{sp} = a_M a_{H^3}^{-3}$); we use standard log solubility products of 8.5 and 2.7 for Al(OH)$_3$ and Fe(OH)$_3$ respectively, and standard enthalpies of precipitation of -107 kJ mol$^{-1}$ and -102 kJ mol$^{-1}$, after Tipping et al. (2003) and Tipping et al. (2002) respectively. The carbonate system may be modelled by assuming equilibrium with atmospheric carbon dioxide or by inputting a measure of the amount of carbonate present. Given that we were attempting to model limed soils, additional code was written to allow the simulation of calcite (CaCO$_3$) precipitation and dissolution. The standard log solubility product ($K_{sp} = a_{Ca} a_{CO_3}$) and
standard enthalpy of precipitation used were -8.48 and -8 kJ mol\(^{-1}\), respectively (Smith et al. 2004).

Results

Characteristics of the investigated soils

All the soils are sandy loams, but due to the different vegetation covers, management practices and distances from the smelter, the soil chemical properties vary (Tables 1 and 2). Significant variations in the contents of TOC, exchangeable Ca and CuCl\(_2\) extractable Al were seen. The Ca accounted for between 75 and 96% of the total CEC. The two largest pH values were found in soils collected from the sites #4 and #8. Both sites are frequently limed (every 5-7 yr), and the relative contribution of Ca to CEC was also the highest in these two soils (Table 2). The content of organic C is lowest in soil #4. The two soils adjacent to the smelter, #3 and #8, had the highest metal (Cu, Zn, Cd) contents (Table 3). Of the two remoter sites, #1 had higher metal contents than #4 as a result of its location downwind of the smelter.

Compared with soils sampled from a forest site in southern Norway (Birkenes) (Lofts et al. 2001a) soils #4 and #8 were notably enriched in exchangeable Ca relative to copper-extractable Al. Ratios of Ca:Al in soils #4 and #8 were 19 and 23 compared to 2 and 0.2 in the Birkenes Oe and Oa horizons. The ratios in soils #1 and #3 were similar to those at Birkenes at 0.8 and 2.1 respectively.

Batch titrations

The observed pH and Ca, DOC, major ions (Mg, K, Al) and trace metals (Cu, Zn, Cd) in the batch titration supernatants are shown in Figures 3, 4, 5 and 6 respectively. Supernatant pH (Figure 3) varied by between two and a half and four pH units depending upon the soil. Dissolved organic carbon concentrations (Figure 4) varied considerably with
The minimum DOC concentration was observed in the ambient systems, except for soil #8 where the DOC at the lowest acid addition was marginally lower than that in the ambient system. In all soils the DOC increased considerably when the base-acid > 0. This has been previously ascribed (Lofts et al. 2001b) to solubilisation of increasingly hydrophobic organic matter due to progressive deprotonation as the pH is increased. Appreciable increases in DOC were also seen in soils #4 and #8 after acid addition; this has tentatively been ascribed (Lofts et al. 2001a) to solubilisation of a portion of the SOM able to bind large amounts of Al and having a net positive charge. Major ion and trace metal solubility varied considerably, both with pH in single soils and among the metals as a proportion of the active pool. Dissolved K varied by up to an order of magnitude depending upon the soil, Mg and Ca by between one and two orders of magnitude, Al and the trace metals by up to three orders of magnitude. At the smallest pH, the dissolved concentrations of Mg, K, Ca, Zn and Cd approached or even reached those expected to result from complete dissolution of the bound metal (as estimated by the various extractions). Dissolved Al and Cu concentrations were notably variable among soils, with solubility relative to the bound pools being relatively large in soil #1, at large pH for both metals and for Al at small pH. In contrast, both metals showed rather low solubility in soil 8, with the highest solution concentration representing less than 10% of the ‘active’ pool, and only about 1% in the case of Cu. The highest Cu concentrations were consistently associated with the large pH end of the titrations, in association with large DOM concentrations. The relative importance of supernatant DOM complexation was seen in the correlations between solution metals (in particular Al and Cu) and DOC concentrations (both expressed as logarithms) – correlation coefficients for Mg, Al, K, Ca, Cu, Zn and Cd were -0.51, 0.80, -0.13, -0.41, 0.93, 0.03 and -0.01 respectively.
These trends in solubility may be interpreted in terms of the binding mechanisms of the metals, and their relative tendencies to bind to solid and dissolved phase ligands. Potassium does not form solution complexes and binds to solid phases by cation exchange; thus competition by protons is less important than it is for cations that bind to specific sites, and the variation in solubility with pH is small. Both Mg and Ca can bind specifically in competition with protons, and so the pH dependence of binding is greater than seen for K. The increase in solubility of these metals above pH 6 in soil #1 may be attributed to solubilisation of organic matter (Figure 4) and its bound metals. This effect becomes more important when considering Zn and Cd, and particularly so for Al and Cu, which would be expected to bind predominantly by specific complexation. Copper in particular exhibits strong binding to both solid phase and dissolved ligands, even at the low end of the studied pH ranges. This results in the observed maximum solubility at the largest pH that is seen particularly in soils #4 and #8. Here the Cu is likely to be predominantly DOM-complexed. Dijkstra et al. (2004) reported the same pH dependency of metal solubility in soil extracts, with a minimum dissolved metal in the pH 4-6 range.

