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1 **Decreasing DOC trends in soil solution along the hill slopes at**
2 **two IM sites in southern Sweden – geochemical modeling of**
3 **organic matter solubility during acidification recovery.**

4
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43 **Keywords:** DOC trends; forest soils; soil water; recovery from acidification; Stockholm
44 Humic Model; integrated monitoring

1 **Abstract**

2 Numerous studies report increased concentrations of dissolved organic carbon (DOC)
3 during the last two decades in boreal lakes and streams in Europe and North America.
4 Recently, a hypothesis was presented on how various spatial and temporal factors affect
5 the DOC dynamics. It was concluded that declining sulphur deposition and thereby
6 increased DOC solubility, is the most important driver for the long-term DOC
7 concentration trends in surface waters. If this recovery hypothesis is correct, the DOC
8 levels should increase both in the soil solution as well as in the surrounding surface
9 waters as soil pH rises and the ionic strength decline due to the reduced input of SO_4^{2-}
10 ions. In this project a geochemical model was set up to calculate the net humic charge and
11 DOC solubility trends in soils during the period 1996-2007 at two integrated monitoring
12 sites in southern Sweden, showing clear signs of acidification recovery. The Stockholm
13 Humic Model was used to investigate whether the observed DOC solubility is related to
14 the humic charge and to examine how pH and ionic strength influence it. Soil water data
15 from recharge and discharge areas, covering both podzols and riparian soils, were used.
16 The model exercise showed that the increased net charge following the pH increase was
17 in many cases counteracted by a decreased ionic strength, which acted to decrease the net
18 charge and hence the DOC solubility. Thus, the recovery from acidification does not
19 necessarily have to generate increasing DOC trends in soil solution. Depending on
20 changes in pH, ionic strength and soil Al pools, the trends might be positive, negative or
21 indifferent. Due to the high hydraulic connectivity with the streams, the explanations to
22 the DOC-trends in surface waters should be searched for in discharge areas and
23 peatlands.

24

25

1 **1. Introduction**

2 Numerous studies report increased concentrations of dissolved organic carbon (DOC)
3 during the last two decades in boreal lakes and streams in Europe, Canada and the US
4 (Erlandsson et al., 2008 ; Evans et al., 2005; Monteith et al., 2007; Skjelkvåle et al.,
5 2005). Many different processes have been proposed to explain these trends e.g.
6 hydrometeorological conditions (Erlandsson et al., 2008; Sarkkola et al., 2009), recovery
7 from acidification due to reduced sulphur deposition (Dawson et al., 2009; Monteith et
8 al., 2007), land cover (Laudon et al., 2009; Sarkkola et al., 2009), forest management and
9 land use (Laudon et al., 2009; Löfgren et al., 2009b; Yallop and Clutterbuck, 2009) etc.
10 Recently, Clark et al. (2010) presented a unifying hypothesis on how various spatial and
11 temporal factors affect the DOC dynamics. They concluded that declining sulphur
12 deposition and thereby increased DOC solubility, is the most important driver for the
13 long-term DOC concentration trends in surface waters, but that the variability between
14 sites is influenced by a multitude of spatial and temporal factors (op. cit.).

15

16 Soils and surface waters in the historically most polluted southern Sweden show clear
17 signs of recovery from acidification since the early 1990's (Karlton et al., 2003; Löfgren
18 et al., 2009a; Skjelkvåle et al., 2005). However, if the recovery hypothesis is correct, the
19 DOC levels should increase both in the soil solution as well as in the surrounding surface
20 waters as soil pH rises and the ionic strength decline due to the reduced input of SO_4^{2-}
21 ions. In contrast to surface waters, however, the soil waters in forested recharge areas
22 (number of monitoring sites (n_{sites}) =68, 50 cm soil depth, podzols) exhibit no change
23 (n_{sites} =32) or decreasing (n_{sites} =31) DOC concentrations during the period 1986-2008 in
24 southern Sweden, indicating increased coagulation of DOC in the upper soil horizon
25 (Zetterberg and Löfgren, 2009, Löfgren and Zetterberg in prep.). In Norway, similar
26 results were obtained, with no change or decreasing DOC trends during the period 1996-
27 2006 in soil water (n_{sites} =18) at 15 and 40 cm soil depth in podzols (Wu et al., 2010). In
28 contrast, increased DOC concentrations were found in soil water at two sites during the
29 period 1994-2007 in the Czech Republic. The latter studies represent soil water under the
30 forest floor at Lysina and in the mineral topsoil at Pluhuv (Hruska et al., 2009). Positive

1 DOC-trends were also found at 5-20 cm soil depth ($n_{\text{sites}}=9$, moorlands and forests)
2 during the period 2000-2005 in the UK (Buckingham et al., 2008).
3
4 Hruska et al. (2009) concluded that the DOC trends in both soil and surface waters were
5 explained by changes in ionic strength, rather than acidity, while Buckingham et al.
6 (2008) considered the UK time series too short, for making a coupling to the surface
7 water DOC trends. Wu et al. (2010) proposed that small changes in the atmospheric
8 deposition during the investigation period could explain the diverging DOC trends in soil
9 and surface waters. However, they also put forward the possibility of competition
10 between mineral anions and DOC for adsorption sites on oxide surfaces, causing a
11 simultaneous decrease of the DOC and SO_4^{2-} concentrations. Zetterberg and Löfgren
12 (2009) hypothesized that processes in discharge areas and peat lands rather than dry soils
13 uphill govern the surface water DOC trends.

14
15 The solubility of DOC is likely to be determined by a number of different biological,
16 chemical and hydrological processes (see Clark et al., 2010 and references therein), but
17 the acidification recovery theory is primarily coupled to the chemical and physical
18 properties of organic matter in soils and water. According to classical DLVO theory for
19 colloidal stability, the surface potential of a charged colloid may be the single most
20 important factor determining its dispersion into the water phase (e.g. Weng et al., 2002).
21 A high surface potential results in more interactions with water molecules and thus a high
22 water solubility. Therefore, different models have been forwarded that relates the DOC
23 solubility either to the surface potential or to the net charge, which is closely related to
24 the surface potential.

25
26 Tipping and Woof (1990) suggested a model for DOC dissolution from soils that assume
27 a nonlinear relationship between the DOC concentration and the net humic charge.
28 According to this model, an increased net charge leads to an increasing DOC
29 concentration. The net charge is calculated using an advanced geochemical model that
30 accounts for the acid-base and metal complexation properties of the organic matter, such
31 as WHAM (Tipping and Woof, op. cit.), NICA-Donnan (Weng et al., 2002) or SHM

1 (Stockholm Humic Model; Gustafsson, 2001). The model of Tipping and Woof (1990)
2 was slightly modified by Lofts et al. (2001) for the WHAM model and by Lumsdon
3 (2004) for the NICA-Donnan model, and after optimization for individual soils it was
4 found to work well in most cases for predicting the DOC concentration, although
5 difficulties were observed in particular for some mineral soils (c.f. the Discussion
6 section).

7

8 A slightly different approach was taken by Weng et al. (2002) who instead related the
9 DOC solubility to the value of a Donnan potential calculated by the NICA-Donnan
10 model, assuming that the Donnan potential was closely related to the surface potential of
11 the humic colloids. These authors found that the magnitude of DOC solubility was related
12 to the Donnan potential in five of six soils, but that acid sandy soils seemed to deviate
13 from the general rule.

14

15 If the DOC concentration is related to the net humic charge, it may provide a tool to
16 understand why the DOC concentrations show no trend or decrease in Swedish soil
17 waters simultaneously with acidification recovery.

18

19 The aim of this project was to set up a geochemical model to calculate the development
20 of the net humic charge with time at the Swedish integrated monitoring (IM) sites
21 Aneboda and Kindla, to investigate whether the observed DOC solubility in soils is
22 closely related to the humic charge, and if so, use the model to examine the factors
23 influencing the humic charge and thus the DOC solubility. The SHM model was tested on
24 soil water data from one transect along the hill slope in each catchment, covering the time
25 period 1996-2007. The transects extend from recharge to discharge areas, making it
26 possible to estimate the net humic charge in both podzols and riparian soils.

