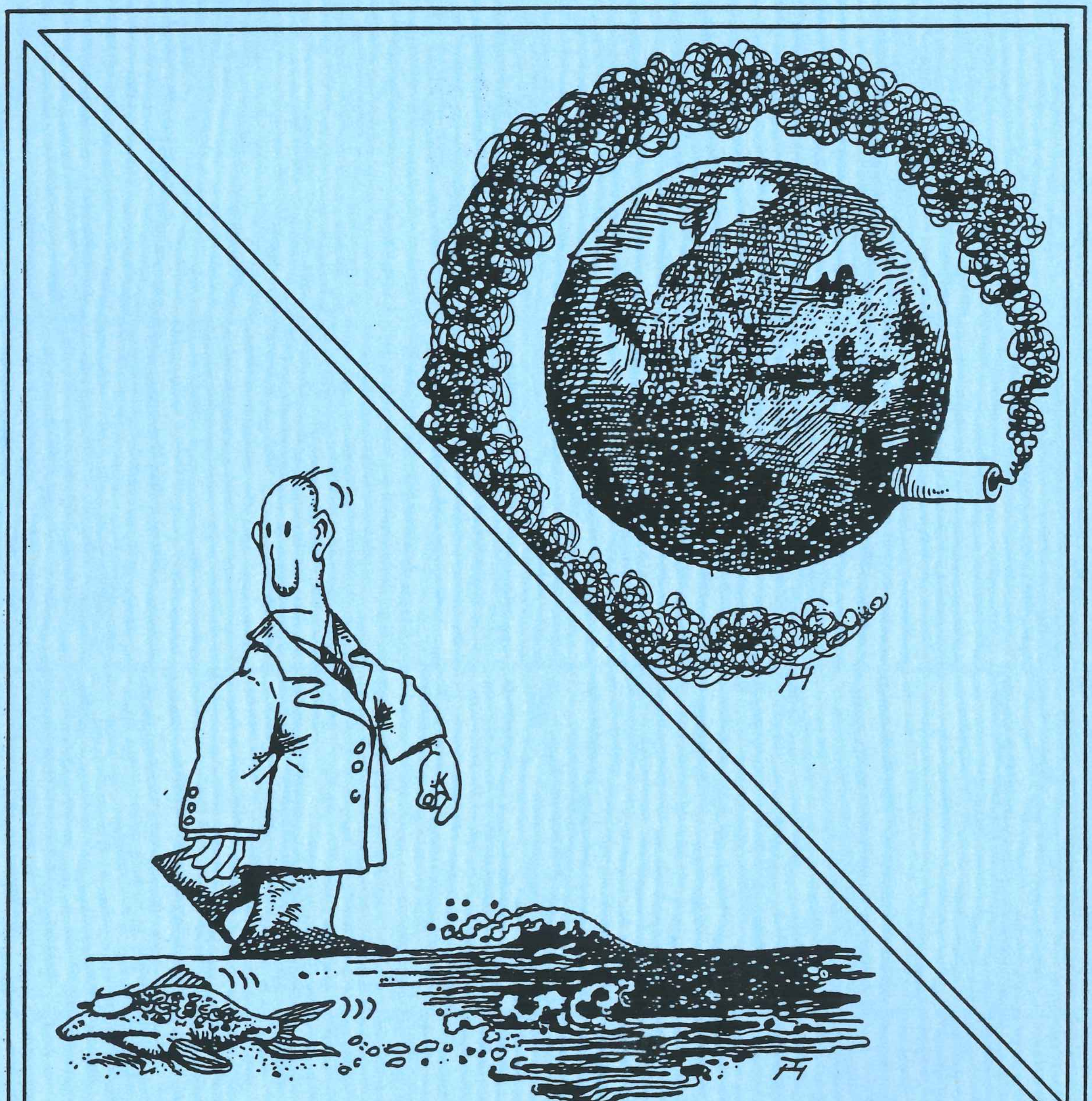
An Experimental Approach to Aluminium Mobilization and Water Flowpaths

At The Birkenes Catchment, Southern Norway



By Rolf David Vogt

AN EXPERIMENTAL APPROACH TO ALUMINIUM MOBILIZATION AND WATER FLOWPATHS AT THE BIRKENES CATCHMENT, SOUTHERN NORWAY

by

Rolf David Vogt

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PREFACE

The work has been carried out at the Central Institute for Industrial Research (SI) and the University of Oslo, by the excellent guidance of Professor Hans Martin Seip. His benevolent confidence in me has been important.

In particular, I thank Dr. Nils Christophersen who provided the opportunity, support, advise and encouragement for this work.

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I am indebted to Dr. Tim Sullivan who initially set up the working facilities and the employees at SI that have let me stay.
The field studies have been conducted in the Birkenes catchment, Aust-Agder. Support in the field was provided by Dag Olav Andersen.
Finally I gratefully acknowledge the support from the Surface Water Acidification Programme (SWAP) and the Norwegian Ministry of Environment.

To Anne and the one to be..

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Appendix

WHAT HAVE THEY DONE TO THE RAIN . . . .

Just a little rain falling all around
The grass lifts its head to the heavenly sound,
Just a little rain, just a little rain
What have they done to the rain ?

Just a little boy standing in the rain,
The gentle rain that falls for years.
And the grass is gone, the boy disappears,
And rain keeps falling like helpless tears,
And what have they done to the rain ?

Just a little breeze out of the sky,
The leaves pat their hands as the breeze blows by,
Just a little breeze with some smoke in its eye,
What have they done to the rain ?

Just a little boy standing in the rain,
The gentle rain that falls for years.
And the grass is gone, the boy disappears,
And rain keeps falling like helpless tears,
And what have they done to the rain ?

- Malvina Reynolds -

Abstract

Streamwater in the Birkenes catchment is highly undersaturated with respect to the mineral gibbsite at high discharge and gradually returns to saturation at low flow. At peak discharge, during saturated hydrological conditions, Al declines and H^+ increases. This indicates that an universal chemical equilibrium with one single mineral Gibbsite phase, or a single Al-H exchange reaction does not apply in Birkenes streamwater.

In spite of considerable research efforts the detailed mechanism involved in acidification, and in particular those controlling aluminium concentrations in water, have not been satisfactorily established. It has been hypothesized that temporal variations in acidity, Al concentrations and Al-mineral saturation indices in stream water are related to variations in Al-controls by changes in flowpaths, and by ionic loadings. In this thesis I will first review earlier work on acidification carried out in the Birkenes catchment in southern Norway.

Addition of sodium bromide to two small soil plots in Birkenes resulted in high concentrations of H^+ in the organic horizon and of Al^{3+} in the eluvial (E) horizon. The data are consistent with the previously postulated ion exchange Al-control in the organic soils and an Al-mineral solubility control in the deeper mineral soils. Time series suggest that this is due to increased residence time in the deeper mineral soils.
From our data we conclude that in the case of a major discharge event, after a prolonged dry period, a lateral water flowpath through upper soil horizons, leads to mobilization of a pool of salts, H^+ and humic acids from the O-horizon, causing a leaching of aluminium from the E-horizon directly to the brook.

It is found that a release of aluminium from the streambed substrate may also account for the observed concentration increase during acid discharge episodes. However in an experimental acidification of the stream we found only a small pool of easily mobilizable aluminium in the Birkenes streambed. In contrast, calcium was released in sufficient amounts to inflict on neutralization processes.

Suggestions for improvement of existing models for calculating stream water concentrations are given in the concluding chapter.

1. INTRODUCTION

Long term anthropogenic deposition of acidity and sulphur compounds (SO_4^{2-}, SO_2) has been identified as the principal cause of acidification of soils and waters in northern Europe and eastern parts of the northern America. Increased soil acidity permits elevated mobilization of aluminium from the edaphic reservoirs to adjacent surface waters (Cronan & Schofield, 1979; Dickson, 1980; Overrein et al., 1980). This observation has triggered considerable research in the acidified areas, particularly because the resulting levels of inorganic aluminium and hydrogen ions in surface waters are potentially bio-toxic (Cronan & Schofield, 1979; Baker & Schofield, 1982; Muniz & Leivestad, 1980).
In spite of persevering research the mechanism involved in controlling the aluminium release to surface waters, have not been satisfactorily established (Sullivan et al., 1986; 1987a; Cronan et al., 1986, Neal, 1988; Seip et al., 1989b). Solubility equilibrium with Al-minerals in soils and surface waters have been suggested (Magistad, 1925; Driscoll et al., 1985), though theoretical work (Neal et al., 1987) and field observations (Hooper & Shoemaker, 1985; Nilsson, 1985; Sullivan et al., 1986) indicate that neither surface water, nor soil solutions from different horizons, are permanently in equilibrium with one single Al-containing mineral.

The Birkenes catchment in southernmost Norway (Fig. 1) is a small acid sensitive low order watershed. Brown trout used to spawn in the brook up to 1950 when a major fish decline occurred; today the streamwater is highly toxic to aquatic biota. The site has been used extensively as a typical acid rain influenced catchment to clarify the important mechanisms in water acidification (Dale et al., 1974; Dovland & Mohn, 1975; Gjessing et al., 1976; Lundquist, 1976; Frank, 1980; Overrein et al., 1980; Christophersen et al., 1982,1985,1985a,b; Sullivan et al., 1986,1987a,b,c; Seip et al., 1989a). The precipitation and water chemistry have been investigated in Birkenes since 1971-1972 by the Norwegian Institute for Air Research (NILU) and the Norwegian Institute for Water Research (NIVA), resulting in one of the longest data records of this kind in the world.
These observations clearly show that the acidity in stream water is positively correlated to discharge. Rosenqvist (1978) hypothesized therefore that the amount of precipitation to a large extent determines the acidity of discharge (cf. Nordø, 1977). There is also a biannual variation in the acidity with the most acidic periods usually observed during snowmelt and in the autumn, particularly when heavy rain occurs after a dry summer (Dale et al., 1974; Gjessing et al., 1976).

Concentrating on the critical periods in autumn and during snowmelt, intense episodic water chemistry studies have been conducted at Birkenes from 1972 to 1975 (Dale et al., 1974; Gjessing et al., 1976) and since 1984 (Sullivan et al., 1986, 1987a, b & c; Seip et al., 1989a; Mulder et al., 1989; Vogt et al., 1989). The data of precipitation, soil water and

stream water has called our attention to the importance of water flowpaths. Based on these data Sullivan et al. (1986) explained the increased acidity during events by postulating that during high runoff conditions lateral flow in the acid upper soils leads the water to bypass the deeper and less acid mineral soil layers. Elaborating this concept Seip et al. (1989) and Mulder et al. (1989) explained the lack of a constant Al-control by stating that different mechanisms regulate the episodic release of aluminium in the various soil-horizons.
The importance of water pathways for the chemistry of stream water has also been confirmed in other studies (Cozzarelli et al., 1987; Lawrence et al., 1988; McAvoy, 1989) however the importance of hydrologic processes in episodic acidification are still largely unknown.

Christophersen et al. (1989a) regarded stream water as a mixture of soil water originating from the surface organic horizon (O), mineral soil (B/C) and deeper soil deposits in the valley bottom (VB or Deep C; DC). They presented a technique to estimate the contributions from each selected soil water class or "endmember" when stream water samples have been collected. As a first approximation the composition of the endmembers were assumed constant.
A recent intensive monitoring of the soil solution chemistry during a transition from dry to wet conditions showed a considerable decrease of the H^+ and Al concentration in soil solutions in the O/H and E layers (cf. variation in Table 7c) (Vogt et al., 1989). This was related to high ionic concentrations in soil water during prolonged dry periods, probably due to evaporative concentration and/or mineralization processes (Reuss & Johnson, 1986).

Henriksen et al. (1987; 1988) found a pool of exchangeable Al associated with streambed materials. They concluded that when aluminium- and calcium rich ground-water in equilibrium with the local CO_2 pressure emerges in streams and lakes, CO_2 degasses due to lower atmospheric CO_2 pressure. Then, pH will increase and aluminium and calcium may hydrolyse forming less soluble forms. Thus, when aluminium- and calcium-rich acid ground-water enters river systems during low flow when pH ≥ 5 and alkalinity positive (Norton & Henriksen, 1983), they may precipitate and/or ionexchange on liverworts in the stream bed. Under high flow conditions low pH values in the stream causes Al and Ca release and an increase of these constituents in solution.
The Birkenes streams are acidic, though during baseflow condition the pH may typically be above 5.0 . The base flow water reservoir is undefined, though recent research (Christophersen et al., 1989a) indicates that the deep bogs in the valley floor, with $5.5 < pH < 7.0$ (Table 7c), may be a significant source of high-pH seepage water. The qualifications that are needed to allow a buildup of an Al-reservoir in the streambed are therefore partially fulfilled. This causes uncertainty if such an Al-reservoir exists in the Birkenes streams.