**Modelling stage 1: solubility controls on Al and Fe(III)**

Solution concentrations of Al and Fe(III) were input to the model along with pH, Mg, K, Ca, Cl and DOM. DOM was assumed to comprise 65% fulvic acid and 35% chemically inert material, after Bryan et al. (2002); this assumption was used throughout. No measurements of solution anions other than Cl (e.g. SO\textsubscript{4}) were available. Given that the electrolyte Cl ought to dominate the solution anions, such other anions were not considered. The carbonate system was assumed to be in equilibrium with atmospheric CO\textsubscript{2}, at a partial pressure of 34.96Pa (3.45 × 10\textsuperscript{-4} atm). Speciation was done by adjusting the Na concentration to force charge balance. Saturation indices (SIs) were initially calculated for hydroxides of Al and Fe(III), using the solubility parameters given in the
Modelling system section. Log SIs for Al(OH)$_3$ ranged from -3.7 to 3.9 and for Fe(OH)$_3$ from -0.5 to 5.9. Thus supersaturation with respect to both minerals was predicted, although for Al the degree of under- or oversaturation was highly pH-dependent. We interpret these finding to indicate the presence of colloidal forms of the minerals in the supernatants, as has been assumed previously (e.g. Tipping et al. 2003). All subsequent calculations were therefore done allowing Al(OH)$_3$\textsubscript{(s)} and Fe(OH)$_3$\textsubscript{(s)} to precipitate.

Modelling stage 2: solubility controls on Ca

The aim of this stage was to examine the possibility that in these limed soils, a solid calcium-containing phase may control the supernatant pH and dissolved Ca. For this purpose we chose calcite (CaCO$_3$) as a model phase, since it is the most soluble of the calcium carbonates. We also assumed that all the measured inorganic C was present as calcite. We then predicted supernatant pH and Ca under three scenarios:

1. Exchangeable calcium and calcite assumed to be ‘active’, i.e. participating in solubility and complexation reactions, in a closed system.

2. As scenario 1, in an open system, i.e. in equilibrium with atmospheric CO$_2$ at a partial pressure of 34.96Pa (3.45 × 10$^{-4}$ atm).

3. As scenario 2, but with calcite not assumed to be ‘active’, i.e. the ‘active’ Ca was set to the measured exchangeable value.