27

28 **2. Site descriptions**

29 Locations and maps of the IM sites Aneboda (19.6 ha, N57°05', E14°32') and Kindla
30 (19.1 ha, N59°45', E14°54') are shown in Figures 1 and 2, respectively. Both sites are

1 protected Norway spruce (*Picea abies*) forests, not affected by forestry during the last
2 century (Lundin et al., 2001). The bedrock consists of granite and glacial till is the
3 dominant parent material with quartz and feldspar (albite, plagioclase, microcline) as the
4 most abundant minerals. At Aneboda, the annual mean temperature is 5.8°C, precipitation
5 750 mm and runoff 280 mm. At Kindla, the same figures are 4.2°C, 900 mm and 450 mm
6 respectively. Between 1996 and 2008, the S-deposition in throughfall has diminished
7 from 6 to 2 kg S ha⁻¹ y⁻¹ at both sites, while the bulk deposition reductions are from 4 to 3
8 kg S ha⁻¹ y⁻¹ at Aneboda and from 4 to 2 kg S ha⁻¹ y⁻¹ at Kindla. In the late 1980's, the S
9 deposition was more than twice these levels (Westling and Lövblad, 2000). Since 1996,
10 the bulk deposition of inorganic N has diminished with ca 1 kg N ha⁻¹ y⁻¹ and is at present
11 approximately 7 and 5 kg N ha⁻¹ y⁻¹ at Anaboda and Kindla, respectively. Compared with
12 the S deposition in the historically, heavily polluted Czech Republic (Lysina and Pluhov
13 Bor), which has experienced total S deposition reductions from 30-40 kg ha⁻¹yr⁻¹ to 7-11
14 kg ha⁻¹yr⁻¹ during the 1990's (Hruska et al., 2009), the S deposition at the Swedish sites
15 are low. Regarding N deposition, the differences are much smaller and at present a couple
16 of kg N ha⁻¹yr⁻¹ higher at the Czech sites. At Aneboda, the throughfall of chloride exhibits
17 large between year variations, with the highest loads in 1999 (20 kg Cl ha⁻¹ y⁻¹) and the
18 lowest in 2005 (7 kg Cl ha⁻¹ y⁻¹), respectively. At Kindla, the interannual variation is less
19 or 7-12 kg Cl ha⁻¹ y⁻¹.

20

21 ***Figure 1***

22

23 ***Figure 2***

24 **3. Methods**

25 The soil and surface water sampling is part of the ordinary IM-program (Lundin et al.,
26 2001, <http://www.environment.fi/default.asp?node=6329&lan=en>). Since 1996, stream
27 water is sampled biweekly at each catchment outlet (Figure 2). In both catchments,
28 lysimeters (ceramic cups P80, 1 µm cut-off) were installed along a hillslope in 1994
29 (Figure 2). In the Aneboda transect, the lysimeters were installed at distances of
30 approximately 1-6 m and 20 m from the stream. Additionally, a group of lysimeters was

1 established 90-110 m from the stream close to the intensive soil and vegetation plots
2 (Figure 2). In the Kindla transect, the distances to the stream were 4-8 m, 20 m and 40 m
3 (Table 1). In recharge areas and intermediate zones (recharge area except for at runoff
4 events with high groundwater levels) with podzols, the lysimeters were installed in the
5 mineral soil just below the O-horizon (E-horizon) and in the centre of the B-horizon. The
6 E- and B-horizon lysimeters were installed pair wise, within a distance of <1m. Multiple
7 such lysimeter pairs were installed within a distance of <6m from each other at each
8 location along the transects (and plot). In the discharge areas, the lysimeters were
9 installed in the peat-covered gleysols and histosols (30 cm and 37 cm, respectively)
10 below soil surface. Soil temperature, measured by termistors (Aanderaa, 30 minutes
11 interval), is available from 10, 32, 44 and 58 cm and 5, 10, 20 and 35 cm soil depths at
12 Aneboda and Kindla, respectively. Soil water has been sampled since 1994, but in order
13 to minimize installation effects on the time series, this study includes data only from the
14 period 1996-2007. If available, soil water was collected 3-4 times per year after snowmelt
15 (April-May) and precipitation events in August and October-November. At Aneboda, few
16 data are available from the E-horizons due to dry conditions in the surface soils.
17 Therefore, the E-horizon data is omitted from this study. The transects cannot be
18 considered as representative for the mosaic of hillslope conditions creating the stream
19 water chemistry, but are rather examples of such conditions.

20

21 The samples were analyzed with Swedish standard methods at the Dept. of Aquatic
22 Sciences and Assessment, Swedish University of Agricultural Sciences (SLU). The
23 analytical methods are accredited by SWEDAC (Swedish Board for Accreditation and
24 Conformity Assessment). Ambient pH was analysed in a semi-closed system. Directly
25 after opening the bottle, the sample was pumped (peristaltic pump) through an airtight
26 cuvette equipped with a combination pH-electrode adapted for low ionic strength waters
27 (Metrohm 6.0253.100). Samples for total organic carbon (TOC) analysis were measured
28 using a Shimadzu TOC 5050 analyzer with ASI-502 sample injector following
29 acidification. Major cations, Fe and Al were analyzed on acidified samples (0.5 ml
30 concentrated HNO₃ per 100 ml sample) by ICP-OES (Varian Vista Ax Pro) and strong

1 acid anions by ion chromatography (LDC Conducto Monitor III). Acid neutralizing
2 capacity (ANC) was calculated according to Reuss and Johnson (1986).

3
4 The non-parametric Seasonal Kendall test (Hirsch and Slack, 1984; Loftis et al., 1991)
5 was used for detecting monotonous trends in measured and simulated (see below)
6 chemical time series. It was visually determined whether the trends were monotonous or
7 not. Thiels slope (Helsel and Hirsch, 1992) was used to quantitatively estimate the trends.
8 Throughout the investigation period soil water data were available only from the months
9 April-May, August and October-November. Hence, these months were used for the trend
10 analyses.

12 **4. Model assumptions**

13 The software Visual MINTEQ (Gustafsson, 2009) employing the Stockholm Humic
14 Model (Gustafsson, 2001) was used to study the acid-base and complexation behavior of
15 organic matter in soils. The overall net charge (Z^-) of the soil organic matter was assumed
16 to influence the DOC mobilization (see Introduction). At each sampling occasion, the pH
17 value as well as the measured dissolved concentrations of ions (Ca^{2+} , Mg^{2+} , SO_4^{2-} , total
18 Al etc.) were entered as fixed in the model, meaning that the model calculated the
19 concentrations of solid-phase organic complexes that were in equilibrium with the given
20 dissolved concentrations. The Z^- value can then be calculated as the sum of the charge
21 contributions from various different organic matter species in the solid phase. As an
22 example, in the simple case of fulvic acid and in the presence of Ca^{2+} and Al^{3+} in the soil
23 solution, the value of Z^- would be given by:

$$25 \quad Z^- = \text{RO}^- - \text{ROCa}^+ - (\text{RO})_2\text{Al}^+ \quad (1)$$

26
27 , where RO^- is a dissociated functional group (usually a carboxylate group), ROCa^+ is a
28 monodentate complex involving one functional group and one Ca^{2+} ion, whereas
29 $(\text{RO})_2\text{Al}^+$ is a bidentate complex involving two functional groups and one Al^{3+} ion. For
30 more detailed information regarding the assumed complex configurations, see Gustafsson

1 (2001) or Gustafsson and Kleja (2005). As seen in equation 1, the value of Z^- indicates
2 the sum of negative charge of the organic matter. Since the negative charge usually
3 predominates, Z^- will take a positive value.

4
5 To set up the model, a number of assumptions were made:

- 6
7 1. The approximate organic matter content of the soil was estimated from different
8 soil samplings carried out during the experimental period at the two sites (data not
9 shown). Thus for the Kindla E horizon the total organic C (TOC_{soil}) content was
10 set to 1.1 %, whereas it was 2.5 % for the Kindla B horizon, 15 % for the peat
11 soils of the Kindla discharge area (lysimeters 6201-6203) and 1.0 % for the wet
12 soils of the same area (lysimeters 6204-6206). In the case of the Aneboda B
13 horizon the TOC_{soil} content was 1.5 %, for the peat soil (lysimeter 7202) 15 % and
14 for the wet soil (lysimeters 7204-7206) 15 %. The results, however, were not
15 sensitive to these assumptions.
- 16
17 2. The water content (g water / g soil) was assumed to be 1 for the peat soils and 0.1
18 for all other soils. Again, however, this was not crucial for the model outcome.
- 19
20 3. It was assumed that the fraction of “active organic matter” (AOM) amounted to
21 50 % of the total organic matter content in all soils. An earlier study found this
22 figure to range between 17 and 84 %, depending on the soil, with the lowest
23 values recorded for mor layers (Gustafsson et al., 2003). Based on these results, it
24 can be estimated that the AOM percentage needed for the model should probably
25 range from 30 to 84 %. However, the exact choice of the AOM percentage did not
26 matter for the model result, and therefore an intermediate value of 50 % was
27 chosen.
- 28
29 4. In the peat soils, 75 % of the AOM was assumed to consist of humic acid and 25
30 % of fulvic acid, whereas in other soils the percentages were 50 % and 50 %,
31 respectively. These figures are based on an earlier detailed evaluation for different

1 soils (Gustafsson et al., 2003). Moreover, all dissolved organic matter (DOM) was
2 assumed to consist of fulvic acid, to be consistent with earlier model
3 optimizations using the SHM (Gustafsson and Kleja, 2005; Gustafsson and van
4 Schaik, 2003).

5

6 5. Besides AOM itself, no other reactive phases in the soils were assumed to
7 influence the net charge. This means, for example, that Fe oxyhydroxides, which
8 could affect the net charge through adsorption of fulvic acid, were disregarded in
9 the calculations. The reason for this is mainly that the interactions between
10 organic matter and oxyhydroxides are very complex and still not completely
11 understood (see e.g. Weng et al., 2007).

12

13 6. The concentration of solid-phase organic matter was assumed to be constant over
14 the entire time period (1996-2007). Because of the large pools of soil organic
15 matter, a change in this property over only eleven years is not expected.