2. SCOPE OF STUDY

The purpose of this study is to investigate soil water flowpaths and possible sources of easily mobilizable aluminium at Birkenes. Important Al-sources are discussed with respect to various mobilization mechanisms.

In order improve our understanding of water pathways and soil Al-processes, we decided to study soil water flow and chemistry response in a podzol and a shallow peat soil-plot after the addition of a neutral salt (NaBr) with a mobile anion, which could be used as a tracer.
By use of the bromide as a tracer I follow the soilwater movement in the examined parts of the edaphic reservoirs and thereby investigate factors controlling the water pathways. Furthermore the changes in the soil solution chemistry caused by the salt effect (Reuss & Johnson, 1986), as well as different Al-controls will be discussed. The short term organic response to the salt pulse will also be treated.

A possible mobilization of aluminium and base cations from the Birkenes streambed during acidic episodes (cf. Henriksen, 1987, 1988) was investigated by artificially acidifying the stream water. During wet autumn and dry summer conditions stream water pH was reduced to 4.1 and 4.2 respectively, and introduced to different stretches of streambed substrate. The consequent release of Al and base cations to the stream water was monitored downstream. The qualitative effect of this Al-release on the Al-concentrations in stream water during acidic episodes will be discussed.

Combining the new information with previous hydrological and chemical data from the Birkenes catchment I describe a flowpath scheme that accounts for the changes in surface water chemistry during an episode at Birkenes, particulary with respect to dissolved aluminium.
Relating to the EMMA-model (End Member Mixing Analysis-model, Christophersen et al., 1989a), the importance of variations in endmember compositions and the liable contribution of the disregarded E-horizon to surface water chemistry, are elucidated in the light of the concluded postulations.

3. BACKGROUND

The study of acid rain and concurrent aluminium mobilization has become an extensive subject. Only a short summary, comprising the concepts and tools directly related to the questions in focus, will therefore be presented as background.

3.1 Chemistry

3.1.1 General mechanisms

A number of mechanisms may control the soil solution and surface water chemistry. Within the solution phase or between the solution and the atmosphere highly diverse processes as protonation / deprotonation, dissolution / precipitation and oxidation / reduction may occur simultaneously. The most important general water chemical concept interrelating these processes is the overall physical principle of electroneutrality. This principle requires the fulfilment of the following charge balance:

Eqn. 1 $\Sigma\ \mu eq/L\ Cation^{+} = \Sigma\ \mu eq/L\ Anion^{-}$

Important interactions between the soil solution and the soil solid phase include the slow dissolution / precipitation of minerals, and the complex and relatively fast cation exchange equilibria (Bolt & Bruggenwert, 1976).

Dissolution or precipitation of minerals are controlled by their thermodynamic equilibrium constant (K_s). Deviations from equilibrium with a given mineral will be discussed later in terms of their saturation index (SI); the SI is a standardized measure of the degree of saturation with respect to a specified mineral.

Eqn. 2 $SI = \log\{ Q_s / K_s \}$

where Q_s is the ion product (based on activities) and K_s the equilibrium constant (solubility product). Positive values indicate oversaturation and may result in precipitation, while negative values denote undersaturation, which may cause a dissolution.

Cation exchange properties depend on a negative surface charge of solid phase particles, which is caused by (I) deprotonation of functional groups of organic acids, or (II) isomorphous substitution in clay minerals. Due to the principle of electroneutrality (Eqn. 1) an excess of cations over anions in close proximity to the solid surface, in the form of a Diffuse Double Layer (DDL), is required (Bolt & Bruggenwert, op cit.). For the following discussion of the cation exchange process we will only consider the general non-specific exchange. In the case of non-specific exchange this pool of cations in the DDL may be exchanged against others, while maintaining the electroneutrality. In the case of organic exchangers decreasing pH values cause the negative charge of exchangers to decrease due to increased protonation of the functional groups. Therefore, depending upon the nature of the soil this configuration gives rise to two types of exchange.

(I) The fixed potential (constant surface potential), characteristic of soil oxides and organics, is dependent on pH and ionic strength, while

(II) fixed CEC (constant surface charge), typical for clay minerals, is independent of pH.

Cation exchange reactions can be modelled using the Gapon equation.
The Gapon equation:

Eqn.3

$$\frac{[H^{+}]}{[M^{2+}]^{1/2}} = K_{sel} \frac{H_a^{+}}{M_a^{2+}}$$

$[H^{+}]$	denote H^{+} activity in solution phase,
H_a^{+}	denote H^{+} fraction of the exchange complex,
$[M^{2+}]$	denote base cation activity in solution phase,
M_a	denote base cation fraction of the exchange complex,
K_{sel}	denote the selectivity coefficient

Other similar equations exist (e.g. Gaines & Thomas). Which equation is used depends upon which empirically describes the exchange data best.

The dissolution of gases in water follows Henrys law. Henrys law states that the amount of dissolved gas is proportional to its partial pressure. A chemically important gas in natural waters is carbon dioxide which produces carbonic acid when dissolved in water;

Eqn. 4 $$CO_{2(g)} + H_2O \leftrightarrow H_2CO_3$$

Eqn. 5 $$H_2CO_3 \leftrightarrow H^{+} + HCO_3^{-}$$

Eqn. 6 $$HCO_3^{-} \leftrightarrow H^{+} + CO_3^{2-}$$

Table 1, in Appendix A, provides the dissociation constants for the carbon dioxide degassing and carbonic acid protonation. A significant acidifying effect of the CO_2 is depended upon the ambient alkalinity and pH.

3.1.2 Aluminium chemistry

The increased mobilization of aluminium from edaphic reservoirs into aquatic systems is of special concern due to the potential bio-toxicity of aluminium. In addition, because Al is amphoteric it may give rise to a strong pH buffering capacity in the pH ranges commonly observed in acid lakes (Bloom et al., 1979).

A simple dissolution and precipitation equilibrium with an aluminium-trihydroxide ($Al(OH)_3$) mineral phase has been described as the major mechanism controlling aluminium concentrations in soil solution and surface waters (Magistad, 1925; Johnson et al., 1981; Driscoll et al., 1985):

Eqn. 7 $$Al(OH)_{3(s)} + 3\ H^+ \leftrightarrow Al^{3+} + 3H_2O$$

thus implying the following solubility relationship:

Eqn. 8 $$[Al^{3+}]\ /\ [H^+]^3 = K_s$$

Al-containing minerals that have been suggested to control the aluminium concentration in solution are synthetic-, natural- and monocrystalline gibbsite as well as amorphous $Al(OH)_3$. See Table 2 in Appendix A for solubility and enthalpy values. All the aluminium hydroxide phases have negative enthalpy values indicating exothermic dissolution. This infers that the minerals are more soluble at low temperatures. Temperature corrected pK_s values are given in Table 3 Appendix.

A major problem with the gibbsite concept is that field observations show large variations in saturation indices (SI), with frequently observed negative values for all the relevant Al-containing minerals (Hooper & Shoemaker, 1985; Nilsson, 1985; Sullivan et al., 1986). This suggests that a universal Al-mineral dissolution equilibria as Eqn. 8 does not exist in nature. Recent detailed soil solution studies suggest instead different Al-controls for the various soil types and horizons (Seip et al., 1989a; Mulder et al., 1989; Vogt et al., 1989). Thermodynamic data for significant mononuclear ion species at equilibrium with aluminium in acid waters are given in Table 4 in Appendix A.

Equation 8 also describes the relationship (K_{sel}) of a simple cation exchange reactions (Reuss and Johnsen, 1986):

Eqn. 9 $$Al_{ex} + 3H^+ \leftrightarrow 3H^+_{ex} + Al^{3+}$$

Though as shown by Bloom et al. (1979) the selectivity constant (K_{sel}) may be lower than the K_s corresponding to synthetic gibbsite.

The possible exchange of hydrolysed Al at both organic matter and permanent charge sites, suggests that less H^+ is consumed in the ion exchange processes per released Al (Bloom, 1979; Coleman & Thomas, 1967).

Eqn.10 $$Al(OH)_x{}^{(3-x)+}{}_{ex} + xH^+_{aq} \leftrightarrow xH^+_{ex} + Al(OH)_x{}^{(3-x)+}{}_{aq}$$

Once in solution the Al-hydroxides will protonate in order to equilibrate with the ambient pH and temperature. In waters with pH below 4.5 the surplus H^+ will therefore be consumed; Eqn. 8 may be applied. At pH values above 4.6 significant amounts of exchanged Al-hydroxides may remain as $Al(OH)_x{}^{(3-x)+}{}_{aq}$.

This may offer one reason for the commonly observed lower K_{sel} in Eqn. 8 .

Some recent studies have also drawn the attention towards minerals containing both sulphate and aluminium to account for SO_4^{2-} retention in soils. The minerals in question are jurbanite, basaluminite and alunite. Cf. Table 5 in Appendix A for their solubility values.

A part of the total aluminium in natural waters is in the form of "dimer" or "polymer" complexes. The aluminium in these compounds does not participate in the fast chemical interactions occurring in the aquatic systems, (though they may release small labile "monomer" species during certain conditions). To discuss aluminium chemistry distinction must be made between these aluminium fractions. This requires detailed thermodynamic evaluation. However at a much simpler level a basic fractionation can be achieved between simple (monomeric) and polymer aluminium compounds by using a simple analytical complexation method described by Barnes (1975) and Driscoll (1984). Driscoll separates Al_{aq} into mainly inorganic monomeric "labile aluminium (Al_i)" and a mainly organically complexed monomeric non-labile aluminium (Al_o)". (Cf. chapter 4.1 for further elaboration).

3.1.3 Hydrochemistry

The seasonal acidity in stream water is positively correlated to discharge. Rosenqvist (1978) therefore emphasized that the amount of precipitation to a large extent determines the acidity of discharge (cf. Nordø, 1977). This has been elaborated by Sullivan et al. (1986), who found that the hydrologic response to stormflow and water soil contact time is important in regulating short-term acidification of streams. McAvoy (1989), found that factors as rainfall volume, intensity, and duration are important in regulating short term acidification of stream water. There is also a variation in the acidity within the seasons with the most acidic periods usually observed during the onset of snowmelt and in the first large discharge event in autumn, particularly after a dry summer (Seip et al., 1989). Vogt et al. (1989) therefore suggested that also the antecedent hydrological conditions are important in determining the major flowpaths in a catchment.

It has not been possible, in spite of considerable research, to explain the physical and chemical aspects of runoff generation within one conceptual model of catchment hydrology (Kennedy et al., 1986; Pearce et al., 1986). Some recent progress is achieved by Seip et al. (1989) and Mulder et al. (1989). They found that different soils or soil layers exhibit different chemical controls on the soil solution composition. During an event, changes in water pathways leading the water from or through these different soil matrices, may therefore qualitatively produce the observed changes in stream water chemistry.

On a catchment scale two fundamentally different concepts, the "fingerprint model" (M. Hauhs, unpublished report) and the "final flowpath horizon model" (N. Christophersen, pers. com.), may be used to explain this mechanism. According to the fingerprint model the soil/soil solution equilibrium reactions are turned off at the point of becoming saturated flow, thus the soil solution conserves the fingerprint chemistry of the soil horizon at the ground water Table. This is based on that saturated flow velocity is too fast to attain chemical equilibria. On the contrary the final flowpath horizon model poses that the soil/soil solution equilibrium reactions may not be turned off. It states instead that the chemistry of the soil solution entering the stream is determined by the last soil matrix in contact with the water (i.e. streambank).

Regardless of both these concepts probable flowpaths have been suggested by different authors working under various hydrological conditions in acid sensitive low order catchments.
Nilsson and Bergkvist (1983), found during the onset of rain a downward flowpath through dry, well-drained soils on the steep hillslopes, followed by upward renewed contact with organic layers near the stream. Oxsygen^{18}- and deuterium-isotope concentration data in the Birkenes catchment suggested that in the case of such a percolation flowpath the new infiltrating water would push out the old soil solution into the stream (the "piston effect") (Christophersen et al., 1985; Christophesen & Rodhe, 1989).
McAvoy (1989) postulated that the infiltration capacity of the B-horizon becomes exceeded during the peak of the storm and that the majority of rain water therefore passes laterally through the upper soil horizons before entering the stream. Vogt et al. (1989) supported this postulation, and suggested that a contributing factor is that shallow soils are mainly situated at the higher elevations furthest away from the streams; the precipitation that reaches these regions drains rapidly into the deeper soil profiles at lower elevations. This large flux of ground water causes a billow on the ground water table that moves rapidly down the hillslope. This wave flushes the organic deposits on its journey. The wave peak reaches the brook and constitutes the maximum discharge.