In scenarios 1 and 2 the total ‘active’ calcium input to the model was the sum of the measured exchangeable pool and the pool assumed to be initially present in calcite, which was calculated from the measured amount of soil inorganic C. In scenario 1 the total carbonate was also calculated from the soil inorganic C. For the open system in scenarios 2 and 3 a total carbonate was not defined. The modelling also required inputs of solid phase concentrations and pools of ‘active’ elements that can partition between solid and...
solution. Pools of Mg and K were taken as the exchangeable values. For Al, we chose to input two pools: a fixed pool of aluminium hydroxide calculated by the difference between the oxalate– and copper–extractable amounts, and an ‘active’ pool, equal to the copper–extractable amount. This is consistent with previous studies where at small pH soil Al solubility has been shown to be controlled by the organically–bound pool (Berggren & Mulder 1995), which is approximated by the copper chloride extraction. The ‘active’ pool was able to precipitate as Al(OH)$_3$, with a chemically active surface. For Fe, no copper–extractable pools were available. However, since the calculations in stage 1 indicated that Fe was consistently close to saturation or oversaturated with respect to Fe(OH)$_3$, we chose to input the oxalate–extractable pool as the ‘active’ pool, allowing it to precipitate with a chemically active surface. For the trace metals, the pools measured by 0.22 M HNO$_3$ were input. SOM was calculated by assuming it to be 50% C and to comprise 50% humic acid and 50% fulvic acid. Initially two sets of clay parameters were used (surface charge density = $10^{-4}$ cmol m$^{-2}$, specific surface area (SSA) = 0.1 m$^2$ kg$^{-1}$ or 1.0 m$^2$ kg$^{-1}$), however preliminary modelling showed that this did not significantly affect any predictions, therefore the surface area was fixed to 0.1 m$^2$ kg$^{-1}$ for all the modelling. The supernatant pH was considered a model fitting parameter, and was adjusted by forcing charge balance. The results are shown in Figure 3. In both soils #1 and #8, the best predictions of both pH and Ca were obtained assuming the exchangeable pool only to control Ca solubility. In soil #3, only small differences among the predictions were found; this is likely because the amount of input Ca derived from calcite was small compared to the exchangeable pool. In soil #4, the pH was consistently and significantly overestimated in all scenarios. Even in scenario 3, dissolved Ca was predicted as being under the control of calcite solubility, even though only the exchangeable pool was input. Considering all four soils together, these
results suggest strongly that Ca solubility in these experiments is not controlled by precipitation-dissolution reactions of calcite, but rather by a pool of exchangeable Ca.

**Modelling stage 3: solubility controls on trace metals**

Solution speciation was re-calculated, using the same assumptions as in Stage 1, allowing Al(OH)₃ and Fe(OH)₃ to precipitate. Saturation indices were calculated for (i) metal hydroxides Cu(OH)₂, am-Zn(OH)₂ and β-Cd(OH)₂ with standard log solubility products (\(K_{so,298} = a_M \cdot a_{OH}^2\)) of -19.83, -15.81 and -14.51 and standard enthalpies of 55.3, 31.4 and 17.2 kJ mol⁻¹, respectively; (ii) metal carbonates CuCO₃, ZnCO₃ and CdCO₃ with standard log solubility products (\(K_{so,298} = a_M \cdot a_{CO_3}\)) of -11.5, -10.00 and -12.00; (iii) the zinc/aluminium layered double hydroxide (LDH) Zn₂Al(OH)₆(CO₃)₀.₅\(\cdot x\)H₂O, with a log solubility product (\(K_{so} = a_{Zn}^2 \cdot a_{Al} \cdot a_{H}^{-6} \cdot a_{CO_3}^{0.5}\)) of 20.8 (Johnson & Glasser 2003). Where enthalpy values were not available enthalpy was assumed to be zero as a first approximation. No saturation with respect to any of these minerals was predicted in the experimental solutions.

**Modelling stage 4: model optimisation and predictions of partitioning**

In the previous three stages we established that control of Ca and the trace metals by solid phases appeared not to be occurring. Thus, for the final stage of modelling we assumed that the solubility of these elements was controlled by complexation to solid phases only. The results of Stage 2 did however indicate that using the measured exchangeable Ca pool did not always predict the supernatant pH well. Therefore, we chose to adjust the exchangeable Ca to fit the pH and dissolved Ca in the ambient supernatants. Optimisation was done by minimising the term

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(pH_{obs} - pH_{calc})^2 + (p[Ca]_{obs} - p[Ca]_{calc})^2,
\]

(1)

where the subscripts ‘obs’ and ‘calc’ refer to the observed and modelled values of pH and
p[Ca], respectively. Following optimisation, solution pH and Mg, Al, K, Ca, Cd, Cu and Zn were predicted for each supernatant in each titration.