16

17 7. Since the temperature was not always measured, the temperature was set to 6°C
18 for all samples. Preliminary model runs showed that the assumed value was not
19 crucial to the model result in the pH (4-6) and temperature ranges (0-14°C)
20 investigated.

21

22 **5. Results**

23 The soil solution was highly acidic with pH<5 and negative ANC at all sites except for in
24 the discharge area at Aneboda and in one of the riparian lysimeters (6203) at Kindla
25 (Table 1a and 1b). In both catchments, Na⁺ was the dominating cation, while Ca²⁺ and
26 Mg²⁺ were of the same levels and generally less than half the concentrations of Na⁺. The
27 Ca²⁺ and Mg²⁺ concentrations increased downslope and exhibited soil solution
28 concentrations close to the stream levels in the riparian soils. Except for the discharge
29 area at Aneboda, exhibiting high concentrations of Cl⁻, SO₄²⁻ was the dominant anion in
30 soil solution. Compared with the mineral soils, lower SO₄²⁻ concentrations were found in

1 the peat (Table 1b). At Aneboda, the Na^+ and Cl^- concentration balance varied between
2 lysimeters, while all lysimeters exhibited excess Na^+ concentrations at Kindla. The DOC
3 concentrations in soil waters were somewhat lower at Aneboda ($5\text{-}9\text{ mg l}^{-1}$) compared
4 with at Kindla ($4\text{-}18\text{ mg l}^{-1}$), while the opposite was true for the streams, 14 compared
5 with 4 mg l^{-1} , respectively. Both catchments had slightly higher DOC concentrations in
6 the riparian soils compared with uphill. The same pattern was found for dissolved Fe,
7 while the highest dissolved Al concentrations were found in dry soils with podzols (Table
8 1a).

9

10 ***Table 1***

11

12 At both sites, several lysimeters experienced decreasing DOC concentrations between
13 1996 and 2007. At Kindla, 7 out of 15 lysimeters had statistically significant decreasing
14 DOC trends ($p < 0.05$), whereas 7 lysimeters did not have any significant change of DOC
15 (Table 2). Only one lysimeter in the discharge area (6202) exhibited an increasing DOC
16 trend. At Aneboda, 3 of 12 lysimeters had statistically significant decreasing DOC
17 concentrations. No lysimeter at any site showed increasing DOC concentrations over this
18 time period (Table 3). As an example, Figure 3 shows the DOC concentrations in the wet
19 soils of the Kindla site for all of which the DOC concentrations decreased.

20

21 ***Table 2***

22

23 ***Table 3***

24

25 ***Figure 3***

26

27 ***Figure 4***

28

29 For individual lysimeters there was often a strong relationship between the calculated net
30 charge of the AOM (Z^-) and DOC, indicating that Z^- is related to DOC solubility. In

1 Figure 4 this relation is presented for the lysimeter 6206 from the Kindla site. This
2 relationship was statistically significant ($p < 0.05$) in 11 out of 27 lysimeters.

3
4 Despite the strong relationship between Z^- and DOC, Z^- did often not decrease by time to
5 the same extent as DOC (Table 2 and 3). In 22 out of 27 lysimeters Z^- stayed more or less
6 constant, verified by no statistically significant ($p < 0.05$) trends. Consequently and
7 especially evident for the Kindla site (Table 2), the ratio of Z^- to DOC often displayed a
8 change in time with increasing trends. This implies that with time, DOC solubility
9 decreased although the net charge did not change appreciably.

10
11 Lumsdon et al. (2005) obtained evidence for an increased hydrophobicity at lower
12 temperatures, which would have led to an increase in the Z^- to DOC ratio. However in
13 our study there was no statistically significant relationship between the ratio of Z^- to DOC
14 and the measured soil temperature in any of the lysimeters (data not shown), which
15 indicates that temperature differences were unlikely to affect the observed deviations
16 between Z^- and DOC.

17
18 The soils at the two sites are subject to recovery from acidification. Hence 15 of the 27
19 lysimeters display statistically significant increases in pH between 1996 and 2007 (Table
20 2 & 3). However, there was one lysimeter at the Aneboda site (no. 7104) that had a
21 decreasing pH trend (Table 3). For all except 3 lysimeters in Kindla, a decrease in the
22 ionic strength was noticed. Examples of this from the B horizon in the intermediate zone
23 are shown in Figure 5. At Aneboda, however, only 50 % of the lysimeters displayed a
24 significantly decreased ionic strength with time. The ionic strength was heavily
25 dependent on SO_4^{2-} , which in many cases decreased considerably at both sites during the
26 investigated time period, as well as on counter-ions such as Ca^{2+} , which also decreased as
27 a result.

28
29 ***Figure 5***

1 Changes in the simulated total Al pool in the soil were not expected due to the large pools
2 involved. With Visual MINTEQ we could simulate the total amount of Al bound to active
3 organic matter. This pool did not change during the time period except for in 6 of the
4 lysimeters, where calculations suggested a slight increase of the modeled Al pool (Table
5 2 & 3).

6
7 The logarithm of the ion activity product of $\text{Al}(\text{OH})_3(\text{s})$ was higher than 9 in the Kindla B
8 horizon, indicating equilibrium with respect to this phase or with imogolite-type materials
9 (Gustafsson et al., 2001). In other lysimeters this value was lower, which might be taken
10 as evidence that Al solubility in these soils was controlled primarily by complexation to
11 organic matter.

12
13 Organically complexed Fe(III) in the soil was also simulated, but as the size of this pool
14 was calculated to be $< 10\%$ of the organically complexed Al pool in almost all cases,
15 Fe(III) is likely to be much less significant than Al in affecting the net humic charge and
16 DOC solubility; these results are therefore not discussed further.

17 18 **6. Discussion**

19 An objective with this study was to understand the soil water trends in DOC solubility
20 using the Visual MINTEQ geochemical model. Since DOC solubility cannot be
21 simulated directly, the modeled net charge Z^- was used as a proxy, using the assumption
22 that Z^- would be directly related to DOC. For individual lysimeters there was indeed a
23 rather strong relationship between these two variables (Figure 4). Despite this, the model-
24 generated Z^- values indicated largely unchanged DOC concentrations for the Kindla site,
25 whereas in reality DOC decreased in most lysimeters.

26
27 Similar results were obtained by Lofts et al. (2001), who used the WHAM model to
28 simulate DOC solubility in soil suspensions from batch experiments using a modified
29 version of the model of Tipping and Woof (1990). They found that for some mineral soil
30 horizons with a comparably high Al content, the model failed to describe correctly the

1 DOC solubility at low pH. These data showed a minimum in the observed DOC solubility
2 between pH 4 and 5, whereas the model indicated ever decreasing DOC with decreasing
3 pH. Similar batch experiment results were obtained by Gustafsson et al. (2003). Figure 6
4 shows batch experiment results from four B horizons in which the pH dependence was
5 varied through additions of acid or base. Similarly to some of the B horizons analyzed by
6 Lofts et al. (2001) a minimum of the DOC concentration was observed between pH 4 and
7 pH 5, depending on the soil.

8
9 ***Figure 6***

10
11 ***Figure 7***

12
13 One of the soils, Tyresta Bs, was analyzed in more detail (for the properties of this soil
14 sample, see Gustafsson et al., 2003). By using the procedures described earlier, Z^- was
15 calculated for the different sample points. As Figure 7 shows, the modeled Z^- did not
16 follow the DOC curve very well, Z^- decreased with decreasing pH until $\text{pH} < 4$. At this
17 point most of the bound Al dissolved, which explains the minimum in Z^- at this point.
18 The results are consistent with the ones of Lofts et al. (2001) for the Waldstein Bw and
19 Bs horizons.

20
21 Lofts et al. (2001) hypothesized, based on WHAM modeling, that the increased DOC at
22 decreasing pH below pH 4 could be due to the development of positive charge on the
23 humic colloids. However, the SHM results did not support this hypothesis since the
24 increase in the simulated Z^- value at very low pH was caused by Al^{3+} desorption, thus
25 leading to a slightly increased net negative charge despite the pH decrease. Interestingly
26 to note is that the increased DOC concentrations in soil solution at the Lysina catchment
27 in the Czech republic (Hruska et al., 2009) occurs at this low pH-interval. Unfortunately,
28 the soil water Al^{3+} concentrations were not reported, but it could be speculated whether
29 the positive DOC trend, besides ionic strength, was affected by an increased net negative
30 charge on the AOM due to a changed solid-solution Al chemistry. There was no trend in
31 pH (op.cit.).

1

2 As a result of the mismatch between DOC and Z^- , the Z^-/DOC ratio increased
3 considerably with increasing pH between pH 4 and pH 5 (Figure 8). This mirrors the
4 results obtained for the lysimeters, since a close inspection of the results in Table 2 and 3
5 reveals that the Z^-/DOC ratio usually (11 out of 15 cases) increased when the pH
6 increased. In the one lysimeter that had a pH decrease (nr. 7104) the Z^-/DOC ratio
7 decreased between 1996 and 2007. This suggests a consistency between the results
8 obtained in equilibrations with soil samples on the laboratory and the lysimeters at the
9 two sites.