The soil is a divers matrix and numerous important soil water flowpaths and concepts are therefore possible. During the following discussion one must therefore keep in mind that any flow scheme hypothesis will be a drastic simplification from the real stormflow generation as a process highly variable in space and time.

3.1.4 Organic interactions

In the upper horizons of the soils, solution composition is determined primarily by interactions between dissolved species and solid organic matter (Krug & Frink, 1983; Bache, 1983). Many investigators dealing with the release of Al from soils have shown that the organic matter exchange sites in acid soils influence the relationship between Al and H^+ concentrations (Bloom et al., 1979; Clark & Nichol, 1966; Evans & Kamprath, 1970; Kittrick, 1966).

Organic matter consists both of water soluble and insoluble compounds. The soluble compounds are produced from organic matter by partial degradation of lignin or synthesized by exoenzymes of certain soil microorganisms. The amount of carbon in soil solution, e.g. the Total Organic Carbon (TOC), consists therefore mainly of water soluble low-molecular weight aliphatic and aromatic acids. The insoluble fraction of interest is produced by humification. Humification is a random resynthesis of the TOC, or further degraded compounds, to less soluble high molecular weight humic polymers. Humic compounds are the end product of the decay of biological material in the soil and is usually referred to as humus.

Dissolved organic compounds may produce low pH, provide mobile anions and be responsible for chelation and transport of aluminium and iron by complexation of the functional groups and non-specific ion-exchange reactions (cf. chap. 3.1.1). Characteristic functional sites on both water soluble and insoluble organic compounds are phenolic and carboxylic groups. Particular combinations of these hydroxyl groups may give strong chelating properties with respect to transition metals and aluminium. Some metal cations, particularly Al and Fe, have relative high affinity to organic compounds. Driscoll (1980) observed that only 30% of the functional sites on natural dissolved organic acids were capable of direct proton transfer, the rest of the sites were complexed with iron and aluminium.
The organic/metal interactions are linked by the net humic charge Z (Tipping & Hurley, 1988). The net humic charge is dependent on the extent of protonation (cf. chap. 3.1.1) and metal complexation. A negative humic charge is counteracted by cations in the DDL on the border between organic matrix and water.

The water soluble organic compounds (TOC) become less soluble the more metals that are complexed or exchanged on to the organic compound (Hayes & Swift, 1978) and the higher the degree of protonation. This lowered solubility is due to the lowered net humic charge (Z, Tanford, 1961), causing a more compressed DDL and reduced repulsion, and thereby permitting (1) enhanced sedimentation and flocculation (Andersen, 1989), and (2) increased polymerization and condensation of TOC to humus (Bolt & Bruggenwert, 1978; Tipping & Hurley, 1988; Reuss & Johnsen, 1986).
The anthropogenic pollutants raise the electrolyte level of the soil and thereby cause a decrease in the soluble organic fraction (Tipping & Hurley, 1988).

Stuanes (1979) discussed the drying of the soil sample in the analytical method for determination of the chemistry in humic soils. He found that due to drying of the soil, higher concentrations of most major cations were eluted by the application of artificial precipitation. The CEC was also found to increase considerably in the dry soil. The electroneutrality constraint further implied an increase in dissolution of organic anions. This increase in TOC is caused by the natural biochemical destruction (mineralization) of microorganisms during drying (or freezing) conditions (Conway, 1982). We may therefore also expect higher CEC and an elevated contribution of salts and organic acids from the organic compartment during natural conditions after a period of dry or freezing weather.

3.2 The Birkenes data base

The highest loadings of anthropogenic sulphur and nitrate acids in Norway are found in the southern most region. In 1971/72 the "Acid Precipitation - Effects on Forest and Fish" (The SNSF-project) initiated a study at the Birkenes catchment (Fig. 1), a 0.41 km^2 forested acid sensitive low order watershed, situated in the centre of this region (58°15'N, 08°15'E, map ref. 37 VPL 556 719 on map Lillesand). The Birkenes catchment has since then obtained the role of a classical "acid rain" influenced watershed, hosting numerous researchers that have played a important part in developing understanding in the science of "acid rain" (e.g. I. Rosenquist, I.P. Muniz, H.M. Seip, N. Christophersen and T.J. Sullivan, see references).

Being a centre for acid rain study the catchment has become well documented with high quality data.
During the SNSF-project the watersheds biology, morphology, topography, hydrology and chemistry was thoroughly mapped (Dale et al., 1974; Dovland & Mohn, 1975; Gjessing et al., 1976; Lundquist, 1976; Frank, 1980; Overrein et al., 1980). The precipitation amount and quality, and discharge and water chemistry have been monitored at Birkenes since the start of the project in 1971-1972 by the Norwegian Institute for Air Research (NILU), the Norwegian Water Resources and Energy Board (NVE) and Norwegian Institute for Water Research (NIVA), resulting in one of the longest data records of this kind in the world. From 1980 the catchment has been part of the Norwegian monitoring programme for polluted, long range transported air and precipitation , operated by the State Pollution Control Authority (SFT).
On the basis of these data Christophersen et al. (1982) constructed the Birkenes model which reproduced major short term and seasonal variations in the observed streamwater chemistry. This work has lead to the requirement for further information for testing hypotheses in the model and to lay the basis for continuous model development. The effort is focused on detailed studies of soils, soil water and streamwater during rainstorms and snowmelt events, with especial concern to the controlling mechanisms of aluminium release (Sullivan et al., 1986, 1987a,b,c; Seip et al., 1989a; Mulder et al., 1989; Vogt et al., 1989).

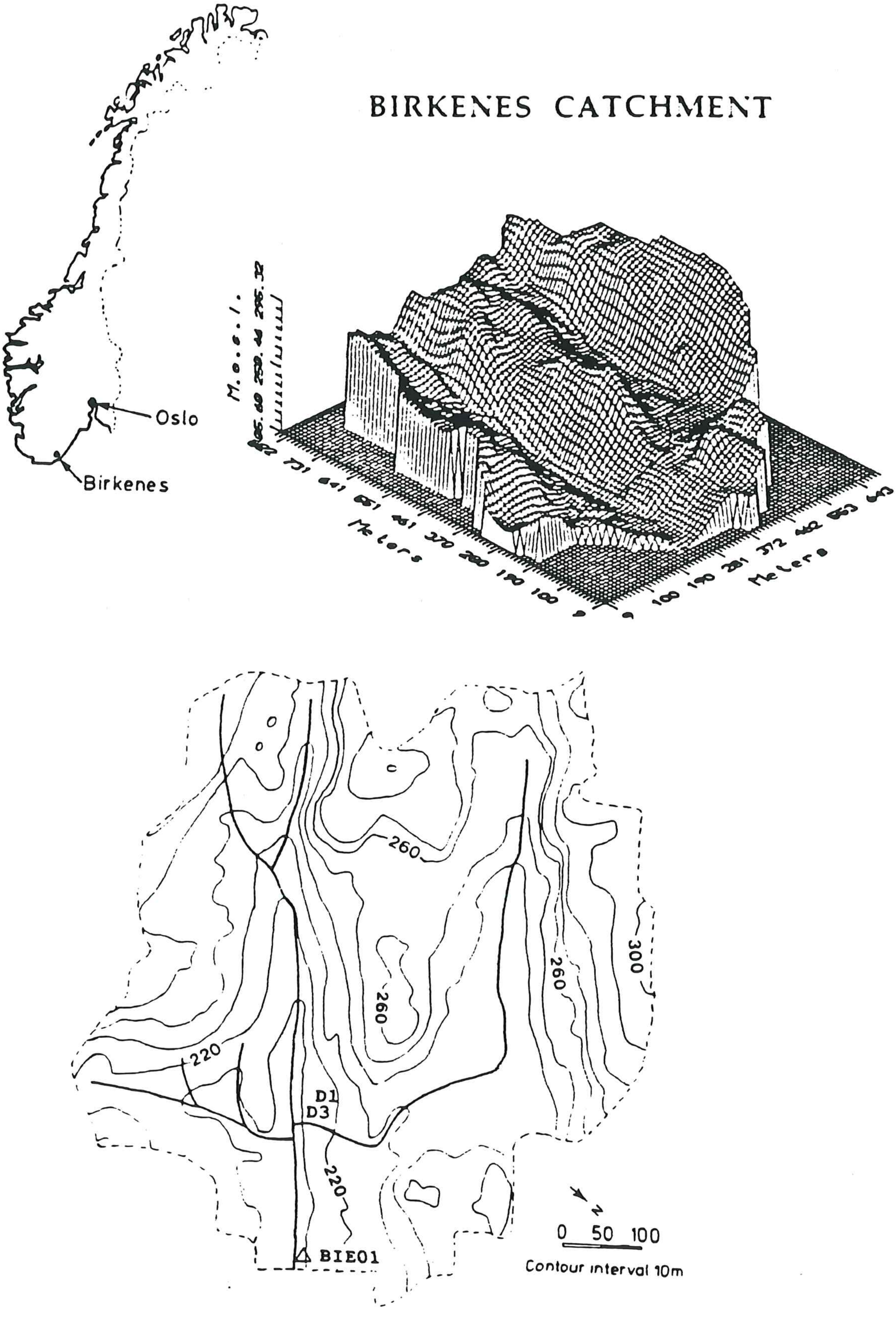

Figure 1. 3 dim. view and topographic map of Birkenes catchment with stream sampling locations (BIE 01, Stream-D) and salt addition plots (D1, D3). Insert shows approximate location in Norway.

Observed temporal variation in acidity and Al-mobility during different episodes led us to conduct a summer episode study where we especially studied changes in the soil solution composition when going from dry to wet conditions (Vogt et al., 1989).
The catchment is now also part of the forest monitoring programme run by the Norwegian Forest Research Institute (NISK).

In chapter 3.2.1 and 3.2.8 I present the relevant biological, morphological, topography, hydrological and chemical data on the catchment, and a review of conclusions and highlights from the episodic studies conducted at Birkenes as well as modelling work.

3.2.1 Climate and atmospheric deposition

Birkenes has a humid climate with an average precipitation of 1370 mm yr^{-1} of which about 1075 mm is discharged as streamwater (SFT, 1986). The length of the growing season (mean daily air temperature > 6 °C) is about 174 days $yr.^{-1}$ (Bruun, 1967) (avg. temp. 6.6°C). Only 50% of the days register precipitation and during the summer months evapotranspiration typically exceed precipitation resulting in generally dry summers with low discharge; the autumns are generally wet with high discharge (Christophersen et al., 1982).
During the winter months the precipitation and its constituents are stored in the catchment as snow, though frequent midwinter melting periods are common. At the onset of snowmelt the meltwater chemistry showed the typical pattern of high initial concentrations of ions followed by a dilution as the melt progressed (Johannessen & Henriksen, 1978; Sullivan et al., 1987b).

The chemical composition of precipitation can be depicted as a mixture of long-range transported components (H^+, SO_4^{2-}, NO_3^-, NH_4^+), marine salts from sea spray (Na^+, Mg^{2+}, Cl^-, SO_4^{2-}) and components from several sources (Ca^{2+}, K^+).
The region has the highest total deposition of anthropogenic atmospheric compounds in Norway (about 6 g SO_4 m^{-2} yr^{-1}, SFT 1988); the volume weighed and the mean pH in precipitation is 4.25 and 4.42 respectively (calculated as H^+). The pH at low precipitation amounts vary greatly with values ranging from 3.2 to 6.2 (NILU, unpublished data). The pH increases typically through a rain event with pH values < 4.5 generally observed at the onset of a storm while pH ≥ 4.5 is commonly found at the end of the period (cf. Sullivan et al., 1987b).
The catchment is situated only 15 km inland from the Skagerak coastline. This causes relative high seasalt aerosol loadings (40% of the ionic sum on an equivalent basis) (Christophersen et al., 1982). Additional input of both acid components and marine salts from the atmosphere comes as dry deposition (approx. 30% based on sulphate) (Christophersen & Wright, 1981). Major anions in the precipitation are chloride and sulphate with average volume weighted concentrations of 56

µeq/L and 68 µeq/L, respectively (SFT, 1986). Concentrations of major ions in precipitation and in stream water are given in Table 6 in Appendix A.

3.2.2 Vegetation

The vegetation of the watershed was mapped by Dale et al. (1974). The forest consists for 89% of coniferous trees with spruce (Picea abies) in the valley bottom and hill slopes, and pine (Pinus sylvestris) essentially on the ridges. Birch (Betula pubescens) and other deciduous trees grow on some south facing slopes. Ground vegetation comprises blueberry-bracken community (Eu-Piceetum myrtilletosum / dryopteridetosum) (58%), pine community (Barbilophozia-Pinetum) (28%), and fern and peat forest (7%).

