

1 *Modelling metal solubility in limed soil with WHAM*

2 **Solubility of major cations and trace metals (Cu, Zn and Cd) in soil**

3 **extracts of some contaminated agricultural soils near a zinc smelter in**

4 **Norway: modelling with a multisurface extension of WHAM**

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11 **Summary**

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

30 **Introduction**

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

35 controlling the concentrations and speciation of metal in the soil solution are key.

36 Downward and lateral movement of metals to surface and groundwater occurs largely by

37 transport in the soil solution. Evidence also strongly suggests that metal speciation in the

38 soil solution controls bioavailability and toxicity to soil organisms (Sauvé 2002), although

39 generalisations must be made with caution since metal uptake routes and regulation

40 processes do vary among organisms. The solid–solution partitioning of metals in soils is

41 commonly quantified by the partition coefficient (K_d) since this is a common parameter in

42 many environmental fate models, or by isotherms such as the Langmuir for which

43 parameters can be obtained in the laboratory. However, there is doubt as to whether K_d

44 values obtained in laboratory experiments using manipulated soil can be realistically

45 transferred to field conditions, due to variations in key parameters such as the soil:water

46 ratio and the solution pH between the field and laboratory. Neither can K_d s or simple

47 isotherms describe the changes in metal partitioning that might result from secondary

48 effects such as soil acidification. Speciation models (e.g. Windermere Humic Aqueous

49 Model, WHAM (Tipping 1994; Tipping 1998) that include descriptions of the chemistry of

50 soil solid phases and solution ligands provide a mechanistic alternative to the use of K_d s or

51 isotherms. Such models are parameterised on laboratory experiments with isolated or

52 synthetic solid phases and ligands and so represent a synthesis of theoretical knowledge for

53 testing against the behaviour of multicomponent systems such as soils. Several authors

54 have applied speciation models to laboratory studies of soil metal solubility (e.g. (Lofts *et*

55 *al.* 2001a; Dijkstra *et al.* 2004; Lumsdon 2004; Fest *et al.* 2005; Ponizovsky *et al.* 2006))

56 with reasonable success. A key finding, reinforced by a number of studies, is the

57 importance of natural organic matter as a binding phase in many soils. The complex

58 chemistry of natural organic matter has presented a significant challenge to modellers, but

59 in recent years sophisticated models for organic matter have been developed, of which the

60 most prominent are the non-ideal competitive adsorption (NICA-Donnan) model
61 (Kinniburgh *et al.* 1996) and Humic Ion Binding Models V and VI (Tipping & Hurley
62 1992; Tipping 1998). As a component of the WHAM speciation model (Tipping 1994),
63 Models V and VI have previously been used to model proton solubility and Al speciation
64 in forest soils (deWit *et al.* 1999; Lofts *et al.* 2001a) and the speciation of radionuclides
65 and trace metals in upland English soils (Tipping *et al.* 1995; Tipping *et al.* 2003). All
66 these studies have focused on speciation and solubility in acid organic soils, where organic
67 matter can robustly be assumed to comprise the solid phase component controlling the
68 solution chemistry (including metal speciation and partitioning). Applications of the
69 model to soils lower in organic matter, and soils of circumneutral pH, have also been made
70 but on a more limited basis (e.g. (Ponizovsky *et al.* 2006). There is thus a need to extend
71 the assessment of the model to such soils.

72 The purpose of this study was to extend the current soil version of WHAM (Tipping *et al.*
73 2003) to consider soil solid phases other than organic matter when modelling major ion
74 and trace metal partitioning, and to apply the model to agricultural soils collected in an
75 area in Norway influenced by a local zinc smelter. The aquatic version of the model has
76 been previously extended to consider solid phases in aquatic suspended particulate matter
77 (Lofts & Tipping 1998; Lofts & Tipping 2000). The soils version of the model developed
78 here is rather similar but also includes precipitation reactions for aluminium and iron(III),
79 both of which elements are important influences on trace metal speciation (Tipping *et al.*
80 2002). Following on from previous studies we firstly seek a description of pH and the
81 major ion concentrations in the soil solutions prior to modelling the solubility of the trace
82 metals.

83

84 **Materials and methods**

85 *Site description*

86 The sampling area is along the “Sørfjorden” fjord near Odda, western Norway (370 km
87 west of Oslo). Due to the topography (Figure 1) local deposition from industry, including
88 the zinc smelter, occurs largely to the valley floor. The zinc smelter was established in
89 1924 and is the main source of Cd and Zn contamination of local soils (Steinnes *et al.*
90 2001). The locations of the sampling sites are shown in Figure 1 and soil properties are
91 given in Table 1. Samples were collected at 2-5 cm depth and subsequently stored moist
92 and cold (at 4°C). Site #1 is an old orchard located 12.3 km north of the zinc smelter,
93 whereas sites #3 and #8 are within a 1 km radius from the smelter. Site #4, located about 5
94 km south of the smelter and partly hidden from it by mountains, has intensive grass
95 production for domestic animals. Site #3 is an actively managed orchard site, whereas site
96 #8 is a garden lawn. Sites #4 and 8 are frequently limed (every 5-7 yr) to maintain
97 favourable soil pH for grass.

98

99 *Soil analysis*

100 Soils were subjected to two extractions for trace metals, using aqua regia and 0.22 M
101 HNO₃, respectively. Subsamples were pulverized by an agate mortar and digested with
102 aqua regia (3:1 concentrated HCl: concentrated HNO₃) in “Erlenmeyer” flasks. Digestion
103 comprised an initial short parboiling, cooling and resting for about 16 hours, boiling for 2
104 hours, evaporation to dryness, and dissolution in 10% HNO₃ (reagent grade). The extract
105 concentrations of Cd were determined using a Perkin-Elmer graphite furnace atomic
106 absorption spectrophotometer (AAS, Perkin-Elmer, Norwalk, CT), whereas for the
107 determination of Cu and Zn, a Thermo Jarrell Ash inductive coupled plasma (ICP, Thermo

108 Jarrell Ash, Franklin, MA) was used. Two grams of field moist soil were shaken in 35 ml
109 0.22 M HNO₃ overnight and the solutions filtered through Whatman glass fibre filters,
110 GF/C (1.2µm). Filtrate metal concentrations were determined using a Quadropole
111 Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Perkin Elmer Elan 6000). Soil
112 pH was measured in deionised water at a solid:solution ratio of 1:2.5. Acid oxalate and
113 pyrophosphate extractable Fe and Al were determined, after the methods of Saunders
114 (1965) and Bascomb (1968) respectively. Copper chloride–extractable Al was determined
115 after (Juo & Kamprath 1979). Aluminium and Fe concentrations were determined using an
116 atomic absorption spectrophotometer (AAS, Perkin-Elmer, Norwalk, CT). Exchangeable
117 base cations and exchangeable acidity (extracted by 1.0 M NH₄NO₃) were also measured.
118 Base cation concentrations were determined using an ICP (Thermo Jarrell Ash, Franklin,
119 MA). Exchangeable acidity was determined by titration with NaOH to pH 7.00. Cation
120 Exchange Capacity (CEC) was computed as the sum of exchangeable base cations and
121 acidity. The inorganic carbon was determined as the difference between total carbon in soil
122 and total organic carbon. Parallel soil samples were repeatedly washed with 2 M HCl to
123 remove inorganic carbon, before total organic carbon was determined using a LECO CHN
124 -1000 analyser. (Leco, St. Joseph, MI). The particle size distribution was measured using
125 the pipette method of Elonen (1971).