10

11 ***Figure 8***

12

13 A question that remains unanswered is what causes this deviation between Z^- and DOC.
14 The model results do not provide any consistent clue to this. However it is clear that the
15 pH value does seem to have an effect such that an increased pH requires a higher net
16 charge for DOC to remain dissolved to the same extent. One possible reason could be
17 related to the coordination of Al^{3+} in organic complexes. If a higher pH causes a higher
18 coordination number for complexed Al^{3+} , then it follows that Al^{3+} could bridge together
19 organic matter molecules more efficiently leading to increased aggregation. This would
20 explain the patterns observed since cation bridging as such would not influence the Z^-
21 value. This may not be the only possible reason, however.

22

23 Concerning factors influencing Z^- , it might be expected that an increased pH value would
24 cause higher DOC concentrations because of increased dissociation of organic matter and
25 hence an increasing net charge. However, other factors affecting the net charge and DOC
26 solubility also need to be taken into account, such as changes in the ionic strength and in
27 the soil Al pool. Figure 9 shows model-generated results for two lysimeters in which the
28 influence of different factors were considered. The scenarios were based on observed data
29 from 1996 and 2006 (see Table 4). An increased pH clearly increased the net humic
30 charge as expected, but the net effect was influenced also by changes in ionic strength
31 and total Al.

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Depending on the soil, the humic charge is dependent on the net result of these different factors. At the Kindla site, Al does not change over time significantly in 13 out of 15 lysimeters (Table 2) and therefore the charge is dependent primarily on the changes in ionic strength and pH, which counteract each other to give a largely unchanged value of Z^- .

Figure 9

Table 4

Figure 9 shows that the concentration of total Al in the soil (mainly as organic complexes) was very important for the net humic charge. This was not unexpected since a larger amount of Al reduces the net charge according to equation 1. At the Aneboda site 3 of 12 lysimeters experienced significant increases in the simulated soil Al pool. The modeling results in Figure 9 show that this might have contributed to the observed decreased humic charge and hence presumably to decreased DOC concentrations. It does not seem likely that this is a “real” increase in complexed Al in the soil, because of the very large pools of Al involved. The result might reflect a change in the hydrological pathways over time, i.e. that the water that enters the lysimeter may be drained from slightly different pores. Based on the annual median water volumes collected by 6 lysimeters during the period 1994-96 (mean 338 ml) and 1998-2010 (450 ml), there are no signs of clogging in the B-horison lysimeters at Aneboda.

Based on these observations, it is evident that the well-documented recovery from acidification does not necessarily have to generate increasing DOC trends in soil solution. Depending on changes in pH, ionic strength and soil Al pools, the trends might be positive, negative or indifferent. The variation in DOC trends between lysimeters can be large within a short distance between the sampling devices and, therefore, it is necessary to have data from many sampling sites in order to assess the general DOC trends in the forested mosaic landscape. The negative DOC trends found in soil solution at many sites

1 in Sweden and Norway (Wu et al., 2010; Zetterberg and Löfgren, 2009) while surface
2 waters in the same regions exhibits positive DOC trends might be explained by non-
3 representative sampling sites, but it might also be a result of other factors as described by
4 Clark et al. (2010). Processes in discharge areas and peatlands seem to be important
5 landscape elements (Köhler et al., 2009; Laudon et al., 2004). Due to the high hydraulic
6 connectivity with the streams, the explanations to the DOC-trends in Scandinavian
7 surface waters should be searched for in such types of landscape elements.

8 **7. Conclusions**

9 In summary, this model exercise has highlighted the following factors of importance for
10 the observed decrease of DOC in many lysimeters of the Aneboda and Kindla sites:

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12 - The increased net charge following the pH increase (because of increased acid
13 dissociation) was in many cases counteracted by a decreased ionic strength, which
14 acted to decrease the net charge and hence the DOC solubility.

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16 - Particularly at the Kindla site, the pH increase induced reduced solubility of DOC
17 despite no or little change in the net humic charge, perhaps because of a change in
18 Al coordination that increased cation bridging effects. This effect could not be
19 verified by the model, but is supported by earlier published results from batch
20 experiments with soil samples from B horizons.

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22 - At the Aneboda site, an increase in the simulated concentrations of the soil Al
23 pool from 1996 to 2007 was obtained in 3 of 12 cases; the model suggested that
24 this might be a major reason to decreased DOC concentrations at this site. It
25 seems unlikely that this result reflects a “real” increase in the soil Al pool. A
26 possible reason might be differences in the hydrological pathways for the water
27 entering the Aneboda lysimeters.

28

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3

4 **References**

5 Buckingham S, Tipping E, Hamilton-Taylor J. Concentrations and fluxes of dissolved
6 organic carbon in UK topsoils. *Sci Total Environ* 2008; 407: 460-470.

7 Clark JM, Bottrell SH, Evans CD, Monteith DT, Bartlett R, Rose R, et al. The importance
8 of the relationship between scale and process in understanding long-term DOC
9 dynamics. *Sci Total Environ* 2010; 408: 2768-2775.

10 Dawson JJC, Malcolm IA, Middlemas SJ, Tetzlaff D, Soulsby C. Is the Composition of
11 Dissolved Organic Carbon Changing in Upland Acidic Streams? *Environ Sci
12 Technol* 2009; 43: 7748-7753.

13 Erlandsson M, Buffam I, Fölster J, Laudon H, Temnerud J, Weyhenmeyer GA, et al.
14 Thirty-five years of synchrony in the organic matter concentrations of Swedish
15 rivers explained by variation in flow and sulphate. *Global Change Biol* 2008; 14:
16 1191-1198.

17 Evans CD, Monteith DT, Cooper DM. Long-term increases in surface water dissolved
18 organic carbon: Observations, possible causes and environmental impacts.
19 *Environ Pollut* 2005; 137: 55-71.

20 Gustafsson JP. Modeling the acid-base properties and metal complexation of humic
21 substances with the Stockholm Humic Model. *J Colloid Interf Sci* 2001; 244: 102-
22 112.

23 Gustafsson JP. Visual MINTEQ ver. 3.0. Web:
24 <http://www.lwr.kth.se/English/OurSoftware/vminteq/index.htm>. Last accessed 2/9
25 2010., 2009.

26 Gustafsson JP, Berggren D, Simonsson M, Zysset M, Mulder J. Aluminium solubility
27 mechanisms in moderately acid Bs horizons of podzolized soils. *Eur. J. Soil Sci.*
28 2001; 52: 655-665.

- 1 Gustafsson JP, Kleja DB. Modeling salt-dependent proton binding by organic soils with
2 the MICA-Donnan and Stockholm Humic models. *Environ Sci Technol* 2005; 39:
3 5372-5377.
- 4 Gustafsson JP, Pechova P, Berggren D. Modeling metal binding to soils: The role of
5 natural organic matter. *Environ Sci Technol* 2003; 37: 2767-2774.
- 6 Gustafsson JP, van Schaik JWJ. Cation binding in a mor layer: batch experiments and
7 modelling. *Eur J Soil Sci* 2003; 54: 295-310.
- 8 Helsel DR, Hirsch RM. *Statistical measures in water research*. Amsterdam: Elsevier
9 Science B.V., 1992.
- 10 Hirsch RM, Slack JR. A Nonparametric Trend Test for Seasonal Data with Serial
11 Dependence. *Water Resour Res* 1984; 20: 727-732.
- 12 Hruska J, Kram P, Mcdowell WH, Oulehle F. Increased Dissolved Organic Carbon
13 (DOC) in Central European Streams is Driven by Reductions in Ionic Strength
14 Rather than Climate Change or Decreasing Acidity. *Environ Sci Technol* 2009;
15 43: 4320-4326.
- 16 Karlton E, Stendahl J, Lundin L. Acid-base status and changes in Swedish forest soils.
17 *KSLAT* 2003; 142: 31-36.
- 18 Köhler SJ, Buffam I, Seibert J, Bishop KH, Laudon H. Dynamics of stream water TOC
19 concentrations in a boreal headwater catchment: Controlling factors and
20 implications for climate scenarios. *J Hydrol* 2009; 373: 44-56.
- 21 Laudon H, Hedtjärn J, Schelker J, Bishop K, Sørensen R, Ågren A. Response of
22 Dissolved Organic Carbon following Forest Harvesting in a Boreal Forest. *Ambio*
23 2009; 38: 381-386.
- 24 Laudon H, Köhler S, Buffam I. Seasonal TOC export from seven boreal catchments in
25 northern Sweden. *Aquat Sci* 2004; 66: 223-230.
- 26 Loftis JC, Taylor CH, Chapman PL. Multivariate Tests for Trend in Water-Quality.
27 *Water Resour Res* 1991; 27: 1419-1429.
- 28 Lofts S, Simon BM, Tipping E, Woof C. Modelling the solid-solution partitioning of
29 organic matter in European forest soils. *Eur J Soil Sci* 2001; 52: 215-226.