3.2.3 Soils

Soils at Birkenes have been studied by Dale et al., (1974), Frank (1980), Brække (1981), Mulder et al., (1989) and by NISK. Selected chemical characteristics for the two major soil profiles at Birkenes are given in Table 7a in Appendix A.

Overlaying a biotite-granitic bedrock 79 % of the catchment is covered by mineral soil, 17 % consists of peat and bogs and 4 % is rock outcrop.
The depth of the mineral deposits typically decreases with increasing elevation from about 1 m at the foot of the slope to zero on the ridges. The glacial deposits consist to a great extent of till, with a clay fraction frequently < 6% and a gravel fraction < 30%. In these deposits, below a organic or humic layer of approximately 10 cm, acid and oligotrophic mineral soils have developed, ranging from true podzols (Spodosols) to acid brown earths.
The areas around the brooks in the valley bottom (7 % of the catchment) are covered by 0.1 m to 2.5 m deep soligenous bogs. In pockets on the slopes smaller patches of soligeneous peat have developed (10 % of the catchment).

The organic soil layers are generally acidic; pH(H_2O) vary from 3.7 measured in the humic layer and bog surface, to 4.2 at approx. 30 cm depth in the bogs. The mineral soils on the slopes are less acid with lowest pH values in the E horizon (4.2), and higher in the B-horizon (4.7-4.8). The highest soil pH is observed below the bog (5.1) in the valley bottom. The cation exchange capacity in the soil is correlated with the amount of organic materials in the soil profile. The CEC values are low in the mineral soils and considerably higher in the organic soil. Typically, the content of insoluble organic material in the podzols is highest in the organic horizon, decreases in the E-horizon, peaks in the Bhs-horizon, and declines with further depth (C) in the soil; the loss on ignition in a similar Birkenes profile is 69.5%, 3.0%, 9.6% and 0.8% respectively. The exchangeable acidity in the B-horizon is dominated by aluminium. In all podzol horizons the base saturation is low; approx. 20% in organic horizon and which only increases slowly during a wetting of the watershed. The bog is therefore considered to contribute significantly to the discharge only during low flow. This was also concluded by Andersen (1989), based on bog water chemical data.

Hauhs (1988) studied hillslope hydrology at Birkenes by monitoring soil water potential in a number of soil profiles. He found great fluctuations in water potential in the soils during precipitation events. In general during events the peat profiles peaked in water content after the mineral soil, but simultaneously with discharge. Based on this time delay between peak flow he contributed differences in discharge contributions from these profiles to the concentration and dilution pattern in the surface waters during storm flow.

3.2.5 Soil solution

The soil solution [H$^+$] generally reaches the highest levels in the organic/humic (O/H) and E-horizons and typically decreases with depth, while the reverse trend was found for [Al^{3+}] (Seip et al., 1989a; Mulder et al., 1989) (cf. Table 7b in Appendix A and Fig. 2). This suggest that neutralization is mainly caused by mobilization of aluminium (Christophersen et al., 1989b). The saturation index with respect to gibbsite increased with pH; as SI varied with respect to synthetic gibbsite from less than -1 to about 1. This shows that the Al^{3+} concentration can not be explained by solubility of only one type of gibbsite (Seip et al., 1989a).

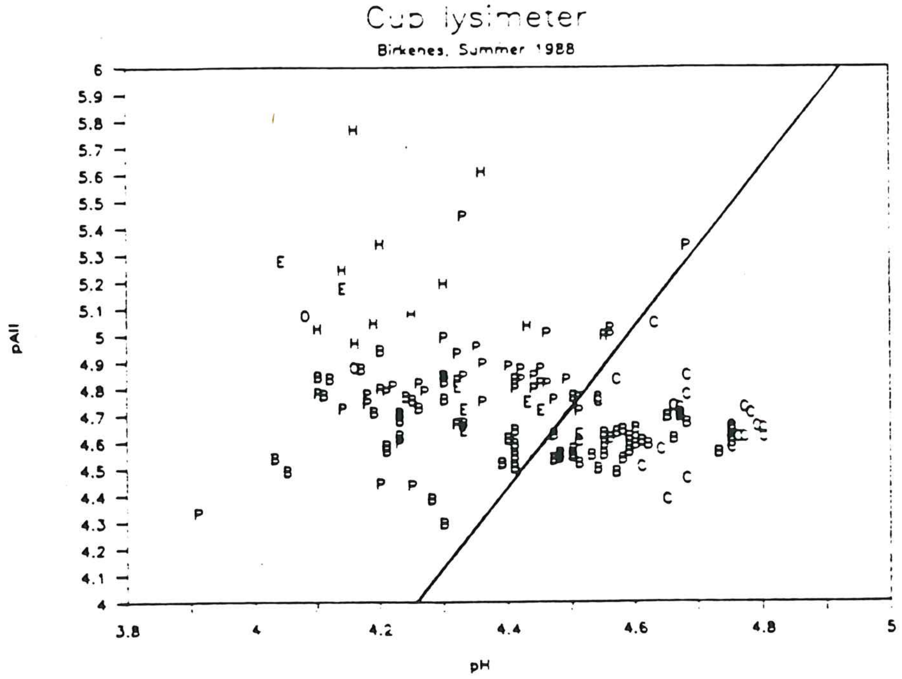

Figure 2. Cup lysimeter data from the summer of 1988 showing soil solution pAli as a function of pH in the H-, O-, P-,E-, B- and C-horizon of the hillslope soils. Letters in graph refer to soil horizon (P=Peat). Natural Gibbsite solubility line using pK$_s$=-8.77 (25°C) is indicated.

only about 5% in the mineral soil. The peat layers on top of the bogs show a large cation exchange capacity (CEC) and the major exchangeable cation is aluminium (CEC = 245 mmol/kg, 78.8% is exchangeable aluminium).

Laboratory experiments adding mineral acids on the Birkenes organic soils by Andersen (1989) reveal an pAl^{3+} vs. pH ratio of 1.7 in autumn soil and 3.1 in summer soil. The mineral soil responded to acid addition by a gibbsite solubility reaction with a constant indicating synthetic gibbsite.

3.2.4 Hydrology

The Birkenes catchment consists of two connected sub-catchment valleys surrounded by steep hillslopes. The elevation ranges from 185 to 275 m a.s.l. The valleys are drained by three second-order streams which merge to form a third-order stream 150 m above a V-notch weir (Fig. 1).

Despite considerable variation in groundwater level on the hillslopes, there was a consistent trend of abrupt rise in water table at onset of storm. With prevailing rain the water table shows a slower increasing trend which frequently intercepts the forest floor. After the precipitation ends the water tables in the deep profiles at the foot of the slope decrease slowly, while the thin soil layers on the ridges drained rapidly (Sullivan et al., 1987a).

Mulder et al. (1989) used a rain event with extremely high seasalt loading to study the effect on soil solution chemistry and the water pathways after an autumn rain storm when the catchment was at its hydrological field capacity. Monitoring the Cl pulse showed that a considerable fraction of the precipitation inputs rapidly flowed laterally through the O/H-horizons to the stream. Vertical percolation of Cl-rich water was slow. Approx. 25% of the incoming rain reached the streams during the discharge event. O^{18}-measurements indicated also that 20 to 30% of the rainfall is transferred directly to the stream during a hygrograph response (Christophersen et al., 1985; Christophersen & Rodhe, 1989).

A billow on the ground water table is typically produced due to rain falling on the shallow soils at the ridges (Vogt et al., 1989). This billow moves rapidly down the hillslope and reaches the brook producing the peak in discharge 2 to 6 hours after the maxima in precipitation intensity.

Lundquist (1976), constructed a hydrologic model for Birkenes. According to the model the till mainly contributes to the discharge during the rising limb of the hygrograph, while the humic compartment is an important source of surface water flow during peak runoff. The bogs in the valley bottom were considered by Lundquist to have a large storage capacity and a long response time. This assumption is also documented by the water table height in the bog (Sullivan et al., 1987a)

Mulder et al. (1989) found that the organic soil solution approximately satisfied Eqn. 8; the relationship between $[Al^{3+}]$ and $[H^+]$ was roughly cubic. Nevertheless the saturation indices with respect to all kinds of gibbsite were highly negative. It therefore seemed reasonable to assume that the Al and H^+ concentrations were determined by cation exchange in organic soils. Laboratory studies of the organic soils confirm this assumption by yielding an exponent in Eqn. 8 of 3.1 for samples taken in the summer. However, experiments on soil collected in the autumn resulted in an exponent of only 1.7 (Andersen, 1989).
The saturation index for mineral soil solution is found by Mulder et al. (op cit.) to be close to zero for synthetic gibbsite, but the exponent in Eqn. 8 was less than 3 (Fig. 2). On the other hand the laboratory studies (Andersen, op cit.) gave an exponent close to 3 both for summer and autumn samples. An Al-mineral dissolution mechanism is therefore a plausible aluminium control in the Birkenes mineral soil.
In the deep deposits along the brook neutralization is probably due to both reduction of sulphate and release of base cations.

The soil solution leachates from sub surface peat layers exhibit high values of sea-salts, TOC and H^+ under dry conditions dropping to moderate values during persistent rainfall (Vogt et al., 1989).
Soil solutions from deeper soil horizons, i.e. DC, B and C horizons show little temporal variation in solute concentrations, despite sampling under varying hydrological conditions (Table 7b).

3.2.6 Surface waters

The streamwater was chronically acidic with a volume-weighted-mean pH in the main brook of 4.5, and inorganic monomeric aluminium (Al_i) is the predominant form of aluminium (Christophersen et al., 1982) (Table 6, Appendix A). The surface waters are highly undersaturated with respect to all forms of gibbsite, $Al(OH)_3$, at high discharge but return gradually to saturation at low flow (Seip et al., 1989a). This indicates that a universal chemical equilibrium with one single mineral gibbsite phase, or an Al-H exchange reaction, does not apply in Birkenes streamwater.
Dramatic elevations in the concentrations of inorganic aluminium and H^+ in the brooks are common during events and especially at the first episode following an extended low discharge period. Though remaining high the $[Al^{3+}]$ in stream water shows a decreasing trend during the subsequent episodes (Fig. 3). During these subsequent episodes streamwater $[Al^{3+}]$ tended to respond negatively with increased runoff (peak 3 and 4 in Fig. 3), whereas $[H^+]$ always shows a maximum at peak discharge. These patterns have been related to the increased contribution of runoff from upper, acidic and aluminium depleted horizons, during events following wet antecedent conditions (Sullivan et al., 1986; Seip et al., 1989a).

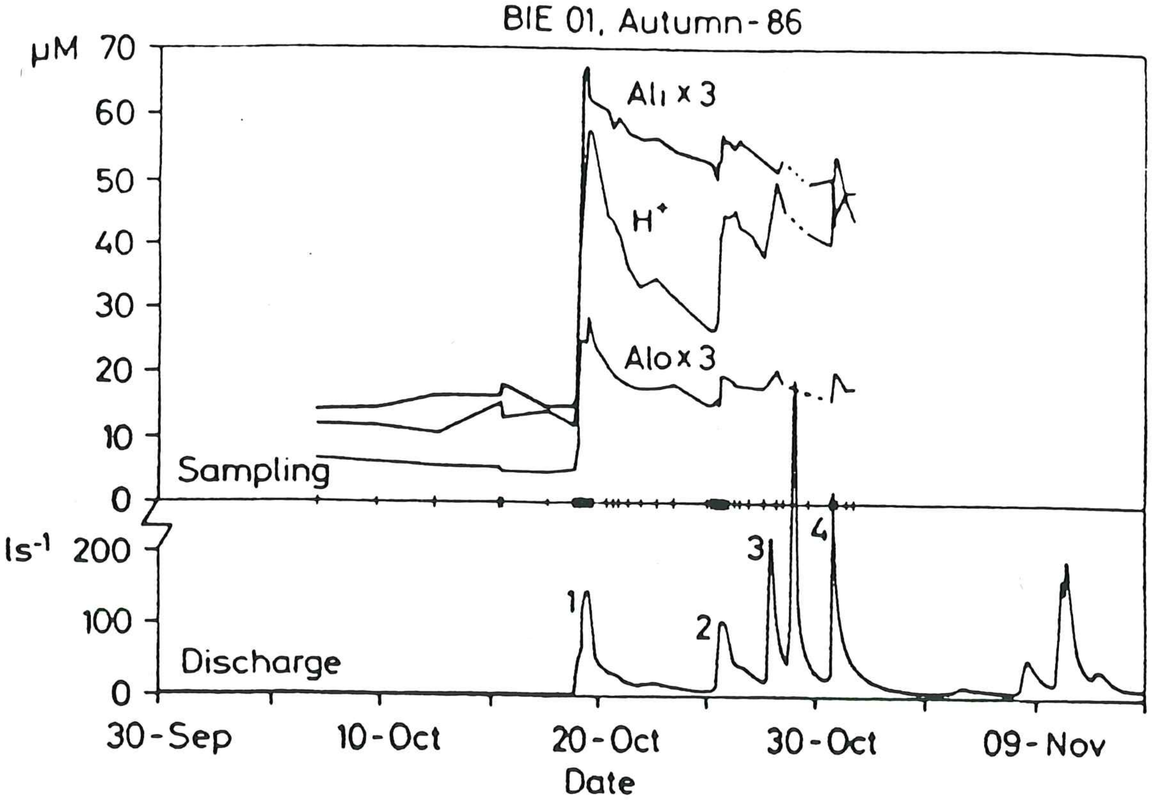

Figure 3. Discharge (L s^{-1}) and concentrations of H^+ and Al^{3+} for the autumn of 1986.