The optimised ‘active’ soil Ca concentration showed no clear pattern in comparison with the Ca extracted using NH$_4$NO$_3$. The largest difference, as might be expected, was observed in soil #4 where the optimised pool was 44% of that measured. In both soils #1 and #3 the optimised pool was higher at 147% and 158% of the measured pool. The least optimisation was required for soil #8 where the optimised pool was 90% of the measured. The modelled pH and p[Ca] agreed reasonably well with the observations. The pH buffering in soils #1, #4 and #8 was well reproduced, particularly so in soil #8 with a root mean squared error (RMSE) of 0.02 for a mean observed pH of 5.93. The pH buffering in soils #1 and soil #3 was somewhat underestimated. Trends in p[Ca] were well reproduced, with soil #8 again showing the best prediction. Trends in p[Mg] and p[K] (Figure 5) were generally well reproduced, although in some cases (p[Mg] in soil #3 and p[K] in soils #3 and #4) predictions were biased. The observed minima in aluminium solubility were reasonably well simulated; however, the model did not reproduce higher dissolved aluminium well, showing a consistent tendency to underestimate solubility at both large and small pH. Underestimation of p[Al] at large pH is likely related to the supersaturation with respect to Al(OH)$_3$ observed in the solution speciation results, implying the presence of colloidal Al(OH)$_3$ in the solutions, which cannot be simulated by the model. Including readily dissoluble Al solids in the active Al by using the oxalate–extractable Al, improved the predictions of dissolved Al (dashed lines in Figure 5) with little effect on predicted p[Ca], p[Mg], p[K] or the trace metals (data not shown). Predicted pH (dashed lines in Figure 3) was also little affected, except for soil #1 where the pH buffering was overestimated somewhat (RMSE in pH was 0.87, compared to 0.48 when copper extractable Al was input).
Trace metal solubility (Figure 6) was generally reproduced very well. Copper was underestimated in soils #1, #4 and #8, indicating that the 0.22 M HNO$_3$ extraction underestimated the active pool. Zinc was underestimated in soil #8 and at small pH in soil #3. Cadmium solubility was consistently well reproduced; particularly in soils #4 and #8 (RMSEs were 0.06 and 0.11 respectively). The model consistently predicted solid phase metal to be predominantly bound to organic matter. Binding to clay and iron or aluminium oxide was relatively unimportant; individual contributions to the total binding were always below 5% and largely below 1%.

Where there was clear bias between observation and prediction we optimised the active soil metal, to establish the difference between the measured optimal active pools. The criterion for optimisation was a mean absolute deviation of greater than 0.4 in log (dissolved metal), thus identifying bias in the predictions as opposed to a poor trend. The soils–metal combinations identified were Cu in soils #1, #4 and #8 and Zn in soils #3 and #8. Optimisation was done by adjusting the active pool of metal to exactly fit the dissolved metal concentration at the ambient pH. The results are shown in Figure 6. Since the bias in the original predictions was consistently to lower dissolved metal concentrations, optimised active pools were all larger than the measured ones. The optimised pools were between two and seven times greater than the 0.22 M HNO$_3$–extracted pools. In all the cases involving copper, and in zinc in soil #3, the optimised pools were greater than the aqua regia–extracted pools. Optimising the metal pools did not produce any significant changes in the trends in predicted log(dissolved metal), thus where the original bias was most consistent, the resulting fits were a notable improvement. This was most clearly seen for Cu in soils #1 and #8 where the RMSEs dropped from 0.47 and 0.60, to 0.21 and 0.15 respectively, on optimisation.
Discussion