- 1 Lumsdon DG. Partitioning of organic carbon, aluminium and cadmium between solid and
2 solution in soils: application of a mineral-humic particle additivity model. *Eur J*
3 *Soil Sci* 2004; 55: 271-285.
- 4 Lumsdon DG, Stutter MI, Cooper RJ, Manson JR. Model assessment of biogeochemical
5 controls on dissolved organic carbon partitioning in an acid organic soil. *Environ*
6 *Sci Technol* 2005; 39: 8057-8063.
- 7 Lundin L, Aastrup M, Bringmark L, Bråkenhielm S, Hultberg H, Johansson K, et al.
8 Impacts from deposition on Swedish forest ecosystems identified by integrated
9 monitoring. *Water Air Soil Poll* 2001; 130: 1031-1036.
- 10 Löfgren S, Cory N, Zetterberg T, Larsson P-E, Kronnäs V. The long-term effects of
11 catchment liming and reduced sulphur deposition on forest soils and runoff
12 chemistry in southwest Sweden. *For Ecol Man* 2009a; 258: 567-578.
- 13 Löfgren S, Ring E, von Brömssen C, Sörensen R, Högbom L. Short-term Effects of
14 Clear-cutting on the Water Chemistry of Two Boreal Streams in Northern
15 Sweden: A Paired Catchment Study. *Ambio* 2009b; 38: 347-356.
- 16 Monteith DT, Stoddard JL, Evans CD, de Wit HA, Forsius M, Hogasen T, et al.
17 Dissolved organic carbon trends resulting from changes in atmospheric deposition
18 chemistry. *Nature* 2007; 450: 537-U9.
- 19 Reuss JO, Johnson DW. Acid deposition and acidification of soils and waters. *Ecological*
20 *studies*. Vol 59: Springer-Verlag, 1986.
- 21 Sarkkola S, Koivusalo H, Lauren A, Kortelainen P, Mattsson T, Palviainen M, et al.
22 Trends in hydrometeorological conditions and stream water organic carbon in
23 boreal forested catchments. *Sci Total Environ* 2009; 408: 92-101.
- 24 Skjelkvåle BL, Stoddard JL, Jeffries DS, Torseth K, Hogasen T, Bowman J, et al.
25 Regional scale evidence for improvements in surface water chemistry 1990-2001.
26 *Environ Pollut* 2005; 137: 165-176.
- 27 Tipping E, Woof C. Humic Substances in Acid Organic Soils - Modeling Their Release
28 to the Soil Solution in Terms of Humic Charge. *J Soil Sci* 1990; 41: 573-586.
- 29 Weng L, Temminghoff EJM, van Riemsdijk WH. Interpretation of humic acid
30 coagulation and soluble soil organic matter using a calculated electrostatic
31 potential. *Eur J Soil Sci* 2002; 53: 575-587.

- 1 Weng L, Van Riemsdijk WH, Hiemstra T. Adsorption of humic acids onto goethite:
2 Effects of molar mass, pH and ionic strength. *J Colloid Interf Sci* 2007; 314: 107-
3 118.
- 4 Westling O, Lövblad G. Deposition trends in Sweden. In: Warfvinge P, Bertills, U.,
5 editor. *The environmental recovery from acidification. Report.* Swedish
6 *Environmental Protection Agency, Stockholm, 2000.*
- 7 Wu YJ, Clarke N, Mulder J. Dissolved Organic Carbon Concentrations in Throughfall
8 and Soil Waters at Level II Monitoring Plots in Norway: Short- and Long-Term
9 Variations. *Water Air Soil Poll* 2010; 205: 273-288.
- 10 Yallop AR, Clutterbuck B. Land management as a factor controlling dissolved organic
11 carbon release from upland peat soils 1: Spatial variation in DOC productivity.
12 *Sci Total Environ* 2009; 407: 3803-3813.
- 13 Zetterberg T, Löfgren S. Decreasing concentrations of dissolved organic carbon (DOC) in
14 the soil solution in southern Sweden during the 1990's. In: Ukonmaanaho L,
15 Nieminen TM, Starr M, editors. *6th International Symposium on Ecosystem
16 Behaviour BIOGEOMON 2009.* 128. Finnish Forest Research Institute, Helsinki,
17 Finland, 2009, pp. 189.
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Table 1a. Lysimeter installation information regarding hydrology, distance to the stream (ΔD), soil type, soil horizon, humus layer thickness (O-hor), depth below soil surface (ΔL), number of observations (n) and the concentrations (mean \pm standard deviation) of DOC, pH, ionic strength, Al and Fe in soil water and stream water at Aneboda and Kindla during the period 1996-2007. nd = no data

Lysimeter	Hydrology*	ΔD (m)	Soil	Horizon	O-hor (cm)	ΔL (cm)	n	DOC mg/l	pH	Ionic strength mmol l ⁻¹	Al μg/l	Fe μg/l
Aneboda												
7101	Rech	105	Podzol	B-hor	8	38	42	6.4±5.5	4.89±0.33	0.21±0.04	410±207	27±24
7102	Rech	101	Podzol	B-hor	8	38	42	6.1±4.3	4.59±0.11	0.56±0.15	1520±244	22±14
7103	Rech	95	Podzol	B-hor	8	38	42	7.1±5.4	4.73±0.14	0.32±0.07	870±263	17±26
7107	Rech	96	Podzol	B-hor	8	38	42	4.8±2.9	4.77±0.18	0.34±0.14	1083±400	16±13
7109	Rech	92	Podzol	B-hor	8	38	40	5.7±1.9	4.65±0.08	0.42±0.15	1184±232	29±17
7113	Rech	101	Podzol	B-hor	8	38	42	7.3±3.9	4.81±0.41	0.40±0.15	1177±346	19±9
7104	Interm	21	Podzol	B-hor	8	38	42	6.0±3.1	4.66±0.37	1.51±0.34	1874±835	20±18
7105	Interm	21	Podzol	B-hor	8	38	42	8.9±3.7	4.38±0.06	2.21±0.21	5427±881	24±18
7204	Disch	6	Gleysol	Mineral	7	37	42	5.6±6.7	4.91±0.16	0.89±0.19	1063±263	26±14
7205	Disch	5	Gleysol	Mineral	7	37	42	7.7±4.1	5.42±0.21	0.70±0.15	438±203	361±499
7206	Disch	4	Gleysol	Mineral	7	37	39	8.6±3.7	5.11±0.26	0.79±0.17	566±141	1722±1358
7202	Disch	1	Histosol	Peat	>50	37	42	25.7±8.2	5.05±0.25	0.60±0.20	681±232	4403±1557
<i>Stream</i>							265	13.6±23**	4.50±0.12	nd	1690±2699	488±274
Kindla												
6004	Rech	40	Podzol	E-hor	15	20	42	18.1±7.2	4.29±0.10	0.40±0.11	1343±328	587±2173
6104	Rech	40	Podzol	B-hor	15	45	35	6.3±3.2	4.77±0.10	0.36±0.08	1210±273	43±108
6105	Rech	40	Podzol	B-hor	15	45	40	12.6±12.0	4.46±0.42	0.42±0.21	1271±315	79±94
6106	Rech	40	Podzol	B-hor	15	45	39	5.2±2.4	4.79±0.07	0.33±0.06	1187±207	36±128
6001	Interm	21	Podzol	E-hor	8	13	42	10.8±3.8	4.41±0.13	0.38±0.08	1276±327	65±36
6002	Interm	21	Podzol	E-hor	8	13	36	7.5±3.2	4.60±0.07	0.39±0.07	1315±308	68±125
6003	Interm	21	Podzol	E-hor	8	13	42	7.0±2.3	4.60±0.05	0.34±0.07	1248±217	25±41
6101	Interm	21	Podzol	B-hor	8	38	39	6.5±3.5	4.61±0.08	0.41±0.08	1384±217	49±26
6102	Interm	21	Podzol	B-hor	8	38	36	4.6±1.6	4.67±0.09	0.42±0.07	1310±235	43±53
6103	Interm	21	Podzol	B-hor	8	38	39	3.8±1.1	4.74±0.07	0.34±0.07	1170±228	30±34
6204	Disch	7	Gleysol	Mineral	20	50	42	11.6±3.0	4.64±0.27	0.35±0.07	914±264	1035±1125
6205	Disch	8	Gleysol	Mineral	20	50	42	7.1±2.4	4.85±0.08	0.32±0.04	945±157	302±302
6206	Disch	5	Gleysol	Mineral	20	50	39	9.5±3.0	4.59±0.07	0.35±0.06	1308±224	72±117
6201	Disch	4	Histosol	Peat	>50	30	42	9.7±2.1	4.45±0.08	0.33±0.06	873±185	105±106
6202	Disch	5	Histosol	Peat	>50	30	42	12.0±2.0	4.88±0.31	0.30±0.12	948±163	529±278
6203	Disch	5	Histosol	Peat	>50	30	42	18.2±3.1	4.58±0.16	0.31±0.13	707±154	716±349
<i>Stream</i>							280	3.8±8.0**	4.58±0.14	nd	497±791	736±166

* Rech = recharge area, Interm = intermediate area, Disch = discharge area

**TOC

Table 1b. Lysimeter number and the concentrations (mean \pm standard deviation) of base cations, mineral acid anions, fluoride and ANC in soil water and stream water at Aneboda and Kindla during the period 1996-2007.