The detailed variations in nitrate and sulphate concentrations are small and inversely correlated to discharge, except during events preceded by dry conditions where $[NO_3^-]$ and $[SO_4^{2-}]$ increases notably with discharge. Cations are in general inversely correlated with episodic discharge (Sullivan et al., 1986).

The outwash of humic substances from the soil may be less than what is produced in the stream waters during stable conditions and we may therefore observe a decline in [TOC] during episodes. Though typically events preceded by dry conditions exhibit larger [TOC] fluctuations and concentrations (Sullivan et al., 1987c).

3.2.7 Seasonal chemical variations

Seasalt

As first pointed out by Rosenqvist (1978) and later by Reuss (1980), and discussed by Skartveit (1981) and Wright et al. (1988), high seasalt concentrations may significantly affect soil solution chemistry primarily through cation exchange.

Seasonal variation in the mobilization of seasalts with a net accumulation during summer and winter, and net release during the autumn and spring, is related to hydrological regime characteristic of these temperate regions.

During the winter months depositions of sea salts and anthropogenic pollutants accumulate in the snowpack at

Birkenes. At the onset of spring melting, surges with high ionic strength originate from the snowpack due to the preferential leaching of the accumulated ionic load with the first meltwater (Johannessen & Henriksen, 1978) (cf. Sullivan et al., 1987b).
During dry periods in the summer an accumulation of seasalts is caused by aerosol sea-spray adsorbed on surfaces and evapotranspiration. These pools of salts may build up in the tree canopies, brush vegetation (Horntvedt & Joranger, 1976) and organic soils (Vogt et al., 1989).

Brække (1980), reported an autumn maxima in acidity in the runoff from the barren rock and mineral soil in Birkenes. He ascribed this acidity to hydrochloric acid caused by seasalts.
A summer salt pool in the Birkenes organic layers was observed by Vogt et al. (1989) (Table 7b, Appendix A). The data exhibit large temporal chemical variations from dry to wet conditions in moss and peat layers, due to the outwash of a pool of ions from tree canopies and peat surface layers.
The Birkenes episode studies in the fall of 1987 happened to include a storm event with a high seasalt loading (bulk concentration 862 µM, Mulder et al., 1989). The deposition of the neutral salt caused a instantaneous displacement of H^+ and Al from the exchange matrix (Reuss & Johnson, 1986) in the organic surface horizons. During following events a small increase in electrolyte level was registered deeper in the mineral soils. Due to uncertainty as to what was causing the results obtained in the field, it was realized in retrospect that insufficient samples were collected for definitive statements to be made concerning mineral soil response to a salt pulse.

Organic anions

In the organic soils a build-up of soluble organic anions by mineralization of organic matter may occur during the winter and dry summer period (Conway, 1982; see chap. 3.1.4.). Vogt et al. (op cit.) observed also a high [TOC] in the organic soils during the dry summer of 1988.

Sulphate

Seasonal variation in sulphate loadings is caused by:
(A) Oxidation of sulphide in deep bogs during periods with low water tables in the winter and summer (Brække, 1980).
(B) Accumulation of anthropogenic loadings as for the seasalts (Christophersen & Wright, 1981).
(C) Increased anthropogenic loadings during winter, caused by increased emission due to domestic heating (SFT, 1986).

Following a period of low water table in the summer, Brække (1980) found an increased acidity during the autumn in the water from the valley bottom bog (Langmyra) in Birkenes. This acidity is due to sulphuric acid released by oxidation, during aerobic conditions above the water table.

3.2.8 Modelling.

A mathematical model was constructed to simulate the major variations in Birkenes streamwater chemistry associated with changes in flow (Christophersen et al., 1982; Stone & Seip, 1989a,b). The model consists of two soil reservoirs and a snow reservoir when appropriate. The upper reservoir gives rise to the acidic and aluminium-rich highflow chemistry and is thought to represent upper and acidic soil layers. The lower reservoir, providing the less acidic baseflow chemistry, represents deeper soil horizons were neutralization takes place. Important chemical processes in the upper reservoir include cation exchange (Eqn. 9) and equilibrium with aluminium hydroxide (gibbsite $Al(OH)_3$) (Eqn. 7). In the lower reservoir the gibbsite equilibrium control is also assumed operative together with weathering reactions consuming acidity and releasing base cations. In the original model, Eqn. 8 was used in both soil reservoirs with the same value for K_s. Later, different constants were used for the two reservoirs, and an exponent of 2 has been tried for the upper one. These changes resulted in some improvements, but the agreement with observations are still not satisfactory. The model is based on the mobile anion concept and include sulphate adsorption, cation exchange, aluminium hydroxide equilibrium, and base cation weathering. For most ions the agreement with observed concentrations are good. However, aluminium presents a problem. For example, the model has so far not reproduced the observed high Al-concentrations in the beginning of the snowmelt (Christophersen et al., 1982).

In the original Birkenes model the water routing was not correct in that too much precipitation entered the stream during events (with a chemistry controlled by terrestrial processes), resulting in simulated O^{18} that were not sufficiently damped. Considerable attention has been given to the problem of modelling this damped behaviour of the chemically conservative species together with the pronounced flow-related variability of the chemically active species (Christophersen et al., 1985; Neal et al., 1988; Hooper et al., 1988; Stone and Seip, 1989a,b; Lundquist et al., 1989).

Based on the work by Hooper et al. (1989), Christophersen et al. (1989a) and Neal & Christophersen (1989) developed a least-squares technique to estimate the contributions to the Birkenes stream from a selected set of "endmembers"; EndMember Mixing Analysis (EMMA). The three major soil solution endmembers in Birkenes were considered to be the organic/humic podzol surface layer (O/H), the podzol mineral soil (B/C) and the deep deposits in the valley bottom (VB) (cf. Table 7b in Appendix A). The EMMA model is able to combine the endmembers to fit measured streamwater concentrations of all major anions and cations satisfactorily except calcium. The compositions of the endmembers were as a first approximation set constant in time.

The large seasonal variations in the upper soil reservoir in the Birkenes model (cf. Christophersen et al., 1982; Stone & Seip, 1989a,b), and in the O/H-horizon endmember in the EMMA concept (Christophersen et al., 1989a), as described in chap. 3.2.7, appear to be of significance when modelling the H^+ and Al concentrations in stream water. The mineral soil solution, referred to as the lower soil reservoir in the Birkenes model or B/C and valley bottom (VB) endmembers in EMMA, showed small temporal variations in $[H^+]$ and $[Al^{3+}]$, compared with variations found in stream water, despite sampling under quite different hydrological conditions (Seip et al., 1989a).

4. EXPERIMENTAL MANIPULATIONS

The knowledge of Al-controls and hydrological flowpathes controlling streamflow chemistry in Birkenes is almost entirely based on data collected during natural conditions. The problem with such data is the lack of control of natural variable factors. On the other hand controlled laboratory experiments contains numerous "bugs".
With the approach of an experimental manipulation of in situ study sites I hoped to limit confusing natural variables, without inflicting changes that may not be accounted for (cf. chap. 6.3).
In the following I will present two experimental manipulations studies; a salt addition to two soil plots to study Al-controls with a mobile anion tracer to track water movements, and a acid addition in a streambed during stable baseflow conditions to qualitatively control the existence of an Al and Ca pool on the streambed substrate.
But first I will describe procedures of sample treatment concerning both studies.

4.1 Sample treatment

To monitor the fluctuations in the Al concentration in natural water it is necessary to minimize storage time and to keep ambient temperature (usually 5-10 °C). An on-site laboratory for immediate processing was therefore set up. Soil solution samples were collected and transported to the field laboratory. For each lysimeter one specific glass-bottle was used continuously to avoid contamination. After immediate processing the remaining solutions were stored in separate clean polyethylene 250 ml bottles (ref. cleansing, Andersen, 1989). Stream samples were collected in clean polyethylene 1000 ml bottles after repetitive rinsing and conditioning with brook water, and transported to the field laboratory.

Immediate processing

Immediate processing in the on-site laboratory consisted of determining pH, temperature, conductivity, UV-absorption (for Total Organic Carbon, TOC, estimation), and fractionation and determination of monomeric aluminium species. Due to small sample volume (<300ml), dilution prior to aluminium fractionation was necessary on the majority of samples collected. The dilution factor is presented together with the data in Appendix B and C, and the scheme used on the basis of sampling volume is presented in Table 8 in Appendix A.
pH was measured potentiometrically using an Orion SA 250 field pH meter with an automatic temperature compensator (ATC), and a Ross Orion glass combination electrode (81-01-SC) especially designed for dilute waters (McQuaker et al., 1983).
Temperature corrected specific conductivity and temperature measurements were conducted using a Wiss. Techn. Werkstatten (WTW) LF-91 Ohm-meter with a WTW KLE 1/T electrode. TOC was

determined by UV-absorbency at 254 nm (Schnitzer & Khan, 1972), with a Shimadzu (UV-120-02) spectrophotometer; calibration curves were constructed from selected samples analyzed by persulphate oxidation (Menzel & Vaccaro, 1964) with IR spectroscopy of the released CO_2 using an Astro Model 1850 carbon analyzer (stream: $r^2 = 0.92$ n = 28, soil: $r^2 = 0.99$ n = 13).
Aluminium fractionation measurements followed the procedure outlined by Driscoll (1980) which involves separation into labile (Al_i) (aquo, OH, F, and SO_4 inorganic complexes) and non-labile (Al_o) (mainly organically complexed) monomeric aluminium. Fractionation was accomplished using the Barnes/Driscoll method (Barnes, 1975; Driscoll, 1980) of pH adjusted Amberlite IR-120 column exchange and monomeric aluminium complexation with 8-hydroxyquinoline, followed by extraction into methylisobutyl ketone (MIBK) at 8.3 (Andersen, 1989). The operationally defined labile monomeric aluminium (Al_i) constitutes the difference between a total sample (Al_a) and an ion exchanged sample (Al_o). The MIBK extracts were measured photometrically and corrected for iron interference. This method has been shown to be free of additional significant interferences (Sullivan et al., 1986). Accuracy is good with a standard deviation of replicate analyses (STD) approximately 1% (Sullivan et al., 1987c). The method precision is treated in chap. 6.3.1.

Full analysis

Selected samples were analyzed for Cl, SO_4, NO_3, Ca, Mg, Na and K and Total-F. Bromide was analyzed in samples from the salt addition experiment; [Cl] determination in the salt addition experiment was conducted but data proved invalid due to interference with bromide. In some cases limited soil solution sample volume restricted the number of parameters obtained.
Sulphate was determined turbidimetrically using an auto-analyzer. The sulphate is precipitated by BaCl but the precipitated $BaSO_4$ is kept in suspension by gelatin and measured photometrically at 400 nm. For nitrate analysis a Flow Injection Analysis method was used were the nitrate is reduced to nitrite. The nitrite reacts with sulfanilamide to give a diazonium salt. The nitrite concentration is determined photometrically by adding Naftylendiammoniumdildorid; a red complex at 520 nm.
Cations were determined by Inductive Coupled Plasma Emission Spectroscopy. Total fluoride was measured using an Orion Expandable Ion-Analyzer (EA 920) with an Orion solid-state fluoride selective electrode after addition of 10% TISAB III buffer to the sample (Andersen, 1989; Orion, 1982). Bromide was analyzed by ion chromatography (Waters ILC1).

4.2 Salt addition to soil

In the autumn of 1988 NaBr was added in situ to two 4 m^2 natural soil plots, a podzol profile and a soligenous peat. These are the two major soil types in the Birkenes catchment (covering 79% and 17% respectively, cf. chap. 3.2.3.) and are considered to affect surface water chemistry during high flow.