Modelling the solid–solution partitioning of elements in soil titrations is one of a number of ways of assessing the abilities of speciation models to reproduce soil chemistry. The approach has the advantage that trends in chemistry are measured in single soils, thus providing quite a rigorous test of the model. Such work also complements studies where single partitioning measurements are made on a larger number of soils from a defined region or area (e.g. Weng et al. 2001; Tipping et al. 2003; MacDonald & Hendershot 2006). Modelling produced highly satisfactory fits to the observed data. The model outputs depend on a large number of input parameters, many of are derived from wet chemical extractions that can only approximate to the conceptual pools of ‘active’ elements and phases that the model requires as inputs. The agreement between observations and predictions is therefore most impressive. To the best of our knowledge, this is the first modelling study of soil titrations where the pH and partitioning of both the native major ions and trace metals have been studied simultaneously. Gustafsson et al. (2003) and Gustafsson and Schaik (2003) have modelled soil pH, major ions and trace metals using batch titrations but added metal salts to achieve defined total concentrations, thus avoiding the need to estimate the active metal. Cances et al. (2003) and Dijkstra et al. (2004) both performed batch experiments without adding metals but fixed pH when modelling. In choosing to model the pH rather than fix it we have tested the model more rigorously than would otherwise have been the case. Given the importance of pH as a control on the trace metal partitioning it provides additional validation of the model framework as a means of simulating not only the control of trace metal partitioning but also the control of pH itself by the major ions and ligands (including solid phases). This would be important if, for example, we wished to model the temporal response of soil metal to variations in soil acidification status.
In common with a previous study on forest soils from southern Norway (Birkenes) (Lofts et al. 2001a) we have chosen to calibrate the model individually to soils. In contrast to this study, the pool of active Ca was selected as the optimal to adjust, whereas previously the active pools of humic substances and Al were adjusted. Taking the four soils together, the modelled soil pH was most sensitive to the value selected for the active Ca pool, which is consistent with the observation that on average Ca made up a larger proportion of the active soil cations relative to Al, than it did in the Birkenes soils. Modelling showed that there was no need to invoke dissolution and precipitation of a solid Ca–containing phase (e.g. CaCO$_3$) in these soils despite the fact that some are known to be limed; this suggests either that the amounts of lime in the soils were not significant for Ca partitioning or that lime dissolution was not significant on the timescale of the experiment. The lime (“Odda lime”) applied to these soils consists mainly of CaOH and CaCO$_3$, and is believed to have both short- and long-term effects due to its composition and particle size distribution (pers. comm., manager at “Odda lime”).

Of the major ions Al was the most poorly simulated by the model. The possible presence of colloidal Al(OH)$_3$ in the supernatants, as indicated by the solution modelling, could explain some of the model discrepancies at large pH. However, dissolved Al at the smallest pH of each titration was underestimated by at least an order of magnitude, indicating that the pool of active Al was too small. In soils #1 and #3 this could be partly accounted for by the overestimation of the smallest pH and the consequent underestimation of proton competition for Al binding to the SOM. However, this cannot explain the results in soils #4 and #8 where the largest pH is well predicted by the model. Increasing the active Al pool by inputting the oxalate–extractable Al consistently increased the predicted supernatant Al and improved the predictions considerably. This is an interesting finding.
since it implies that readily dissoluble Al solid phases (i.e. those extracted by oxalate but not by copper chloride) are part of the active Al in these soils. This contrasts with the findings of studies on Al solubility control in acid forest soils of the region (e.g. Berggren & Mulder 1995; Lofts et al. 2001a) where short-term solubility was controlled solely by the pool of organically-bound Al. The reasons for this discrepancy are not clear. From the perspective of this study, Al is less important than Ca in controlling the chemistry of these soils and does not appear to be highly significant in influencing the trace metal solubility by competition.