126

127 *Batch titration*

128 Between four and six subsamples (20 g) of each field moist soil were suspended in <50 ml
129 0.01 M NaCl to which small volumes of NaOH (0.1 M) or HCl (1.0 M or 0.1 M) were added
130 to adjust pH. The final total solution volume was 50.0 ml, including the soil water, 0.01 M
131 NaCl extract and acid/base added to adjust pH. The volumes of acid and base were chosen,
132 based on range–finding tests, to achieve a final pH range of 1–2 units above and below that

133 pH obtained without addition of acid or base (the ambient pH). Soil–solution mixtures
134 were shaken continuously (100 strokes min⁻¹) for 55 hours, and the supernatants removed
135 and filtered through Whatman glass fibre filters, GF/C, 1.2 µm). No attempt was made to
136 exclude the atmosphere from the samples during the experiments. The pH and
137 concentrations of dissolved organic carbon (DOC), Mg, Al, K, Ca, Cu, Zn, and Cd were
138 measured in the supernatants. Metal concentrations were determined using a Quadropole
139 Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Perkin Elmer Elan 6000). A
140 Shimadzu TOC-5000 analyser (Shimadzu Scientific, Columbia, MD) was used to
141 determine supernatant DOC. pH was measured using a combination electrode.

142

143 **Modelling**

144 *Humic Ion Binding Model VI*

145 A full description of Humic Ion Binding Model VI (hereafter referred to as Model VI) is
146 given by Tipping (1998). Briefly, Model VI is a discrete site/electrostatic model for
147 simulating cation binding to humic substances. Binding of cations can occur either at
148 discrete binding sites (specific binding) or electrostatic accumulation adjacent to the
149 molecular surface. Heterogeneity of binding is provided for by having a number of distinct
150 site types each with its own binding strength. The range of metal binding strengths is
151 extended by allowing multidentate binding at specific combinations of two and three sites,
152 and further by empirically increasing the binding strengths of subsets of these sites.
153 Binding strengths are further modified by the (electrostatic) effect of charge development
154 at the molecular surface resulting from ion binding and release. Electrostatic accumulation
155 of ions adjacent to the molecular surfaces (non-specific binding) is simulated using
156 Donnan type expressions. The relative affinity of ions for accumulation may be adjusted

157 using selectivity coefficients. Here we have set the selectivity coefficients for the ions
158 Na^+ , Mg^{2+} , Al^{3+} , AlOH^{2+} and Al(OH)_2^+ to 0.25, 0.75, 0.5, 0.5 and 0.5 respectively, after
159 Tipping *et al.*, (1995). All other ions have selectivity coefficients of unity.

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

164 *Mineral surfaces*

165 We have chosen three mineral surfaces for modelling: iron oxide, aluminium oxide and an
166 idealised clay cation-exchanger. Iron and aluminium oxide surface chemistry are
167 simulated by a surface complexation model originally used by Lofts and Tipping (1998) as
168 a component of the SCAMP (Surface Chemistry Assemblage Model for Particles) model
169 for aquatic suspended particulate matter. In this model the oxide surfaces possess
170 amphoteric hydroxyl groups. These groups are homogenous with respect to the strengths
171 of proton binding and release. Metals can bind monodentately to any surface group. Metal
172 binding is heterogeneous, with three metal binding strengths: strong, medium and weak,
173 applying to 0.9%, 9% and 90.1% of the surface groups respectively. We assume the oxides
174 to be in large surface area, amorphous forms; surface areas were set to the default values of
175 $0.6 \text{ m}^2 \text{ kg}^{-1}$ and $0.4 \text{ m}^2 \text{ kg}^{-1}$ for iron and aluminium oxides respectively. Electrostatic
176 effects on ion binding, and electrostatic accumulation of ions adjacent to the surface, are
177 handled by submodels similar to those found in Model VI. Parameters for proton and
178 metal binding are those calculated by Lofts and Tipping (1998).

179

180 Cation binding to the idealised cation-exchanger is calculated using the model introduced
181 by Tipping (1994). Binding is by electrostatic accumulation only, using Donnan type
182 expressions. Selectivity of binding is possible, but is not invoked here. Binding capacity
183 is expressed by a surface charge density (in $\text{cmol}_c \text{kg}^{-1}$) and a specific surface area (in
184 $\text{m}^2 \text{kg}^{-1}$).

185 *Modelling system*

186 Model VI, the surface complexation model, cation exchanger model and a solution
187 speciation submodel were combined as shown in Figure 2. Organic matter, comprising
188 humic and fulvic acids, can be present in the solid phase as soil organic matter (SOM) or in
189 the solution phase as dissolved organic matter (DOM). The default binding parameters in
190 all the models were not adjusted in this study. The relationship between the measured
191 amounts of organic matter on the soil solids, and the amounts of humic and fulvic acid
192 input to the model to represent these phases, can be set *a priori* or input as fitting
193 parameters. Input Al and Fe(III) can be specified as a mixture of ‘fixed’ hydroxides that
194 have chemically active surfaces but cannot dissolve, and of ‘active’ element that can
195 participate in solution and surface equilibria. The latter if desired can precipitate as
196 hydroxides, and if desired the precipitates can possess chemically active surfaces.
197 Hydroxide precipitation is simulated by conventional solubility products ($K_{\text{sp}} = a_{\text{M}} \cdot a_{\text{H}}^{-3}$);
198 we use standard log solubility products of 8.5 and 2.7 for $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$
199 respectively, and standard enthalpies of precipitation of -107 kJ mol^{-1} and -102 kJ mol^{-1} ,
200 after Tipping *et al.* (2003) and Tipping *et al.* (2002) respectively. The carbonate system
201 may be modelled by assuming equilibrium with atmospheric carbon dioxide or by
202 inputting a measure of the amount of carbonate present. Given that we were attempting to
203 model limed soils, additional code was written to allow the simulation of calcite (CaCO_3)
204 precipitation and dissolution. The standard log solubility product ($K_{\text{sp}} = a_{\text{Ca}} \cdot a_{\text{CO}_3}$) and

205 standard enthalpy of precipitation used were -8.48 and -8 kJ mol^{-1} , respectively (Smith *et*
206 *al.* 2004).

207 **Results**

208 *Characteristics of the investigated soils*

209 All the soils are sandy loams, but due to the different vegetation covers, management
210 practices and distances from the smelter, the soil chemical properties vary (Tables 1 and 2).
211 Significant variations in the contents of TOC, exchangeable Ca and CuCl_2 extractable Al
212 were seen. The Ca accounted for between 75 and 96% of the total CEC. The two largest
213 pH values were found in soils collected from the sites #4 and #8. Both sites are frequently
214 limed (every 5-7 yr), and the relative contribution of Ca to CEC was also the highest in
215 these two soils (Table 2). The content of organic C is lowest in soil #4. The two soils
216 adjacent to the smelter, #3 and #8, had the highest metal (Cu, Zn, Cd) contents (Table 3).
217 Of the two remoter sites, #1 had higher metal contents than #4 as a result of its location
218 downwind of the smelter.

219 Compared with soils sampled from a forest site in southern Norway (Birkenes) (Lofts *et al.*
220 2001a) soils #4 and #8 were notably enriched in exchangeable Ca relative to copper-
221 extractable Al. Ratios of Ca:Al in soils #4 and #8 were 19 and 23 compared to 2 and 0.2 in
222 the Birkenes Oe and Oa horizons. The ratios in soils #1 and #3 were similar to those at
223 Birkenes at 0.8 and 2.1 respectively.