The soil solution chemistry in the different horizons was monitored by means of ceramic cup lysimeters using a variable vacuum less than 50 kPa.
We used the bromide concentration as an accurate measure of the amount of salt in the soil solution and the soil solution movement. Both chloride and bromide are suitable as water tracers in Birkenes soils, but I decided to use NaBr since the natural background of Br^- is below the detection limit. The specific conductivity of soil solutions is used as an indicative substitute parameter where bromide concentrations were lacking.
Based on the achieved data and earlier studies I discuss Al-controlling mechanisms during highly varying chemical conditions in the different compartments of the soil profile. I follow the soil solution movement as bromide was transported between these compartments.
Special attention is also given to the Total Organic Carbon (TOC) variations.

4.2.1 Site description and instrumentation

Two adjacent sites, on the southeast facing slopes up from the main brook (Fig. 1) were selected, a podzol acid brown earth profile (Plot D 1) and a soligenous peat layer with a sandy layer at the bottom (Plot D 3) (Mulder et al., 1989).
The sites were instrumented with ceramic cup suction lysimeters for soil solution sampling (655X1-B1M3, Soil Moisture Corp.,Santa Barbara,CA)) using a non constant tension of max. 50 kPa.
See Table 7a and b in Appendix A for soil and soil solution chemical data, and Table 9 in Appendix A for description on lysimeter placing.
Tensiometers for monitoring the soil water potential were installed but failed prior to the field season due to software error and will not be further discussed in this thesis.

The Podzol profile

The podzol profile studied is situated on a gentle slope. It is 50 cm deep, with a 10 cm thick organic layer and a 13 cm deep E-horizon.
Representative soil samples have been collected in close vicinity of the plot (Frank, 1980; Mulder, et al., 1989). The organic deposits have the lowest pH(H_2O) (3.7) but highest CEC and base saturation of the profile. The E-horizon has a loss on ignition of only 3%. The illuvial horizon contains more organic deposits (loss on ignition of 6-10%) giving raise to

higher CEC values (60 mmol kg-1). The pH(H_2O) of the mineral soil increases with depth from 4.0-4.2 in the E-horizon to 4.7-5.1 in the B-horizon.
In the summer of 1987 this plot was equipped with 6 ceramic cups. In the O/H-horizon cup lysimeter 10 is situated 2 cm down in the partly decomposed material. Two cup lysimeters, CL11 and CL12, are placed in the eluvial horizon. These are situated 13 and 12 cm respectively below the O/H-horizon cup, or 5 and 4 cm down in the mineral soil. Three lysimeters are placed in the B-horizon. Cup lysimeter 13 is situated 17 cm down in the mineral soil in a layer that contains illuvial organic matter (Bhs). Cup lysimeter 14 is placed in the horizon that contains diffuse accumulations of illuvial iron (Bs). In the bottom of the profile, partly in Bs and parent material (C), cup lysimeter 15 is installed at 32 cm depth (8 cm above bed-rock).

The Peat profile

The peat profile is situated in a pocket on the slope. It consists mainly of 50 cm deep peat with a 2 cm sandy layer at the bottom overlying the Biotite-granitic bedrock.
In lack of relevant data for soil chemical characteristics of the peat profile we may apply the results obtained from the top layer of the deep bogs in the valley bottom. These results show that the soiligen bogs are more acidic than the mineral soils. Furthermore the bog is extremely high in exchangeable Al, whereas exchangeable protons are reduced.
In the spring of 1988 3 ceramic cups, as used at plot D 1, were installed. Cup lysimeter 21 is installed 5 cm below the surface in the partly decomposed organic matter (root layer). Cup 22 is situated 20 cm deeper still in the organic peat, though here the organic matter is completely fermented. In the bottom of the profile 1 cm in the 2 cm deep mineral layer cup 23 is located.
The pF curves constructed by Hauhs (1988) reveal the general peat picture of linear increase in interstitial soil water content with decreasing pF. 27 w/w % water was left at pF 4.25 while 83 % remained at pF 0.75

4.2.2 Field study

100 litres of 5.0 mM solutions of NaBr were prepared and added to the plots by use of conventional watering cans. This procedure was chosen due to its handling ease and good spreading ability. 10 litres were applied over each plot every half hour, starting at 10.15 hr. on Oct. 14, for a total of 5 times (completed at 12.15 hr.). This corresponds to an overall addition of 12.5 mm of 5.0 mM NaBr, amounting to 62.5 meq m^{-2}, over a 2 hour period.
From the point of sodium bromide addition (Time = 0) the soil solution was sampled and analyzed every second hour if enough soil solution (≥200 ml) had been collected by the lysimeters. When the variation in soil solution composition decreased the sampling frequency was also decreased gradually; at the end of the day following NaBr addition, samples with enough volume

were collected only every half day. From day 4 to 7 only daily samples were collected and were sampling still was possible (i.e. soil water suction < applied tension, see chap. 5.1) also a sample at day 9 was collected. On the evening of day 12 an 30 mm event set in and intensive monitoring was re-initiated until the soil solution composition stabilized again in the evening of the next day. Samples were further collected every half day, until the field study was completed on day 14. Additional samples were then collected after the subsequent consecutive events on the day 27 and day 35.

4.3 Acid addition to stream

Four acidification experiments at different stream locations just outside the Birkenes catchment was conducted. The first in the autumn of 1987 during high flow and three during a low runoff period in the summer of 1988. These localities comprised different types of substrate (moss, sand, gravel). 5 or 20 meters downstream grab samples were collected of brook water and examined for released Al or base cations from a conceivable streambed reservoir.
See Table 12 in Appendix A for detailed site description.

4.3.1 Instrumentation

At each location a weir was installed at the head of the stream stretch to be acidified. Stream water was led through a plastic tubing into a 10 L. plastic mixing chamber. A peristaltic pump was set up to add 0.125 M sulphuric acid to the stream water inside the plastic tubing. A pH meter (cf. chap. 4.1) was placed in the mixing chamber. The pH was reduced down to 4.0 - 4.2 in the stream water by means of the course setting of the peristaltic pump (based on calculations) and adjustments according to measured pH in the mixing chamber. Great effort was made to assure that no stream water of pH<4.0 made contact with streambed sediments. A conductivity meter was set to record in-stream variations of ion activity at the down stream sampling locations. Samples were initially collected manually. During stable chemical conditions the sampling was conducted by an auto sampler (Maning, S-4400 Portable Discrete Sampler).

4.3.2 Field study

The field studies were conducted over two periods. The first study was held during thoroughly wet conditions on the 25 Oct. 1987, exercises 2-4 were performed during extremely low base flow conditions from 21 to 25 of June, 1988. Sampling intensity was set according to changes in streamwater conductivity at the sampling location. Typical frequency was every other minute during stream increase in ion activity down to once every 7.5 hours at end of monitoring period.
While exercise 1 was only conducted for 5 hours, exercise 2 to 4 were continued for about 20 hours.

5.0 RESULTS

The data from the salt addition and acid addition experiments are presented in Appendix B and C respectively.

5.1 Salt addition

A concept based on the actual soil solution movement through mineral and organic soil pores (cf. Brustad & Njøs, 1980; Brække, 1980) is applied to describe the hydrology during the experiment.
Two soil water classes are discriminated on the basis of soil pore diameter (d) to describe soil solution movement and chemistry; large pore flow ($d \geq 30$ µm) and small pore flow (6 µm $< d <$ 30 µm). This pore size distinction was selected on the basis of previous work (Brustad & Njøs, op cit.) though the lower limit is slightly adjusted to coincide with the range of pore size water that theoretically may be sampled by the lysimeters. The upper limit is defined by pF_2 (field capacity) were pores of 30 µm still hold water.
Large pore water may move fast through the soil when the soil moisture is at or above its field capacity. The large pores may be created by dead roots or coarse material in the upper parts of the soil profile. The water has little contact with the soil surface resulting in possible non-equilibrium transport. This flow permits fast transport and a low degree of dilution when the soil water content is below the field capacity (i.e. large pores are drained).
Small pore flow constitutes soil solution in close contact with the matrix and the DDL, and is therefore presumably in approximate equilibrium with the matrix. The lower soil pore diameter is operationally defined by the tension set on the lysimeters; max tension suction = 50 kPa ≈ suction from a 500 cm water column, or pF = 2.7. At pF = 2.7 only the pores of 6 µm and smaller contain water. Water flow through small pores occurs due to gradients in soil water pressure. Small pores are common in fine soil texture, organic deposits and compact soil. The soil solution moving in small pores becomes highly mixed with the resident small pore solution.

The moisture content of the soil is an hydrological parameter which was missing due to instrumental failure. The sampling efficiency of the cup lysimeters was used as a indication of the prevailing soil hydrological conditions. Dry conditions are expressed by no water sampling and indicate empty large and small pores at the applied soil water pressure (50 kPa) (cf. chap. 6.1.1). "Wet soil" is used to characterize soils that give difficult sampling (less than 350 ml/day). This situation illustrates a soil water content less than the field capacity. It is one of empty large pores, but with soil solution present in small pores ($d \geq 6$ µm). The value of 350 ml/day is empirically chosen on the basis of the relation between sampling efficiency and water potential measured at the plots during the summer of 1988 (Andersen, 1989). When the soil moisture is above the field capacity the sampling was efficient (more than 350 ml/day). Now the large pores (d ≥ 30 µm) may become filled and the soil water suction is zero. At supersaturation the soil profile was discharging large volumes of soil water.

The antecedent hydrological conditions were generally wet, with a 15.9 mm precipitation event on the preceding day (pH = 4.46). Just prior to and during the salt addition 1.3 mm of highly acid rain (pH = 3.72) precipitated. A minor acid drizzle (0.7 mm) after 7 days without rain is not considered sufficient to be of significance nor to penetrate the soil. 28 mm rain of around average pH (22.1 mm of pH = 4.46 and 6 mm of pH = 4.95, avg.pH = 4.5) precipitated on day 12 and 13 (Table 11, Appendix A) (NILU, unpublished data).

5.1.1 The Podzol profile

Variations in concentrations of Br^- in time and depth for the podzol profile are given in the 3-dimensional Fig. 4. Variations in time of TOC, $[Al^{3+}]$ and $[H^+]$ in cup lysimeter 10 to 15 are given in Figs. 5 to 10, respectively. Statistical chemical and physical relations are listed in Table 10a and c in Appendix A.

General remarks

Prior to the NaBr addition the podzol profile showed the expected increase in $[Al^{3+}]$ and decrease in $[H^+]$ with depth, cf. chap. 3.2.5. After the salt addition, the $[Al^{3+}]$ was generally highest in the E-horizon (>100 µM).
The $[H^+]$ is well correlated with $[Na^+]$, Σ[Base Cations] and $[Br^-]$. $[Na^+]$ increased as may be expected with increasing bromide concentrations, though due to consumption by ion exchange a good correlation is disturbed. The fluoride concentration has a linear correlation to [Al] and $[Br^-]$; Al^{3+} regression calculations with F-tot yield r^2 values of 0.86 for the O/H horizon and 0.91 for the E horizon, though no correlation was found in the B/C horizon. Calculated free fluoride is an insignificant part of [F-tot]. In average the fluoride complexes account for 36% of the $[Al_i]$ in the O/H horizon, and from 12 to 15 % in the other horizons. The total organic carbon (TOC) in soil solution was permanently highest in the O/H-horizon and lowest in the Bhs-layer. High concentrations of TOC and sulphate are only observed during low concentrations of cations, though no good correlation was found. The $[Al_o]$ follows the $[Al_i]$ at high Al concentrations. At low Al concentrations Al_o appears also to be controlled by TOC. Nitrate is generally low or below detection limit (7.1 µeq/L) except in the organic horizon.
The soil temperature in the profiles during the field season varied between 2.5 - 12 °C, with an average temperature of 8.1 °C.