The trace metal modelling results indicate that short-term solubility of Cu, Zn and Cd in these soils is controlled by binding to organic matter. Other binding phases, and metal precipitates, are indicated to have an insignificant or negligible role in controlling solubility. This is in clear accordance with similar modelling studies involving these metals (Weng et al. 2001; Dijkstra et al. 2004). Generally the model reproduced the observed solubility well. Directly predicting the metal solubility as we have done here is a means of assessing the extraction method for estimating the active soil metal. Where there was significant bias between observations and predictions, it was readily possible to fit the model by adjusting the active pool. Dilute acid extractions of the type used here are popular for estimation of the active metal, and there is no reason to believe from the modelling that the measured active pools show any general bias. A standard wet chemical extraction for active soil metal would be useful from the point of view of modelling since it would improve consistency of data among studies. Wider acceptance of any single wet chemical extraction method will, however, require application and validation against a wider range of soil types than has currently been done. None of the metals appeared to be controlled by any of the solid phases considered. This is rather interesting in the case of the Zn/Al LDH, since this material solid has previously been identified as comprising 20% of
the total Zn in a soil contaminated by smelting activities, of quite similar pH (5.6) and organic matter content (14%) to our soils (Juillot et al. 2003). Clearly there is a potential for such solids to form an appreciable portion of the Zn in contaminated soils. However, they appear to exert no influence on short–term Zn solubility in these soils. The optimisation of selected metal pools to fit the observations produced some intriguing results. In particular, the observation that optimised pools of Cu, in three of the soils, were greater than the pool obtained by aqua regia extraction, deserves attention. Aqua regia extraction is considered to extract some tightly bound mineral metal as well as surface bound metals, and thus should overestimate the active pool. This suggests that the optimised Cu pools are unrealistically large and that the underestimation of dissolved Cu when using the 0.22 M HNO₃ extracted pool is due to model error. Given the complexity of the model, the source of such error is difficult to ascertain without further work. It is notable that Cu solubility depends strongly on the solubility of the soil organic matter and thus on the relative affinity for SOM and DOM for the metal. Predictions are therefore expected to be sensitive to both the intrinsic binding affinity of the model humic and fulvic acids and to a priori assumptions made about the activity of the SOM and DOM. But without more detailed experimental data (such as free metal ion activities in the supernatants) it is not appropriate to explore this further in this study. The mobility of DOM was clearly a significant influence on trace metal solubility in these experiments, particularly so for Cu and also to a lesser extent for Zn and Cd at largest pH. This is again in clear accordance with current knowledge about the binding of these metals to organic matter. It ought to be realised that the concentrations of DOM encountered in the batch titration supernatants are likely to be higher than those encountered in field soil solutions or local surface waters; this is an increasingly recognised phenomenon in soil experimentation in the laboratory (e.g. (Tipping et al. 2003). The supernatant metal
concentrations cannot therefore be taken as representative of the concentrations that we would expect to encounter in field samples. The data are better viewed as providing a test of the mechanistic underpinning of the model and of its ability to describe how the supernatant chemistry varies as a result of experimental manipulation.

As noted in the Introduction, the use of $K_d$s to quantify metal partitioning remains common since many transport and fate models require the $K_d$ as an input parameter, but there are significant difficulties inherent in measuring $K_d$s that are suitably representative of field conditions. Coupled speciation–transport models (e.g. (Tipping et al. 2006), incorporating other longer term metal input and loss processes such as mineral weathering, provide an alternative approach to simulating the transport and fate of metals in the soil environment.

It is clear from the results of this and previous studies that speciation models have great potential in simulating trace metal partitioning in soils. The further work needed to establish relationships between analytical measurements and model inputs would be best achieved by analysing and modelling as wide a range of soils as possible. A criticism sometimes made of speciation modelling is the richness of input data required, compared for example to a single $K_d$ value. While this is certainly the case, it is also true that speciation model outputs are richer in that they provide a framework to describe metal partitioning in the context of other changes in soil chemistry (e.g. pH and DOM concentration). A goal of terrestrial metal modelling should be to link the partitioning and fate of contaminant metals to major soil processes such as acidity buffering and carbon cycling. Only by doing this can we begin to assess the effects of large scale environmental change on trace metals in soils.

Acknowledgements

We want to thank Dr. Oddvar Røyseth at the Norwegian Institute for Water Research, Oslo, for assistance with ICP-MS analysis and fruitful discussions. This was a
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References


Tipping, E. 1994. WHAM - a chemical equilibrium model and computer code for waters, sediments and soils incorporating a discrete site/electrostatic model of ion-binding by


Table 1 Some important properties of the soils sampled from the four sampling sites arranged with increasing distance from smelter. North is towards the mouth of the fjord, whereas South is further into the fjord and up the valley behind.