224 *Batch titrations*

225 The observed pH and Ca, DOC, major ions (Mg, K, Al) and trace metals (Cu, Zn, Cd) in
226 the batch titration supernatants are shown in Figures 3, 4, 5 and 6 respectively.
227 Supernatant pH (Figure 3) varied by between two and a half and four pH units depending
228 upon the soil. Dissolved organic carbon concentrations (Figure 4) varied considerably with

229 acid/base addition. The minimum DOC concentration was observed in the ambient
230 systems, except for soil #8 where the DOC at the lowest acid addition was marginally
231 lower than that in the ambient system. In all soils the DOC increased considerably when
232 the base-acid > 0. This has been previously ascribed (Lofts *et al.* 2001b) to solubilisation
233 of increasingly hydrophobic organic matter due to progressive deprotonation as the pH is
234 increased. Appreciable increases in DOC were also seen in soils #4 and #8 after acid
235 addition; this has tentatively been ascribed (Lofts *et al.* 2001a) to solubilisation of a portion
236 of the SOM able to bind large amounts of Al and having a net positive charge. Major ion
237 and trace metal solubility varied considerably, both with pH in single soils and among the
238 metals as a proportion of the active pool. Dissolved K varied by up to an order of
239 magnitude depending upon the soil, Mg and Ca by between one and two orders of
240 magnitude, Al and the trace metals by up to three orders of magnitude. At the smallest pH,
241 the dissolved concentrations of Mg, K, Ca, Zn and Cd approached or even reached those
242 expected to result from complete dissolution of the bound metal (as estimated by the
243 various extractions). Dissolved Al and Cu concentrations were notably variable among
244 soils, with solubility relative to the bound pools being relatively large in soil #1, at large
245 pH for both metals and for Al at small pH. In contrast, both metals showed rather low
246 solubility in soil 8, with the highest solution concentration representing less than 10% of
247 the 'active' pool, and only about 1% in the case of Cu. The highest Cu concentrations
248 were consistently associated with the large pH end of the titrations, in association with
249 large DOM concentrations. The relative importance of supernatant DOM complexation
250 was seen in the correlations between solution metals (in particular Al and Cu) and DOC
251 concentrations (both expressed as logarithms) – correlation coefficients for Mg, Al, K, Ca,
252 Cu, Zn and Cd were -0.51, 0.80, -0.13, -0.41, 0.93, 0.03 and -0.01 respectively.

253 These trends in solubility may be interpreted in terms of the binding mechanisms of the
254 metals, and their relative tendencies to bind to solid and dissolved phase ligands.
255 Potassium does not form solution complexes and binds to solid phases by cation exchange;
256 thus competition by protons is less important than it is for cations that bind to specific
257 sites, and the variation in solubility with pH is small. Both Mg and Ca can bind
258 specifically in competition with protons, and so the pH dependence of binding is greater
259 than seen for K. The increase in solubility of these metals above pH 6 in soil #1 may be
260 attributed to solubilisation of organic matter (Figure 4) and its bound metals. This effect
261 becomes more important when considering Zn and Cd, and particularly so for Al and Cu,
262 which would be expected to bind predominantly by specific complexation. Copper in
263 particular exhibits strong binding to both solid phase and dissolved ligands, even at the low
264 end of the studied pH ranges. This results in the observed maximum solubility at the
265 largest pH that is seen particularly in soils #4 and #8. Here the Cu is likely to be
266 predominantly DOM-complexed. Dijkstra *et al.* (2004) reported the same pH dependency
267 of metal solubility in soil extracts, with a minimum dissolved metal in the pH 4-6 range.

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

269 Solution concentrations of Al and Fe(III) were input to the model along with pH, Mg, K,
270 Ca, Cl and DOM. DOM was assumed to comprise 65% fulvic acid and 35% chemically
271 inert material, after Bryan *et al.* (2002); this assumption was used throughout. No
272 measurements of solution anions other than Cl (e.g. SO₄) were available. Given that the
273 electrolyte Cl ought to dominate the solution anions, such other anions were not
274 considered. The carbonate system was assumed to be in equilibrium with atmospheric
275 CO₂, at a partial pressure of 34.96Pa (3.45×10^{-4} atm). Speciation was done by adjusting
276 the Na concentration to force charge balance. Saturation indices (SIs) were initially
277 calculated for hydroxides of Al and Fe(III), using the solubility parameters given in the

278 *Modelling system* section. Log SIs for Al(OH)₃ ranged from -3.7 to 3.9 and for Fe(OH)₃
279 from -0.5 to 5.9. Thus supersaturation with respect to both minerals was predicted,
280 although for Al the degree of under- or oversaturation was highly pH-dependent. We
281 interpret these finding to indicate the presence of colloidal forms of the minerals in the
282 supernatants, as has been assumed previously (e.g. Tipping *et al.* 2003). All subsequent
283 calculations were therefore done allowing Al(OH)_{3 (s)} and Fe(OH)_{3 (s)} to precipitate.

284 *Modelling stage 2: solubility controls on Ca*

285 The aim of this stage was to examine the possibility that in these limed soils, a solid
286 calcium-containing phase may control the supernatant pH and dissolved Ca. For this
287 purpose we chose calcite (CaCO₃) as a model phase, since it is the most soluble of the
288 calcium carbonates. We also assumed that all the measured inorganic C was present as
289 calcite. We then predicted supernatant pH and Ca under three scenarios:

- 290 1. Exchangeable calcium and calcite assumed to be ‘active’, i.e. participating in
291 solubility and complexation reactions, in a closed system.
- 292 2. As scenario 1, in an open system, i.e. in equilibrium with atmospheric CO₂ at a
293 partial pressure of 34.96Pa (3.45×10^{-4} atm).
- 294 3. As scenario 2, but with calcite not assumed to be ‘active’, i.e. the ‘active’ Ca was
295 set to the measured exchangeable value.

296 In scenarios 1 and 2 the total ‘active’ calcium input to the model was the sum of the
297 measured exchangeable pool and the pool assumed to be initially present in calcite, which
298 was calculated from the measured amount of soil inorganic C. In scenario 1 the total
299 carbonate was also calculated from the soil inorganic C. For the open system in scenarios
300 2 and 3 a total carbonate was not defined. The modelling also required inputs of solid
301 phase concentrations and pools of ‘active’ elements that can partition between solid and

302 solution. Pools of Mg and K were taken as the exchangeable values. For Al, we chose to
303 input two pools: a fixed pool of aluminium hydroxide calculated by the difference between
304 the oxalate- and copper-extractable amounts, and an 'active' pool, equal to the copper-
305 extractable amount. This is consistent with previous studies where at small pH soil Al
306 solubility has been shown to be controlled by the organically-bound pool (Berggren &
307 Mulder 1995), which is approximated by the copper chloride extraction. The 'active' pool
308 was able to precipitate as $\text{Al}(\text{OH})_3$, with a chemically active surface. For Fe, no copper-
309 extractable pools were available. However, since the calculations in stage 1 indicated that
310 Fe was consistently close to saturation or oversaturated with respect to $\text{Fe}(\text{OH})_3$, we chose
311 to input the oxalate-extractable pool as the 'active' pool, allowing it to precipitate with a
312 chemically active surface. For the trace metals, the pools measured by 0.22 M HNO_3 were
313 input. SOM was calculated by assuming it to be 50% C and to comprise 50% humic acid
314 and 50% fulvic acid. Initially two sets of clay parameters were used (surface charge
315 density = 10^{-4} $\text{cmol}_c \text{ m}^{-2}$, specific surface area (SSA) = $0.1 \text{ m}^2 \text{ kg}^{-1}$ or $1.0 \text{ m}^2 \text{ kg}^{-1}$), however
316 preliminary modelling showed that this did not significantly affect any predictions,
317 therefore the surface area was fixed to $0.1 \text{ m}^2 \text{ kg}^{-1}$ for all the modelling. The supernatant
318 pH was considered a model fitting parameter, and was adjusted by forcing charge balance.
319 The results are shown in Figure 3. In both soils #1 and #8, the best predictions of both pH
320 and Ca were obtained assuming the exchangeable pool only to control Ca solubility. In
321 soil #3, only small differences among the predictions were found; this is likely because the
322 amount of input Ca derived from calcite was small compared to the exchangeable pool. In
323 soil #4, the pH was consistently and significantly overestimated in all scenarios. Even in
324 scenario 3, dissolved Ca was predicted as being under the control of calcite solubility, even
325 though only the exchangeable pool was input. Considering all four soils together, these