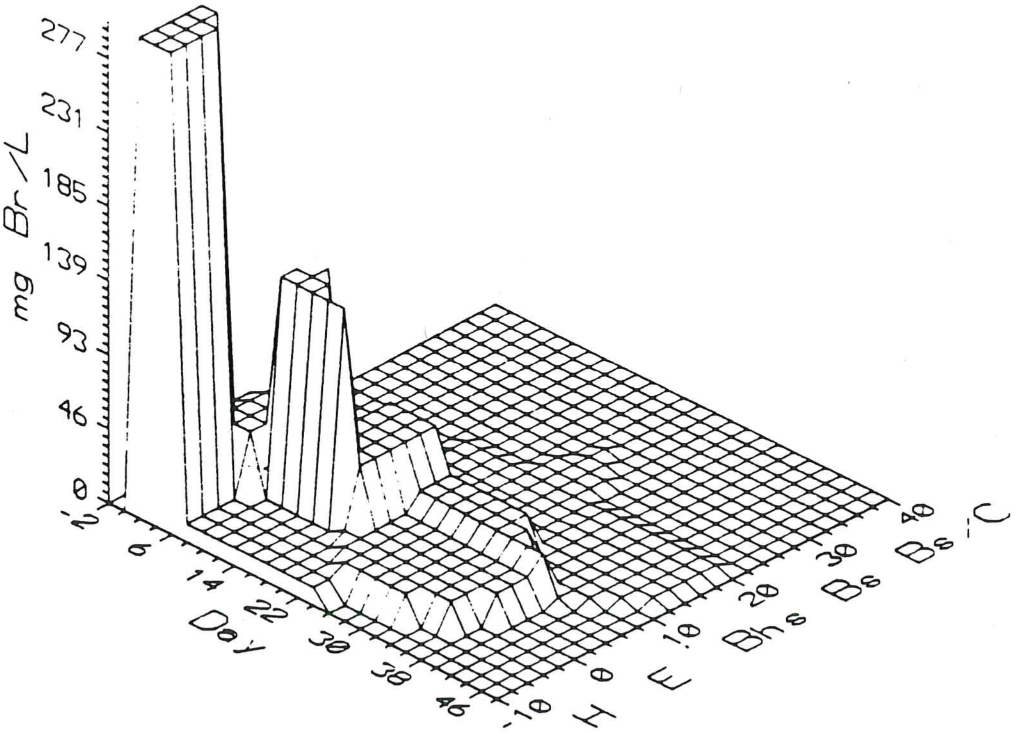

Figure 4. 3-dim. plot of soil water bromide vs. time and the sampling location at the podzol profile. The plot is based on 18 data points and smoothed slightly.

O/H-horizon

The lysimeter 2 cm down in the organic horizon gave an almost immediate response to the NaBr addition. The first sample after the salt was added contained 3.75 mM Br- documenting an initial 25 % dilution of the sodium bromide pulse. Accompanying the bromide a dramatic increase in $[H^+]$ occurred (282 µM). Once the salt addition ceased the pulse became more diluted but stabilized at pH ≈ 3.9. At the onset of the day 12 and 13 event the salt pulse is flushed out from the depth of the O/H-horizon lysimeter and the [Br-] was depleted down to 0.15 mM. Aluminium was found in varying, though moderate, amounts, with initial values of Al_i up to 24 µM. When the soil became wet after the event on days 12 and 13, there was a slight increase in $[H^+]$, but essentially no change in $[Al^{3+}]$.

pAl^{3+} (the negative logarithm to the Al^{3+} activity) and pH were poorly correlated ($r^2 = 0.53$), with a gradient of +0.66 (Fig. 11). We calculate an average $pQ = pAl^{3+}-3pH = -7.11$, but the standard deviation (STD) was high (1.19); the pQ values decrease with increasing pH from -5.62 during the salt pulse to -9.17 during the day 12 event (Fig. 12).
The sulphate and nitrate vary greatly, from 218 µeq/L down to 25 µeq/L and from 228 µeq/L down to 29 µeq/L respectively, low concentrations were experienced during high electrolyte levels (high specific conductivity) or in highly diluted samples. TOC varied considerably with low values during the salt pulse and with high concentrations during the following event.

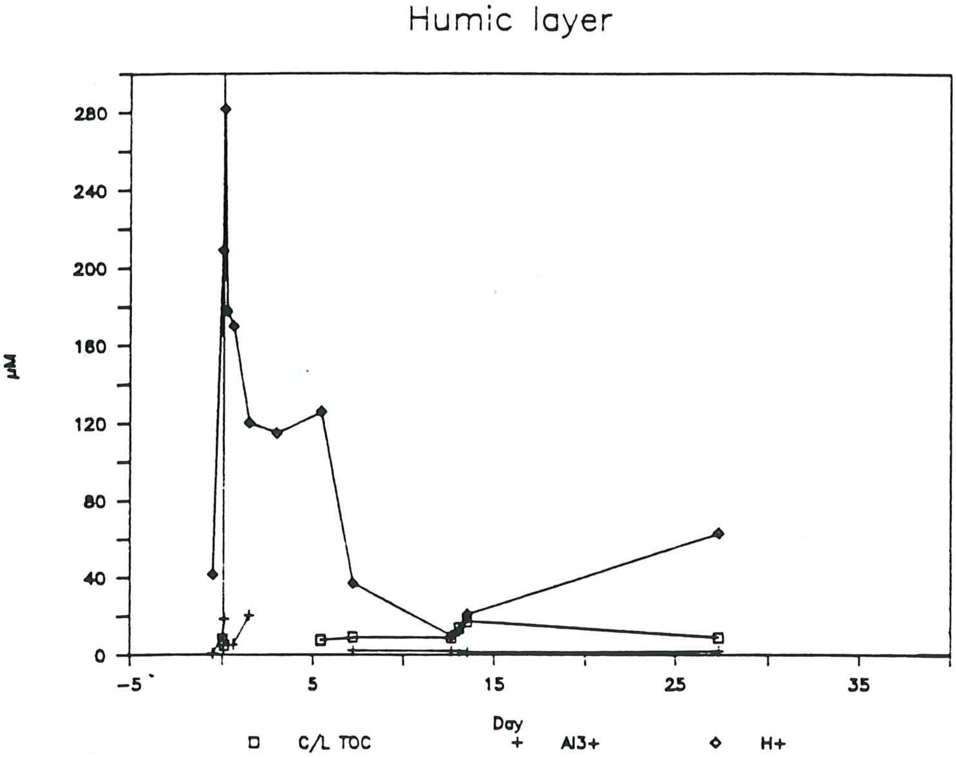

Figure 5. Total organic carbon, [Al^{3+}] and [H^+] vs. time at the cup lysimeter 10 in the O/H-horizon of the podzol profile. TOC is given as µM Carbon.

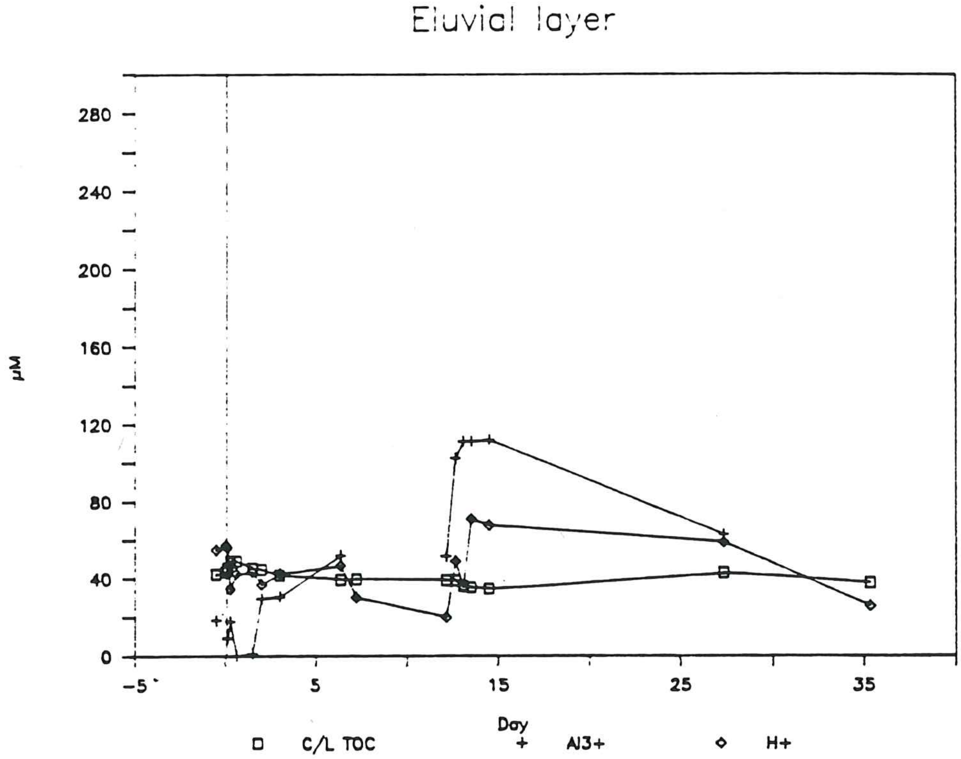

Figure 6. Total organic carbon, [Al^{3+}] and [H^+] vs. time at the cup lysimeter 11 in the E-horizon of the podzol profile. TOC is given as µM Carbon.

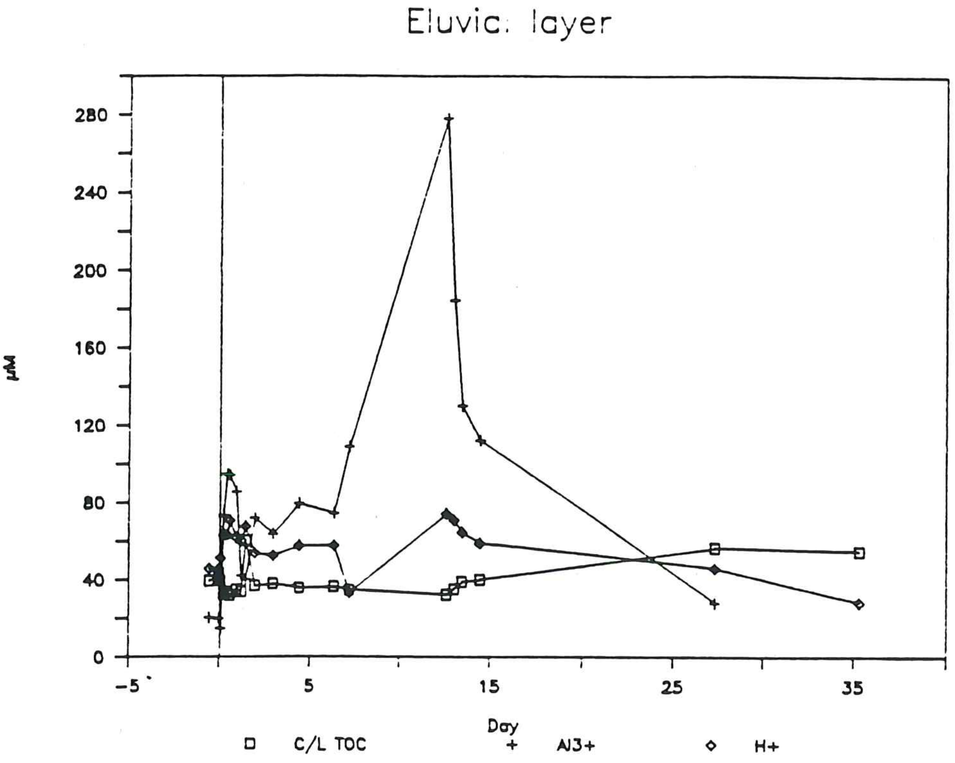

Figure 7. Total organic carbon, [Al^{3+}] and [H^+] vs. time at the cup lysimeter 12 in the E-horizon of the podzol profile. TOC is given as µM Carbon.

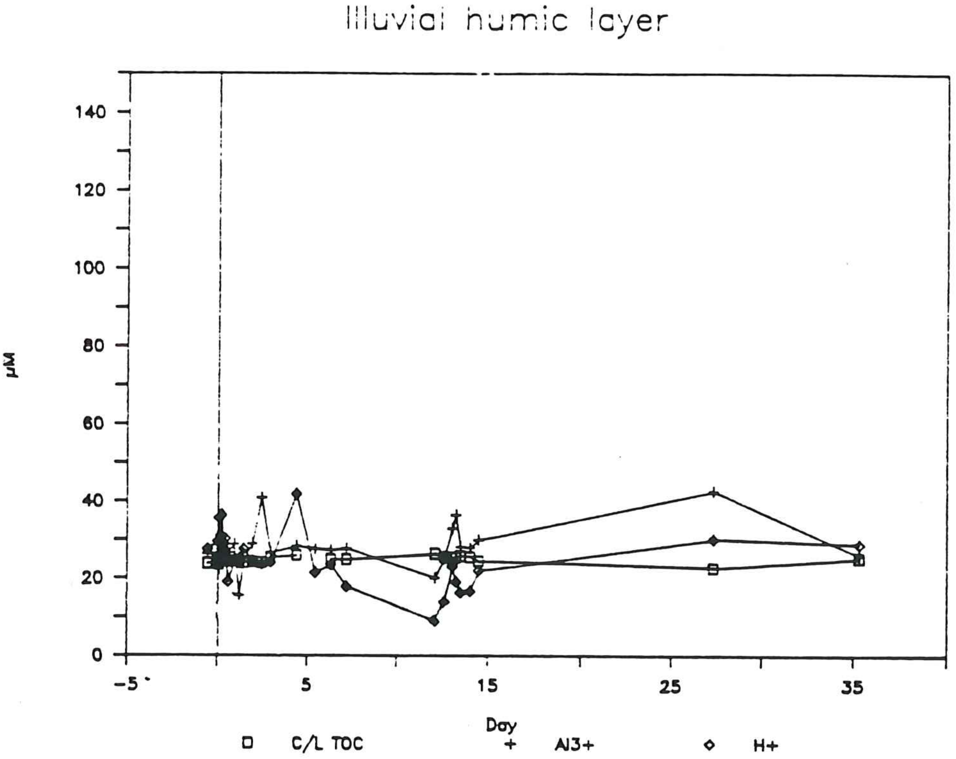

Figure 8. Total organic carbon, [Al^{3+}] and [H^+] vs. time at the cup lysimeter 13 in the Bhs-horizon of the podzol profile. TOC is given as µM Carbon.