<table>
<thead>
<tr>
<th>Cultivation/vegetation cover</th>
<th>Distance from smelter</th>
<th>$\text{pH}_{\text{H}_2\text{O}}$</th>
<th>CEC</th>
<th>Clay</th>
<th>Organic C</th>
<th>Inorganic C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil #1 Old orchard</td>
<td>12.3</td>
<td>N</td>
<td>5.1</td>
<td>11.9</td>
<td>4.0</td>
<td>4.2</td>
</tr>
<tr>
<td>Soil #4 Meadow, intensive grass</td>
<td>5.0</td>
<td>S</td>
<td>6.4</td>
<td>31.7</td>
<td>3.5</td>
<td>2.0</td>
</tr>
<tr>
<td>production and partly pasturage</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil #3 Young orchard</td>
<td>1.0</td>
<td>SW</td>
<td>5.4</td>
<td>25.1</td>
<td>6.8</td>
<td>7.7</td>
</tr>
<tr>
<td>with permanent grass cover</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil #8 Garden lawn</td>
<td>0.9</td>
<td>NW</td>
<td>6.6</td>
<td>54.9</td>
<td>5.0</td>
<td>6.3</td>
</tr>
</tbody>
</table>
Table 2. Concentrations of exchangeable base cations and solid phase fractions of Al and Fe in the soils.

<table>
<thead>
<tr>
<th></th>
<th>exchangeable cations</th>
<th>oxalate-extractable Al &amp; Fe</th>
<th>copper-extractable Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na</td>
<td>Mg</td>
<td>K</td>
</tr>
<tr>
<td>Soil #1</td>
<td>0.74</td>
<td>7.35</td>
<td>1.09</td>
</tr>
<tr>
<td>Soil #4</td>
<td>nd b</td>
<td>4.84</td>
<td>2.36</td>
</tr>
<tr>
<td>Soil #3</td>
<td>nd</td>
<td>17.6</td>
<td>6.10</td>
</tr>
<tr>
<td>Soil #8</td>
<td>nd</td>
<td>22.9</td>
<td>6.08</td>
</tr>
</tbody>
</table>

a values are brackets are the % of the CEC due to Ca.

b not detectable
Table 3  Aqua Regia and 0.22 M HNO3 extractable Cd, Cu and Zn.

<table>
<thead>
<tr>
<th></th>
<th>Aqua Regia extractable (mmol kg⁻¹)</th>
<th>0.22 M HNO₃ extractable (mmol kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Soil 1</td>
<td>Soil 4</td>
</tr>
<tr>
<td>Cd</td>
<td>0.0057</td>
<td>0.0033</td>
</tr>
<tr>
<td>Cu</td>
<td>0.48</td>
<td>0.15</td>
</tr>
<tr>
<td>Zn</td>
<td>2.2</td>
<td>1.8</td>
</tr>
</tbody>
</table>
Figure captions

Figure 1. Locations of the sampling sites. The ▲ - symbols illustrates high mountains on both side of the fjord (between 1000 and 1400 m altitude above sea level). Shaded areas indicate the lower edge of glacier. An arrow outside the small map of Norway indicates the study area.

Figure 2. Schematic representation of the reactions simulated in WHAM/Model VI. Double arrows represent the equilibria simulated. Precipitation equilibria of Al, Fe(III) and Ca are denoted by dotted lines.

Figure 3. Observed and modelled pH and dissolved Ca in the batch titration supernatants. Solid lines: predictions obtained by optimising the ‘active’ Ca in modelling stage 4. The remaining lines show the predictions obtained under the scenarios of Ca solubility control investigated in modelling stage 2. Double dot–dashed lines: scenario 1; Dot–dashed lines: scenario 2; Dashed lines: scenario 3. See main text for details of the scenarios. Note the different pH scale for soil #4.

Figure 4. Observed DOC concentrations in the batch titrations. Solid circles, soil #1; open circles, soil #3; Solid triangles, soil #4; Open triangles, soil #8. The lines are for guidance.

Figure 5. Observed and modelled dissolved Mg, Al and K in the batch titrations, following model fitting. The dashed lines on the Al plots represent the modelled Al when inputting oxalate–extractable Al as the active pool.

Figure 6. Observed and modelled dissolved Cu, Zn and Cd in the batch titrations, following model fitting. The tick horizontal lines represent the dissolved metal concentration corresponding to the active pool. Dashed lines represent the
predicted dissolved metal, and active pool, obtained by optimisation, where this was done (see text for details).
Figure 1.
Figure 2.
Figure 4
Figure 5.
Figure 6.