326 results suggest strongly that Ca solubility in these experiments is not controlled by
327 precipitation–dissolution reactions of calcite, but rather by a pool of exchangeable Ca.

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

329 Solution speciation was re–calculated, using the same assumptions as in Stage 1, allowing
330 Al(OH)₃ and Fe(OH)₃ to precipitate. Saturation indices were calculated for (i) metal
331 hydroxides Cu(OH)₂, am–Zn(OH)₂ and **b**–Cd(OH)₂ with standard log solubility products
332 ($K_{so, 298} = a_M \cdot a_{OH}^2$) of -19.83, -15.81 and -14.51 and standard enthalpies of 55.3, 31.4 and
333 17.2 kJ mol⁻¹, respectively; (ii) metal carbonates CuCO₃, ZnCO₃ and CdCO₃ with standard
334 log solubility products ($K_{so, 298} = a_M \cdot a_{CO_3}$) of -11.5, -10.00 and -12.00; (iii) the
335 zinc/aluminium layered double hydroxide (LDH) Zn₂Al(OH)₆(CO₃)_{0.5}·xH₂O, with a log
336 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
337 enthalpy values were not available enthalpy was assumed to be zero as a first
338 approximation. No saturation with respect to any of these minerals was predicted in the
339 experimental solutions.

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

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

$$348 \quad (pH_{obs} - pH_{calc})^2 + (p[Ca]_{obs} - p[Ca]_{calc})^2, \quad (1)$$

349 where the subscripts ‘obs’ and ‘calc’ refer to the observed and modelled values of pH and

350 p[Ca], respectively. Following optimisation, solution pH and Mg, Al, K, Ca, Cd, Cu and
351 Zn were predicted for each supernatant in each titration.

352 The optimised 'active' soil Ca concentration showed no clear pattern in comparison with
353 the Ca extracted using NH_4NO_3 . The largest difference, as might be expected, was
354 observed in soil #4 where the optimised pool was 44% of that measured. In both soils #1
355 and #3 the optimised pool was higher at 147% and 158% of the measured pool. The least
356 optimisation was required for soil #8 where the optimised pool was 90% of the measured.

357 The modelled pH and p[Ca] agreed reasonably well with the observations. The pH
358 buffering in soils #1, #4 and #8 was well reproduced, particularly so in soil #8 with a root
359 mean squared error (RMSE) of 0.02 for a mean observed pH of 5.93. The pH buffering in
360 soils #1 and soil #3 was somewhat underestimated. Trends in p[Ca] were well reproduced,
361 with soil #8 again showing the best prediction. Trends in p[Mg] and p[K] (Figure 5) were
362 generally well reproduced, although in some cases (p[Mg] in soil #3 and p[K] in soils #3
363 and #4) predictions were biased. The observed minima in aluminium solubility were
364 reasonably well simulated; however, the model did not reproduce higher dissolved
365 aluminium well, showing a consistent tendency to underestimate solubility at both large
366 and small pH. Underestimation of p[Al] at large pH is likely related to the supersaturation
367 with respect to $\text{Al}(\text{OH})_3$ observed in the solution speciation results, implying the presence
368 of colloidal $\text{Al}(\text{OH})_3$ in the solutions, which cannot be simulated by the model. Including
369 readily dissolvable Al solids in the active Al by using the oxalate-extractable Al, improved
370 the predictions of dissolved Al (dashed lines in Figure 5) with little effect on predicted
371 p[Ca], p[Mg], p[K] or the trace metals (data not shown). Predicted pH (dashed lines in
372 Figure 3) was also little affected, except for soil #1 where the pH buffering was
373 overestimated somewhat (RMSE in pH was 0.87, compared to 0.48 when copper
374 extractable Al was input).

375 Trace metal solubility (Figure 6) was generally reproduced very well. Copper was
376 underestimated in soils #1, #4 and #8, indicating that the 0.22 M HNO₃ extraction
377 underestimated the active pool. Zinc was underestimated in soil #8 and at small pH in soil
378 #3. Cadmium solubility was consistently well reproduced; particularly in soils #4 and #8
379 (RMSEs were 0.06 and 0.11 respectively). The model consistently predicted solid phase
380 metal to be predominantly bound to organic matter. Binding to clay and iron or aluminium
381 oxide was relatively unimportant; individual contributions to the total binding were always
382 below 5% and largely below 1%.

383 Where there was clear bias between observation and prediction we optimised the active
384 soil metal, to establish the difference between the measured the optimal active pools. The
385 criterion for optimisation was a mean absolute deviation of greater than 0.4 in log
386 (dissolved metal), thus identifying bias in the predictions as opposed to a poor trend. The
387 soils–metal combinations identified were Cu in soils #1, #4 and #8 and Zn in soils #3 and
388 #8. Optimisation was done by adjusting the active pool of metal to exactly fit the dissolved
389 metal concentration at the ambient pH. The results are shown in Figure 6. Since the bias
390 in the original predictions was consistently to lower dissolved metal concentrations,
391 optimised active pools were all larger than the measured ones. The optimised pools were
392 between two and seven times greater than the 0.22 M HNO₃–extracted pools. In all the
393 cases involving copper, and in zinc in soil #3, the optimised pools were greater than the
394 aqua regia–extracted pools. Optimising the metal pools did not produce any significant
395 changes in the trends in predicted log(dissolved metal), thus where the original bias was
396 most consistent, the resulting fits were a notable improvement. This was most clearly seen
397 for Cu in soils #1 and #8 where the RMSE's dropped from 0.47 and 0.60, to 0.21 and 0.15
398 respectively, on optimisation.

399 **Discussion**

400 Modelling the solid–solution partitioning of elements in soil titrations is one of a number
401 of ways of assessing the abilities of speciation models to reproduce soil chemistry. The
402 approach has the advantage that trends in chemistry are measured in single soils, thus
403 providing quite a rigorous test of the model. Such work also complements studies where
404 single partitioning measurements are made on a larger number of soils from a defined
405 region or area (e.g. Weng *et al.* 2001; Tipping *et al.* 2003; MacDonald & Hendershot
406 2006). Modelling produced highly satisfactory fits to the observed data. The model
407 outputs depend on a large number of input parameters, many of are derived from wet
408 chemical extractions that can only approximate to the conceptual pools of ‘active’ elements
409 and phases that the model requires as inputs. The agreement between observations and
410 predictions is therefore most impressive. To the best of our knowledge, this is the first
411 modelling study of soil titrations where the pH and partitioning of both the native major
412 ions and trace metals have been studied simultaneously. Gustafsson *et al.* (2003) and
413 Gustafsson and Schaik (2003) have modelled soil pH, major ions and trace metals using
414 batch titrations but added metal salts to achieve defined total concentrations, thus avoiding
415 the need to estimate the active metal. Cances *et al.* (2003) and Dijkstra *et al.* (2004) both
416 performed batch experiments without adding metals but fixed pH when modelling. In
417 choosing to model the pH rather than fix it we have tested the model more rigorously than
418 would otherwise have been the case. Given the importance of pH as a control on the trace
419 metal partitioning it provides additional validation of the model framework as a means of
420 simulating not only the control of trace metal partitioning but also the control of pH itself
421 by the major ions and ligands (including solid phases). This would be important if, for
422 example, we wished to model the temporal response of soil metal to variations in soil
423 acidification status.