Lysimeter	Ca	Mg	Na	K	SO ₄ μeq l ⁻¹	Cl	NO ₃	F*	ANC
<u>Aneboda</u>									
7101	12±5	8±18	74±17	19±7	78±22	76±44	0.8±1.1	5.9±1.7	-31±41
7102	32±11	18±47	128±51	14±9	222±62	153±84	1.3±3.7	4.1±0.9	-154±52
7103	14±6	8±19	68±18	7±7	129±37	75±37	2±4.6	2.2±0.5	-92±26
7107	21±17	13±29	73±19	9±8	137±64	92±51	0.8±1.7	1.6±0.2	-98±59
7109	26±37	22±37	89±22	9±13	145±55	113±61	0.6±1	3±0.6	-98±31
7113	41±16	17±31	69±24	14±17	163±68	97±59	0.4±0.4	1.9±0.4	-104±57
7104	32±13	37±98	778±289	20±10	375±155	824±334	0.3±0.3	7.7±2.3	-251±121
7105	73±14	34±160	771±331	20±12	953±103	682±289	1.1±2.5	7.4±2.5	-614±105
7204	62±27	29±97	451±149	3±2	274±49	391±167	1.1±1.1	10.6±1.1	-52±88
7205	98±27	29±103	314±58	5±3	183±63	299±89	0.7±0.8	9.9±1	40±44
7206	90±30	28±101	351±77	6±3	205±87	364±103	1.2±2.8	12±3.2	-16±105
7202	96±26	31±100	243±36	9±3	114±121	264±51	1.2±2.2	6.9±0.8	79±62
<i>Stream</i>	96±18	88±18	223±20	13±17	153±69	187±28	2.5±4.7	5.4±1.2	78±57
<u>Kindla</u>									
6004	15±7	7±24	108±31	11±7	134±54	83±47	0.5±0.5	2.8±0.5	-58±66
6104	15±5	5±20	91±20	12±7	142±37	73±36	1±1.7	3.8±0.2	-77±36
6105	10±6	6±17	98±34	5±3	141±42	106±189	0.8±1	2.9±0.7	-111±186
6106	11±4	4±17	88±15	5±1	125±33	71±35	0.5±0.5	4±0.6	-77±29
6001	14±6	9±20	98±23	6±4	145±39	75±27	1.2±4.9	3.3±0.6	-85±34
6002	14±7	6±17	104±26	5±3	152±38	77±39	1±1.5	3.2±0.6	-85±30
6003	10±3	4±15	90±17	4±3	135±31	65±26	0.7±1.1	3.4±0.4	-81±29
6101	21±30	5±18	95±19	5±3	160±33	76±20	0.5±0.5	4.6±0.6	-95±42
6102	18±6	4±19	98±19	5±1	177±34	66±18	0.5±0.7	4.5±1	-107±29
6103	11±4	3±15	86±13	3±1	140±29	57±18	0.7±1.2	4±0.6	-81±30
6204	31±9	8±27	96±12	6±2	141±31	67±44	0.6±0.9	3.4±1	-48±23
6205	32±6	4±23	90±11	4±1	132±21	49±10	0.6±0.7	4.4±0.8	-33±16
6206	17±4	5±20	94±14	4±3	136±29	60±18	0.8±0.8	3.6±0.4	-62±25
6201	26±7	6±24	93±12	3±3	130±27	51±12	0.7±0.8	4.1±0.4	-36±17
6202	29±13	9±24	99±14	4±2	100±84	62±15	0.8±1	1.7±0.3	-3±36
6203	36±23	15±28	102±14	3±2	86±71	61±12	0.9±1.7	4±0.9	22±32
<i>Stream</i>	31±9	26±6	96±11	4±8	117±37	58±11	0.8±1.9	5.7±1.4	-19±30

*2005-2007

Table 2. Simulated results and comparisons with observed pH and DOC trends for individual lysimeters at Kindla during the years 1996-2007.

Kindla E horizon

Lysimeter no.	Mean pH	pH trend ^a	Mean DOC (mg/l)	DOC trend ^a	Mean calc. Z ⁻ (mol/kg AOM)	Z ⁻ trend ^a	Z ⁻ /DOC trend	Mean calc. Al _{tot} (mol/kg AOM)	Al _{tot} trend ^a	Mean log IAP, Al(OH) ₃ (s) ^b	Ionic strength trend
6001	4.40	+	10.8	-	0.093	0	+	1.23	0	8.13	-
6002	4.61	0	7.2	0	0.065	0	0	1.58	0	8.93	-
6003	4.60	+	7.1	-	0.067	0	+	1.55	0	8.82	-
6004	4.29	0	17.8	0	0.123	0	0	0.95	0	7.60	-

Kindla B horizon

Lysimeter no.	Mean pH	pH trend ^a	Mean DOC (mg/l)	DOC trend ^a	Mean calc. Z ⁻ (mol/kg AOM)	Z ⁻ trend ^a	Z ⁻ /DOC trend	Mean calc. Al _{tot} (mol/kg AOM)	Al _{tot} trend ^a	Mean log IAP, Al(OH) ₃ (s) ^b	Ionic strength trend
6101	4.61	+	6.3	-	0.065	0	+	1.59	+	8.94	-
6102	4.68	+	4.7	0	0.059	0	0	1.71	0	9.20	-
6103	4.74	+	3.8	-	0.055	0	+	1.76	0	9.33	-
6104	4.78	+	6.1	-	0.067	0	+	1.75	0	9.29	-
6106	4.79	0	5.1	0	0.060	0	0	1.79	0	9.38	0

Kindla discharge area

Lysimeter no.	Mean pH	pH trend ^a	Mean DOC (mg/l)	DOC trend ^a	Mean calc. Z ⁻ (mol/kg AOM)	Z ⁻ trend ^a	Z ⁻ /DOC trend	Mean calc. Al _{tot} (mol/kg AOM)	Al _{tot} trend ^a	Mean log IAP, Al(OH) ₃ (s) ^b	Ionic strength trend
6201	4.46	0	9.7	0	0.078	0	0	0.99	0	7.92	-
6202	4.87	+	11.9	+	0.094	+	+	1.21	+	8.46	-
6203	4.57	0	18.0	0	0.146	0	-	0.56	0	7.17	0
6204	4.64	+	11.6	0	0.162	+	+	1.48	0	7.91	0
6205	4.85	+	7.0	-	0.086	0	+	1.74	+	9.14	-
6206	4.59	+	9.5	-	0.079	0	+	0.85	0	8.68	-

^a+, Statistically significant if p<0.05 (Mann-Kendall); direction defined by Theil slope;

^b; IAP, Al(OH)₃(s) defined as: {Al³⁺}/ {H⁺}³

Table 3. Simulated results and comparisons with observed pH and DOC trends for individual lysimeters at Aneboda during the years 1996-2007.

Aneboda B horizon

Lysimeter no.	Mean pH	pH trend ^a	Mean DOC (mg/l)	DOC trend ^a	Mean calc. Z ⁻ (mol/kg AOM)	Z ⁻ trend ^a	Z ⁻ /DOC trend	Mean calc. Al _{tot} (mol/kg AOM)	Al _{tot} trend ^a	Mean log IAP, Al(OH) ₃ (s) ^b	Ionic strength trend
7101	4.86	+	5.1	0	0.158	0	0	1.24	0	8.15	-
7102	4.60	+	5.9	0	0.077	0	0	1.59	0	8.90	-
7103	4.73	0	4.9	0	0.086	0	0	1.60	+	8.91	-
7104	4.60	-	5.2	-	0.082	-	-	1.71	0	9.18	0
7105	4.39	0	8.2	0	0.062	-	0	1.60	0	8.91	0
7107	4.78	+	4.6	-	0.071	0	+	1.72	0	9.19	-
7109	4.65	+	5.7	-	0.068	0	0	1.63	+	9.04	-
7113	4.73	+	7.4	0	0.095	0	0	1.57	0	8.96	-

Aneboda discharge area

Lysimeter no.	Mean pH	pH trend ^a	Mean DOC (mg/l)	DOC trend ^a	Mean calc. Z ⁻ (mol/kg AOM)	Z ⁻ trend ^a	Z ⁻ /DOC trend	Mean calc. Al _{tot} (mol/kg AOM)	Al _{tot} trend ^a	Mean log IAP, Al(OH) ₃ (s) ^b	Ionic strength trend
7202	5.04	0	25.6	0	0.310	+	0	0.52	0	7.53	0
7204	4.90	0	5.0	0	0.130	0	0	0.81	0	9.39	0
7205	5.41	0	7.0	0	0.381	0	0	1.81	0	8.72	0
7206	5.16	0	8.6	0	0.324	0	+	0.98	+	8.55	0

^a+, Statistically significant if p<0.05 (Mann-Kendall); direction defined by Theil slope;

^b; IAP, Al(OH)₃(s) defined as: $\{Al^{3+}\}/\{H^+\}^3$

Figure legends

Figure 1. Location of the two Swedish IM sites Aneboda and Kindla.

Figure 2. Lysimeter transect localizations in the catchments of Kindla (left) and Aneboda (right). Black square = lysimeter plot at Aneboda, grey surface = peat land, solid black line = surface water/stream, hatched line = water divide, solid grey line = equidistance isoline above sea level (m).

Figure 3. DOC concentrations and smoothed trend lines (cubic spline, JMP 8.0.1) in three lysimeters (6204-6206) at the Kindla site between 1996 and 2007.