424 In common with a previous study on forest soils from southern Norway (Birkenes) (Lofts
425 *et al.* 2001a) we have chosen to calibrate the model individually to soils. In contrast to this
426 study, the pool of active Ca was selected as the optimal to adjust, whereas previously the
427 active pools of humic substances and Al were adjusted. Taking the four soils together, the
428 modelled soil pH was most sensitive to the value selected for the active Ca pool, which is
429 consistent with the observation that on average Ca made up a larger proportion of the
430 active soil cations relative to Al, than it did in the Birkenes soils. Modelling showed that
431 there was no need to invoke dissolution and precipitation of a solid Ca-containing phase
432 (e.g. CaCO_3) in these soils despite the fact that some are known to be limed; this suggests
433 either that the amounts of lime in the soils were not significant for Ca partitioning or that
434 lime dissolution was not significant on the timescale of the experiment. The lime (“Odda
435 lime”) applied to these soils consists mainly of CaOH and CaCO_3 , and is believed to have
436 both short- and long-term effects due to its composition and particle size distribution
437 (pers. comm., manager at “Odda lime”).

438

439 Of the major ions Al was the most poorly simulated by the model. The possible presence
440 of colloidal $\text{Al}(\text{OH})_3$ in the supernatants, as indicated by the solution modelling, could
441 explain some of the model discrepancies at large pH. However, dissolved Al at the
442 smallest pH of each titration was underestimated by at least an order of magnitude,
443 indicating that the pool of active Al was too small. In soils #1 and #3 this could be partly
444 accounted for by the overestimation of the smallest pH and the consequent underestimation
445 of proton competition for Al binding to the SOM. However, this cannot explain the results
446 in soils #4 and #8 where the largest pH is well predicted by the model. Increasing the
447 active Al pool by inputting the oxalate-extractable Al consistently increased the predicted
448 supernatant Al and improved the predictions considerably. This is an interesting finding,

449 since it implies that readily dissolvable Al solid phases (i.e. those extracted by oxalate but
450 not by copper chloride) are part of the active Al in these soils. This contrasts with the
451 findings of studies on Al solubility control in acid forest soils of the region (e.g. Berggren
452 & Mulder 1995; Lofts *et al.* 2001a) where short-term solubility was controlled solely by
453 the pool of organically-bound Al. The reasons for this discrepancy are not clear. From the
454 perspective of this study, Al is less important than Ca in controlling the chemistry of these
455 soils and does not appear to be highly significant in influencing the trace metal solubility
456 by competition.

457 The trace metal modelling results indicate that short-term solubility of Cu, Zn and Cd in
458 these soils is controlled by binding to organic matter. Other binding phases, and metal
459 precipitates, are indicated to have an insignificant or negligible role in controlling
460 solubility. This is in clear accordance with similar modelling studies involving these
461 metals (Weng *et al.* 2001; Dijkstra *et al.* 2004). Generally the model reproduced the
462 observed solubility well. Directly predicting the metal solubility as we have done here is a
463 means of assessing the extraction method for estimating the active soil metal. Where there
464 was significant bias between observations and predictions, it was readily possible to fit the
465 model by adjusting the active pool. Dilute acid extractions of the type used here are
466 popular for estimation of the active metal, and there is no reason to believe from the
467 modelling that the measured active pools show any general bias. A standard wet chemical
468 extraction for active soil metal would be useful from the point of view of modelling since it
469 would improve consistency of data among studies. Wider acceptance of any single wet
470 chemical extraction method will, however, require application and validation against a
471 wider range of soil types than has currently been done. None of the metals appeared to be
472 controlled by any of the solid phases considered. This is rather interesting in the case of the
473 Zn/Al LDH, since this material solid has previously been identified as comprising 20% of

474 the total Zn in a soil contaminated by smelting activities, of quite similar pH (5.6) and
475 organic matter content (14%) to our soils (Juillot *et al.* 2003). Clearly there is a potential
476 for such solids to form an appreciable portion of the Zn in contaminated soils. However,
477 they appear to exert no influence on short-term Zn solubility in these soils.

478 The optimisation of selected metal pools to fit the observations produced some intriguing
479 results. In particular, the observation that optimised pools of Cu, in three of the soils, were
480 greater than the pool obtained by aqua regia extraction, deserves attention. Aqua regia
481 extraction is considered to extract some tightly bound mineral metal as well as surface
482 bound metals, and thus should overestimate the active pool. This suggests that the
483 optimised Cu pools are unrealistically large and that the underestimation of dissolved Cu
484 when using the 0.22 M HNO₃ extracted pool is due to model error. Given the complexity
485 of the model, the source of such error is difficult to ascertain without further work. It is
486 notable that Cu solubility depends strongly on the solubility of the soil organic matter and
487 thus on the relative affinity for SOM and DOM for the metal. Predictions are therefore
488 expected to be sensitive to both the intrinsic binding affinity of the model humic and fulvic
489 acids and to a *a priori* assumptions made about the activity of the SOM and DOM. But
490 without more detailed experimental data (such as free metal ion activities in the
491 supernatants) it is not appropriate to explore this further in this study.

492 The mobility of DOM was clearly a significant influence on trace metal solubility in these
493 experiments, particularly so for Cu and also to a lesser extent for Zn and Cd at largest pH.
494 This is again in clear accord with current knowledge about the binding of these metals
495 to organic matter. It ought to be realised that the concentrations of DOM encountered in
496 the batch titration supernatants are likely to be higher than those encountered in field soil
497 solutions or local surface waters; this is an increasingly recognised phenomenon in soil
498 experimentation in the laboratory (e.g. (Tipping *et al.* 2003). The supernatant metal

499 concentrations cannot therefore be taken as representative of the concentrations that we
500 would expect to encounter in field samples. The data are better viewed as providing a test
501 of the mechanistic underpinning of the model and of its ability to describe how the
502 supernatant chemistry varies as a result of experimental manipulation.

503 As noted in the Introduction, the use of K_d s to quantify metal partitioning remains common
504 since many transport and fate models require the K_d as an input parameter, but there are
505 significant difficulties inherent in measuring K_d s that are suitably representative of field
506 conditions. Coupled speciation–transport models (e.g. (Tipping *et al.* 2006), incorporating
507 other longer term metal input and loss processes such as mineral weathering, provide an
508 alternative approach to simulating the transport and fate of metals in the soil environment.
509 It is clear from the results of this and previous studies that speciation models have great
510 potential in simulating trace metal partitioning in soils. The further work needed to
511 establish relationships between analytical measurements and model inputs would be best
512 achieved by analysing and modelling as wide a range of soils as possible. A criticism
513 sometimes made of speciation modelling is the richness of input data required, compared
514 for example to a single K_d value. While this is certainly the case, it is also true that
515 speciation model outputs are richer in that they provide a framework to describe metal
516 partitioning in the context of other changes in soil chemistry (e.g. pH and DOM
517 concentration). A goal of terrestrial metal modelling should be to link the partitioning and
518 fate of contaminant metals to major soil processes such as acidity buffering and carbon
519 cycling. Only by doing this can we begin to assess the effects of large scale environmental
520 change on trace metals in soils.

521 **Acknowledgements**

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

524 postdoctoral fellowship which, including all analytical cost, was financed by the
525 Norwegian Research Council.

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

	Cultivation/vegetation cover	Distance from smelter		pH _{H2O}	CEC	Clay	Organic C	Inorganic C
		km	direction					
Soil #1	Old orchard	12.3	N	5.1	11.9	4.0	4.2	1.9
Soil #4	Meadow, intensive grass production and partly pasturage	5.0	S	6.4	31.7	3.5	2.0	1.4
Soil #3	Young orchard with permanent grass cover	1.0	SW	5.4	25.1	6.8	7.7	0.2
Soil #8	Garden lawn	0.9	NW	6.6	54.9	5.0	6.3	0.8

3

1 **Table 2.** Concentrations of exchangeable base cations and solid phase fractions of Al and Fe in the soils.

	exchangeable cations				oxalate-extractable Al & Fe		copper-extractable Al	
	Na	Mg	K	Ca ^a	Al	Fe	Al	
/mmol kg ⁻¹								
Soil #1	0.74	7.35	1.09	44.5	(75)	132	188	52.9
Soil #4	nd ^b	4.84	2.36	152	(96)	26.1	43.1	7.50
Soil #3	nd	17.6	6.10	102	(81)	114	115	49.3
Soil #8	nd	22.9	6.08	249	(91)	37.8	120	11.3

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

3 ^b not detectable

4

1 **Table 3** Aqua Regia and 0.22 M HNO₃ extractable Cd, Cu and Zn.

	Aqua Regia extractable (mmol kg ⁻¹)				0.22 M HNO ₃ extractable (mmol kg ⁻¹)			
	Soil 1	Soil 4	Soil 3	Soil 8	Soil 1	Soil 4	Soil 3	Soil 8
Cd	0.0057	0.0033	0.057	0.070	0.0031	0.0023	0.016	0.019
Cu	0.48	0.15	0.92	1.7	0.27	0.05	0.24	0.55
Zn	2.2	1.8	15	15	0.76	0.63	4.0	4.9

2

1 **Figure captions**

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

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

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

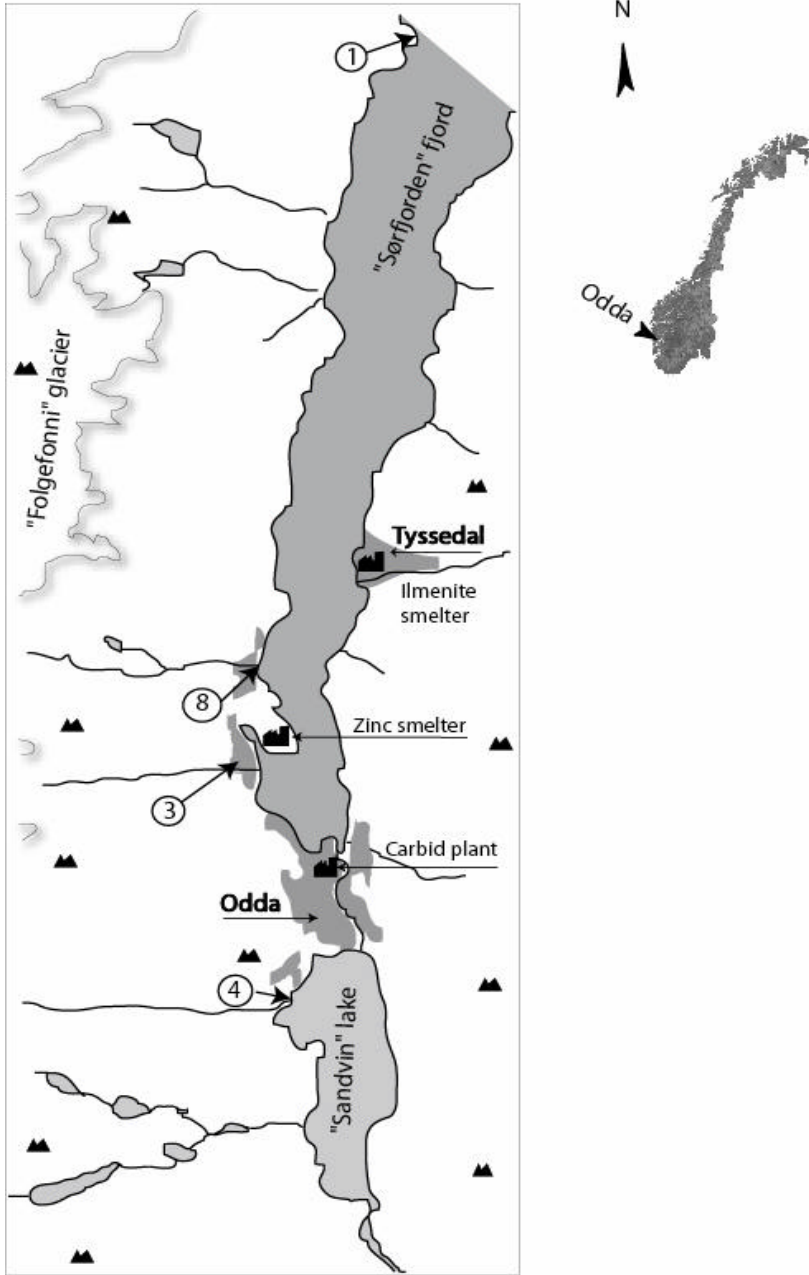
15 Figure 4. Observed DOC concentrations in the batch titrations. Solid circles, soil #1; open
16 circles, soil #3; Solid triangles, soil #4; Open triangles, soil #8. The lines are for
17 guidance.

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

21 Figure 6. Observed and modelled dissolved Cu, Zn and Cd in the batch titrations,
22 following model fitting. The tick horizontal lines represent the dissolved metal
23 concentration corresponding to the active pool. Dashed lines represent the