Figure 4. The relationship between DOC and the modeled net charge (Z) of the AOM at the Kindla site, lysimeter 6206.

Figure 5. Ionic strength (M) and smoothed trend lines (cubic spline, JMP 8.0.1) in three lysimeters (6101-6103) at Kindla (top) and in three lysimeters (7101-7103) at Aneboda (bottom) between 1996 and 2007.

Figure 6. Solubility of dissolved organic carbon (DOC) as a function of pH for four B horizons from central Sweden. Data from Gustafsson et al. (2003).

Figure 7. Solubility of dissolved organic carbon in Tyresta Bs, and the calculated Z^- value, as a function of pH.

Figure 8. The Z^-/DOC ratio as a function of pH for the Tyresta Bs soil sample.

Figure 9. Average effects of increased pH, decreased ionic strength (IS) and/or increased total Al concentrations on the net humic charge in soils. See Table 4 for model parameters.

A) Kindla, lysimeter no. 6206

B) Aneboda, lysimeter no. 7105.



Figure 1.

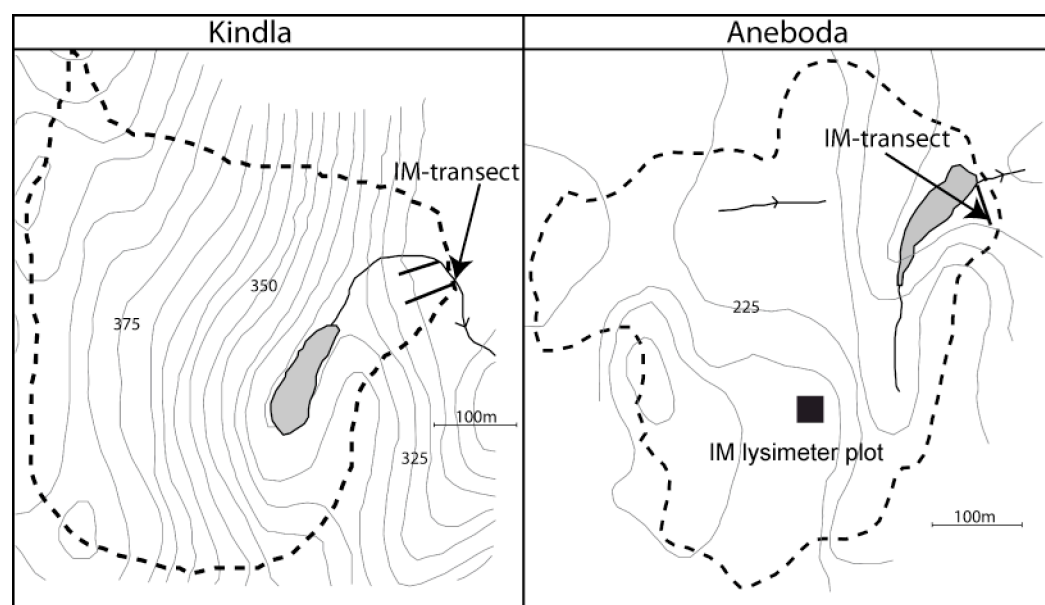


Figure 2.

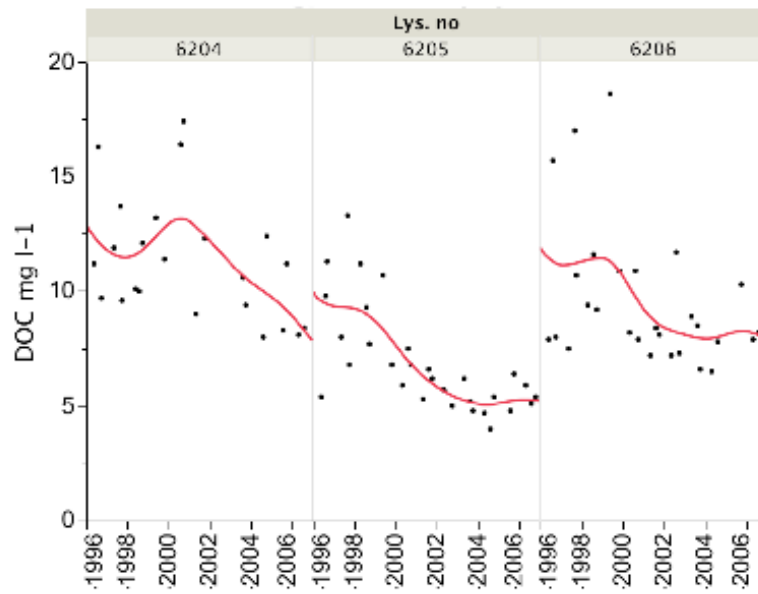


Figure 3.

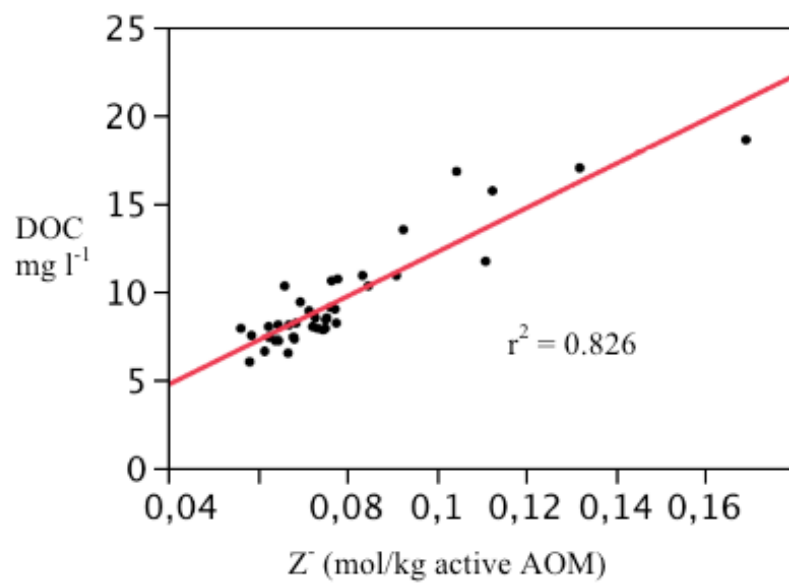


Figure 4.

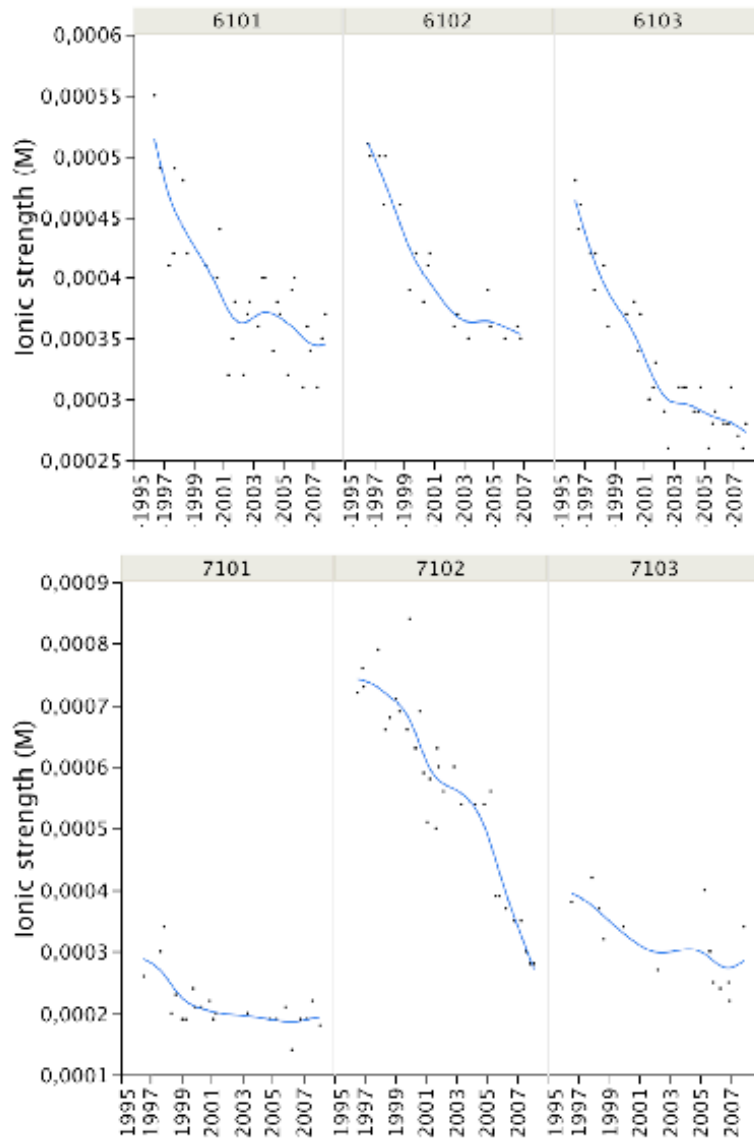


Figure 5.