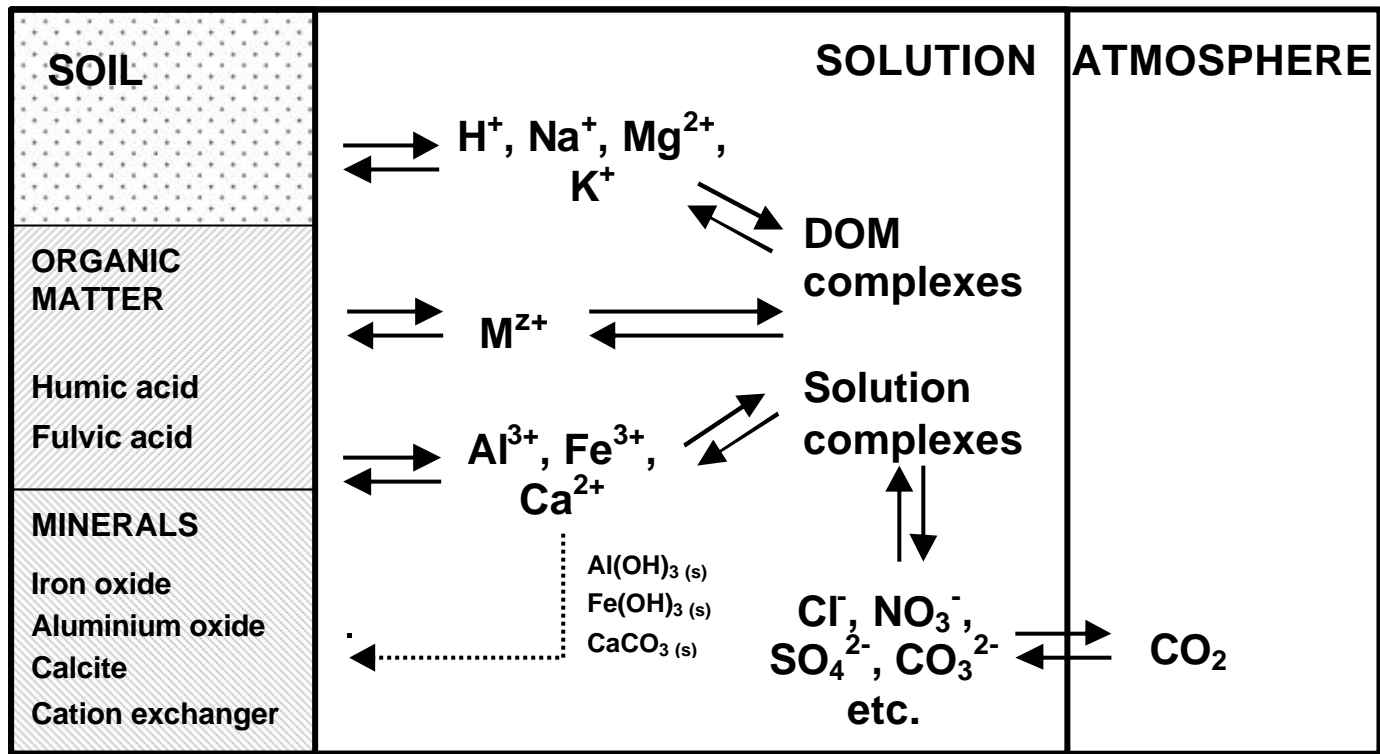
1 predicted dissolved metal, and active pool, obtained by optimisation, where this
2 was done (see text for details).

1



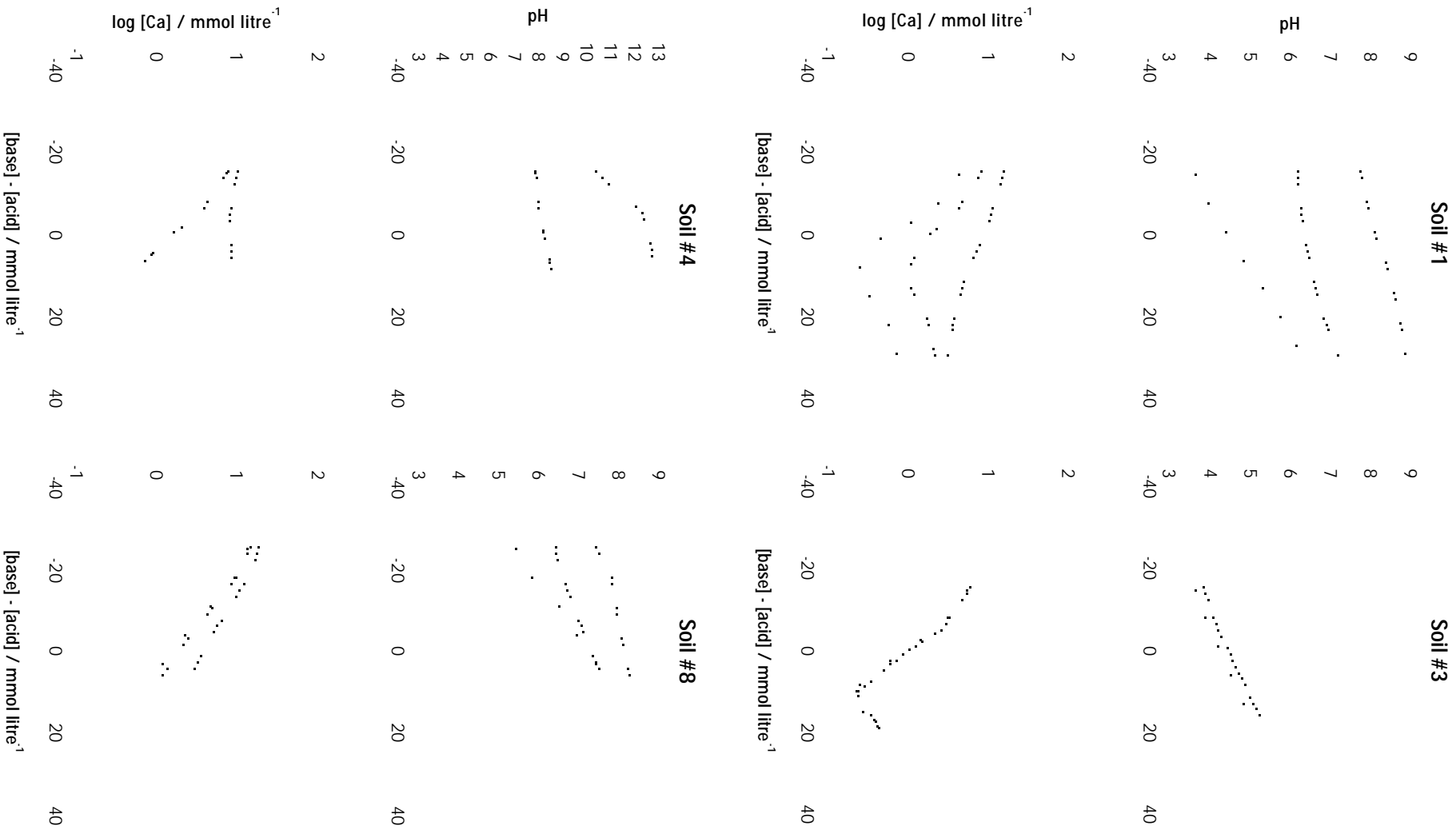
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3 **Figure 1.**

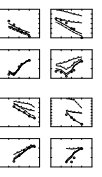


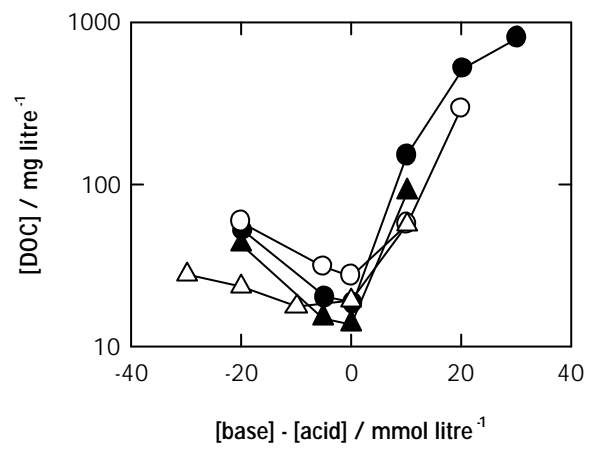
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2 Figure 2.



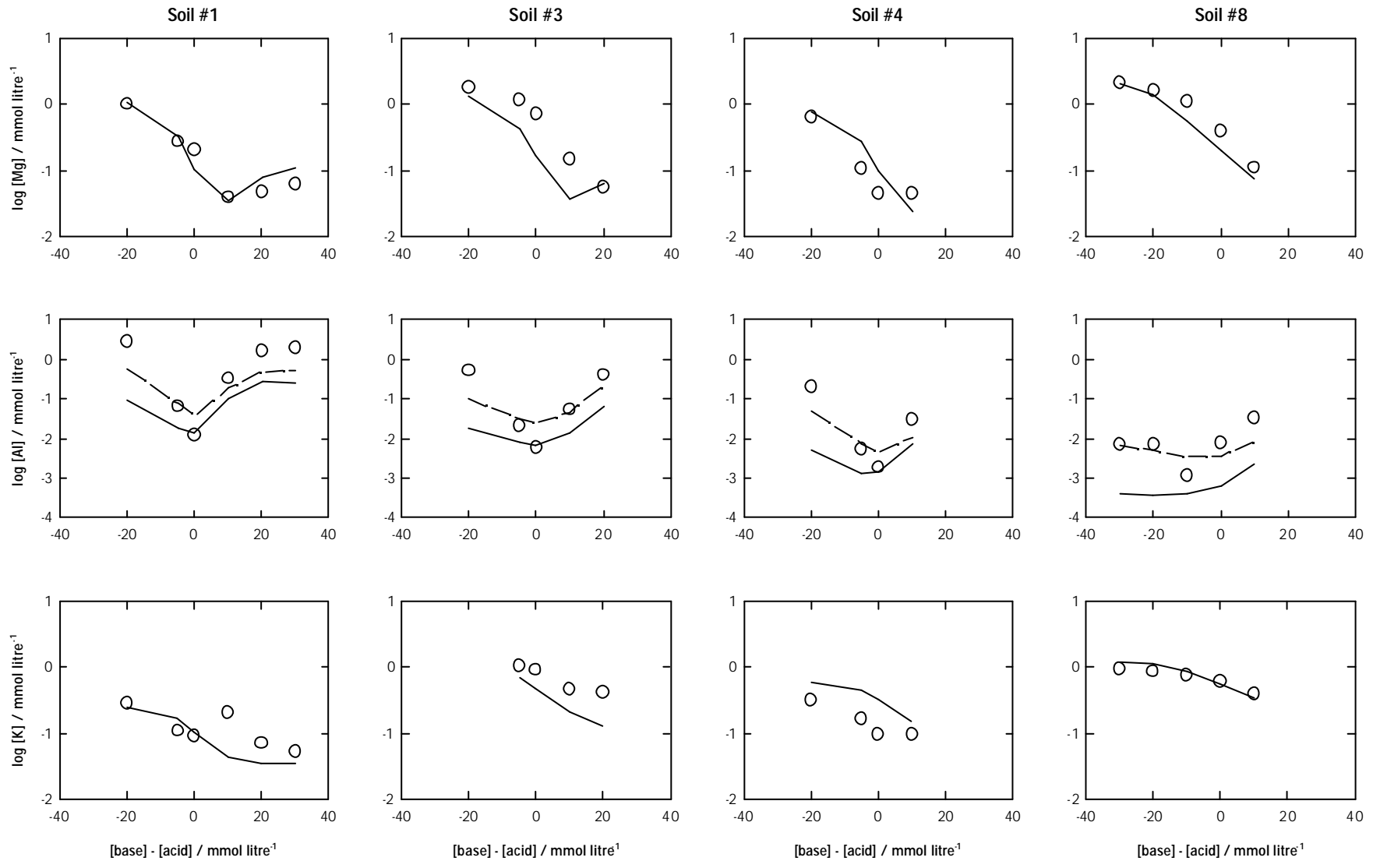
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2 **Figure 3.**





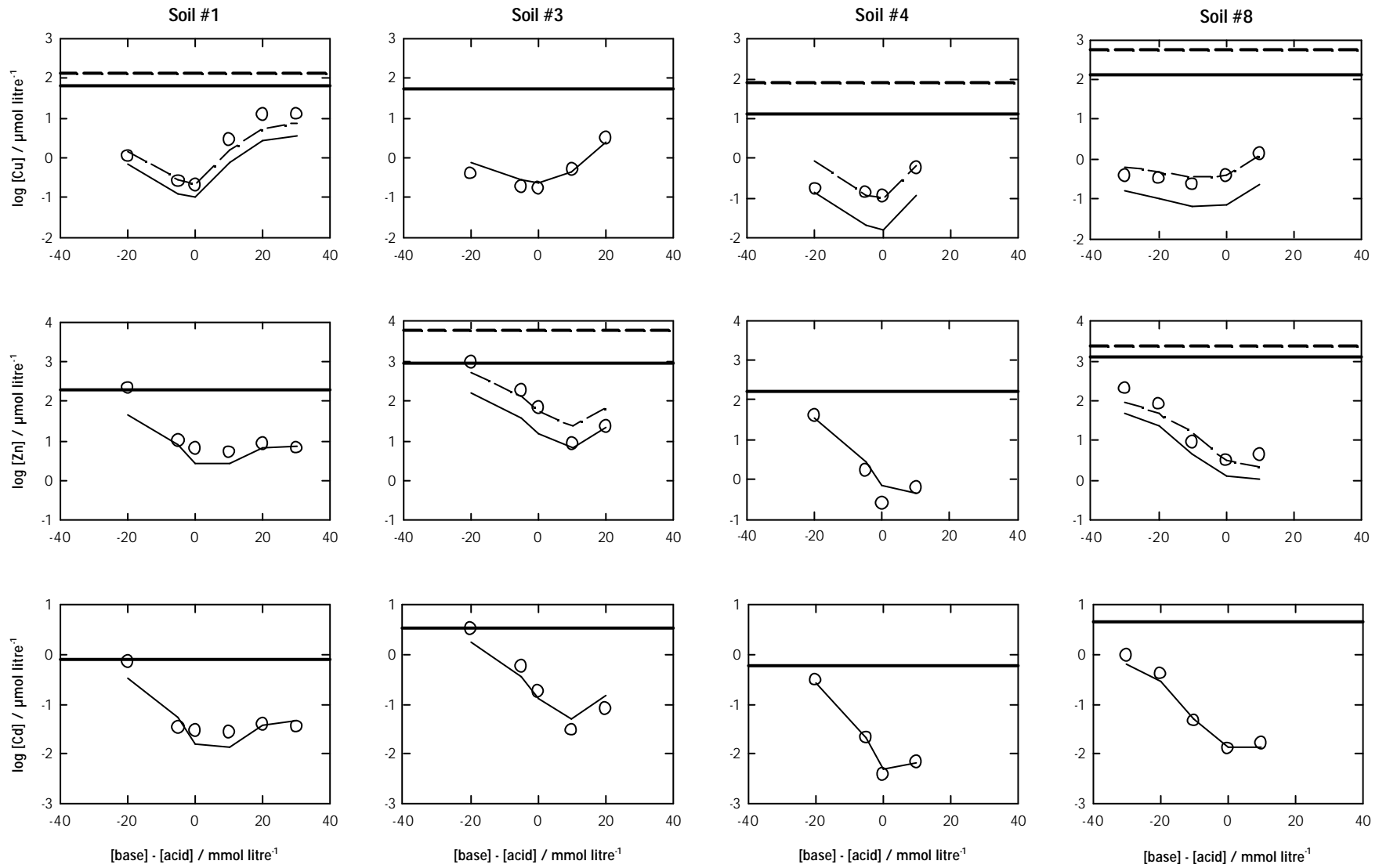
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2 **Figure 4**



1

2 **Figure 5.**



1

2 **Figure 6.**

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