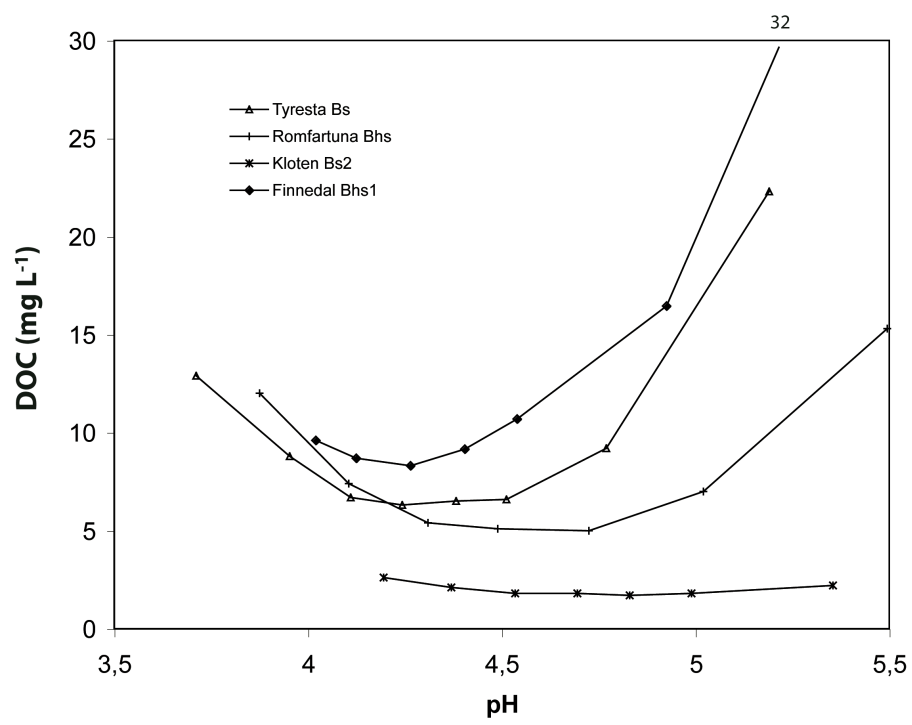


Figure 6

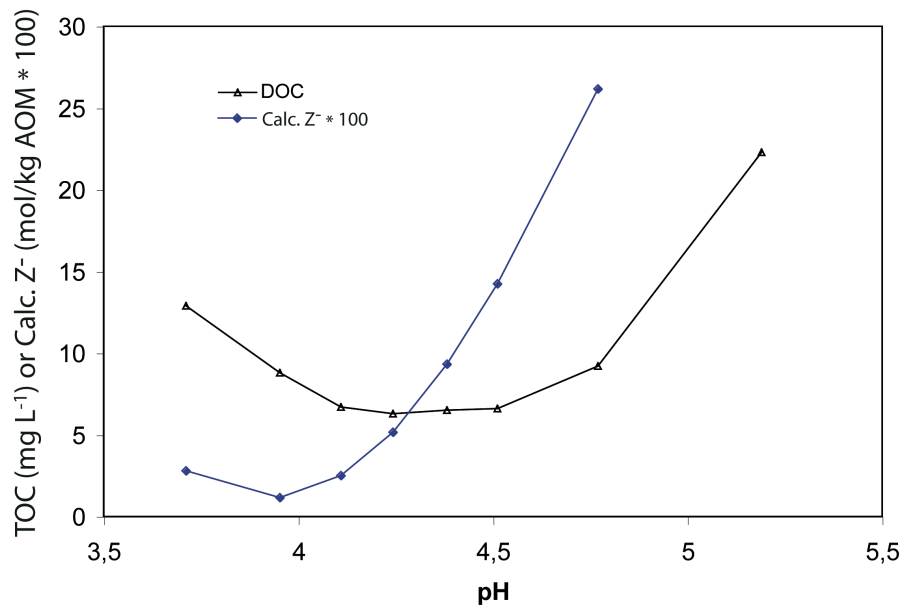


Figure 7

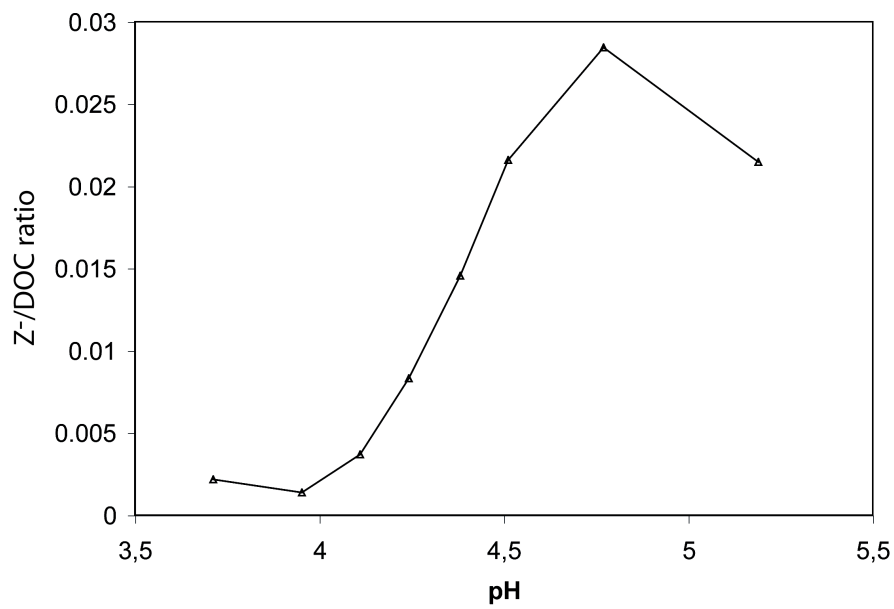


Figure 8

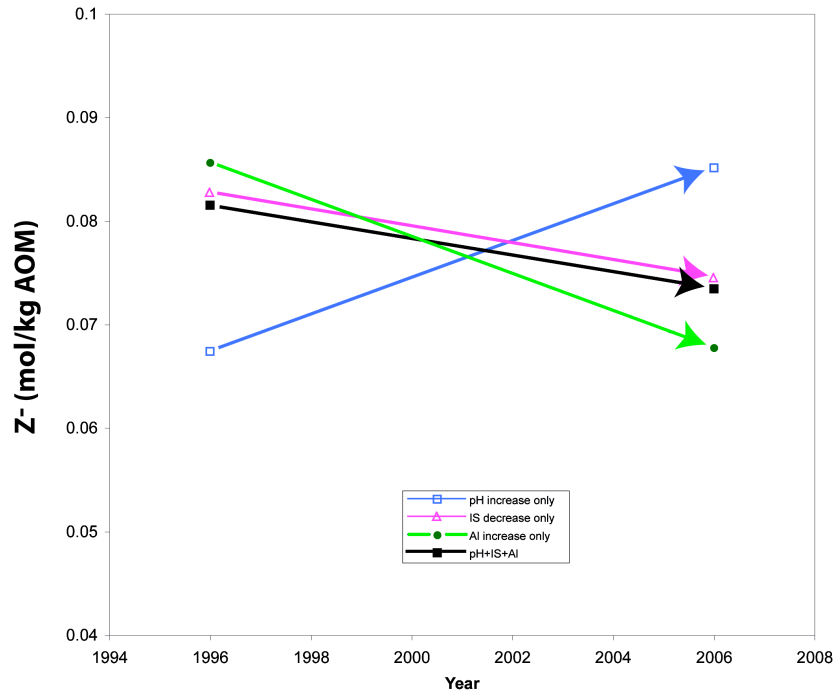


Figure 9a

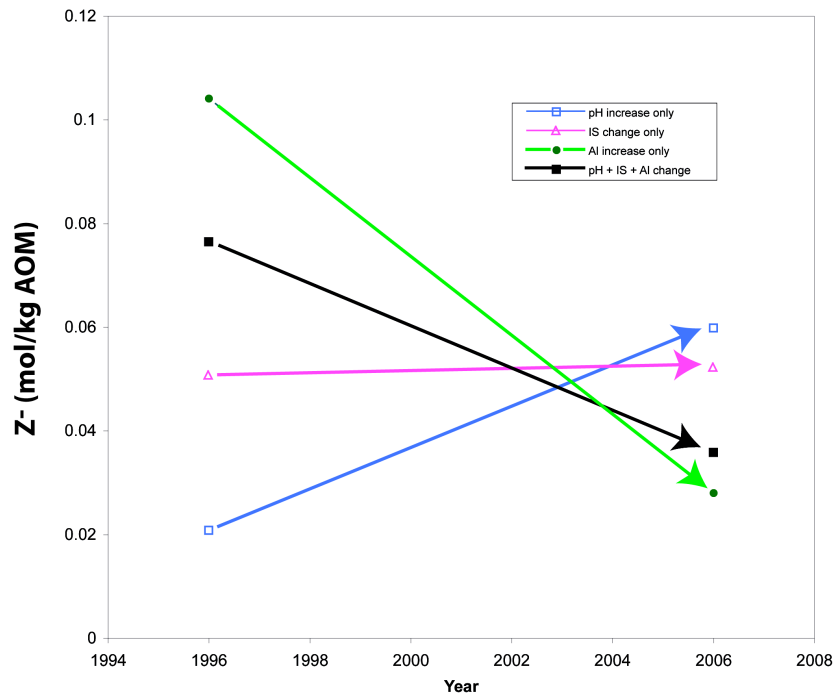


Figure 9b