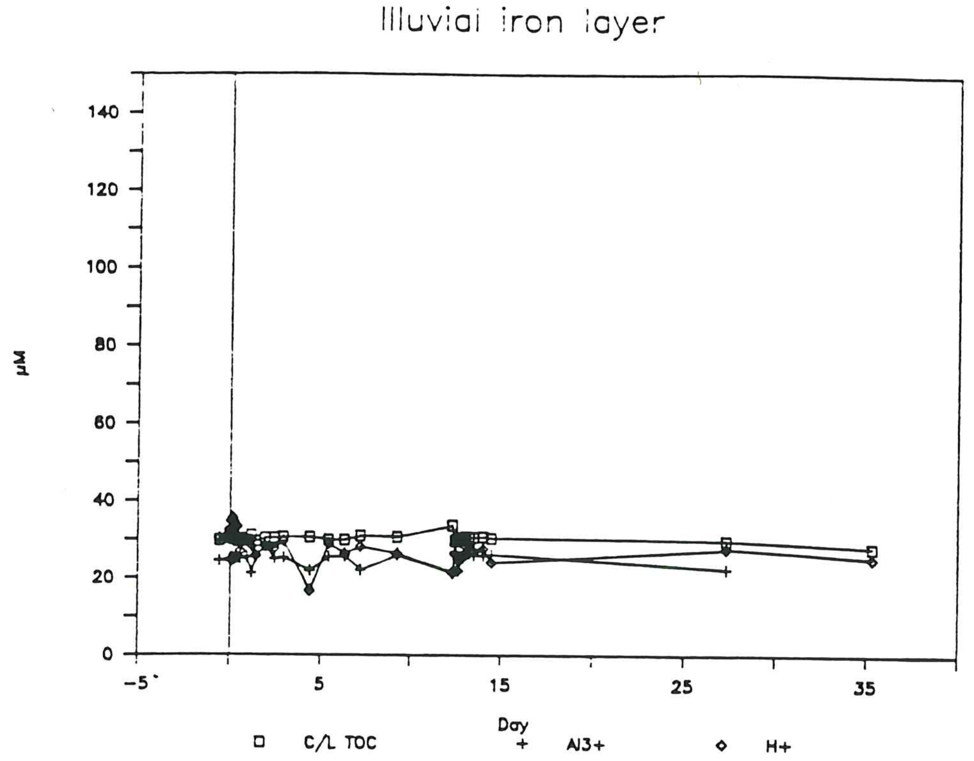

Figure 9. Total organic carbon, [Al^{3+}] and [H^{+}] vs. time at the cup lysimeter 14 in the Bs-horizon of the podzol profile. TOC is given as µM Carbon.

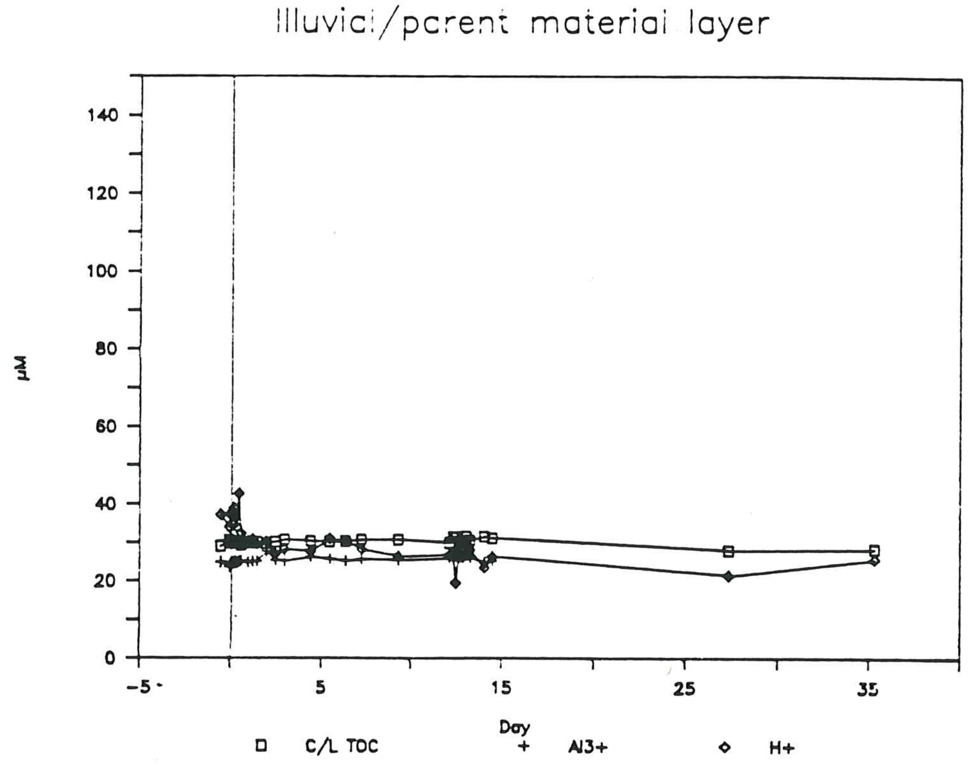

Figure 10. Total organic carbon, [Al^{3+}] and [H^{+}] vs. time at the cup lysimeter 15 in the B/C-horizon of the podzol profile. TOC is given as µM Carbon.

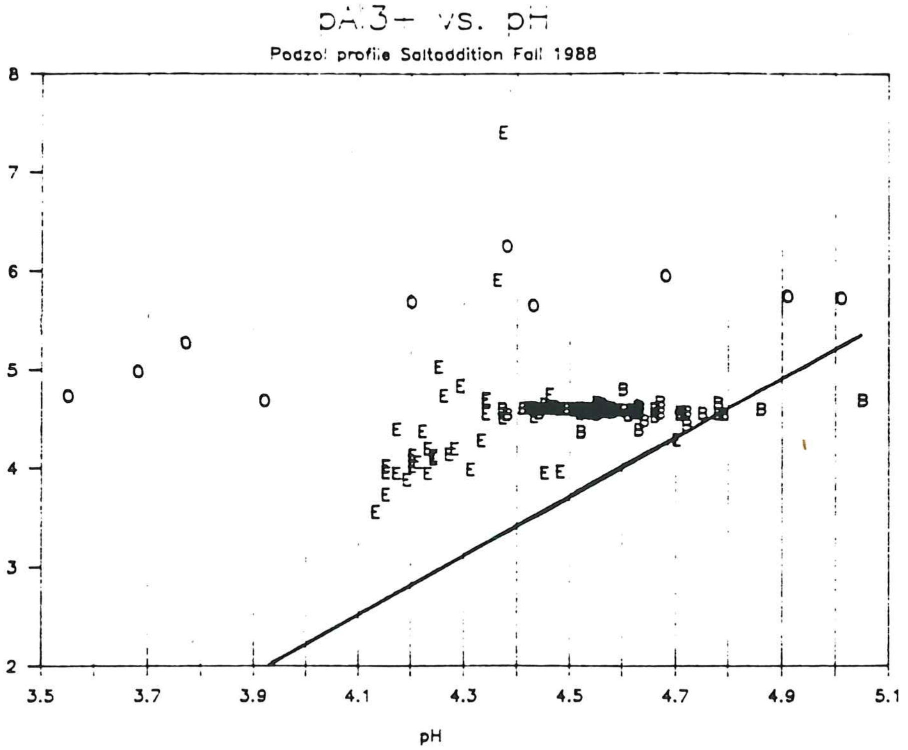

Figure 11. Plot of soil solution pH vs. pAl^{3+} at all sampling location in the podzol profile. Natural Gibbsite solubility line using $pK_s=-9.79$ (temp. corrected to mean temp.=8.1°C) is indicated.

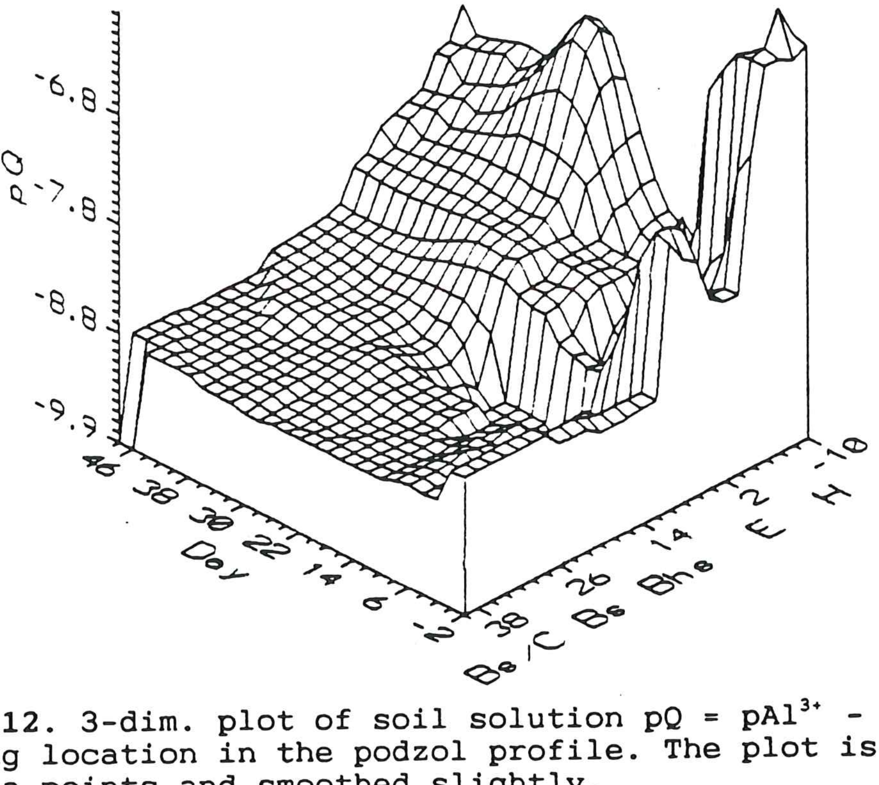

Figure 12. 3-dim. plot of soil solution $pQ = pAl^{3+} - 3pH$ at all sampling location in the podzol profile. The plot is based on 128 data points and smoothed slightly.

E-horizon

The immediate response to the salt addition in the E-horizon was small. The E-horizon water, rich in Al^{3+}, was replaced by O/H-horizon leachate richer in H^+ at both cups upon becoming more unsaturated on day 1. The cup lysimeters situated 4 and 5 cm down in the mineral soil then collected a bromide concentration of only 0.55 and 0.01 mM respectively. In the period from day 1 to day 11 no significant precipitation occurred. The NaBr front seeps down into the soil following the decline in groundwater table, causing elevated ion strength.
At the 28 mm precipitation event on day 12 and 13 (Table 11 Appendix A) the centre of the sodium bromide pulse passed the E-horizon lysimeters and gave an dramatic increase in $[Al^{3+}]$. The $[Al^{3+}]$ in the highest cup increased strongly during the onset of rain and decreased rapidly during the peak runoff, while $[Al^{3+}]$ in the deeper cup followed the stream discharge. The maximum concentrations measured were about 278 µM at the highest cup-lysimeter and 112 µM in the lower. The lack of successful sampling of the highest cup lysimeter prior to the event indicates dry conditions at this location (e.g. soil pores diameter > 6 µm are drained).
According to maximum bromide levels the salt pulse was diluted by a factor of 3 and 8 for the highest and deepest cup respectively upon passage. At the next large episode on day 27 the salt pulse had passed these lysimeters and further dilution was experienced, but now the highest cup was more diluted (1:24) than the lower (1:15).

pAl^{3+} vs. pH from both E-horizon cup lysimeters gave no significant correlation ($r^2 = 0.09$) (Fig. 11). The mean SI was negative with respect even to synthetic gibbsite ($pQ_s = -8.30$, STD = 0.66). During stable hydrological conditions prior to the day 12 event, SI increased to about 0.5 (cf. pQ Fig. 12). Low sulphate concentrations were experienced during high electrolyte levels (high specific conductivity). This is especially evident in the highest E-horizon cup during the day 12 and 13 event where the conductivity reaches a maximum of 323 µS/cm and sulphate is down to below the detection limit (25 µeq/L). High TOC value in the E-horizon soil solution was only observed where Na^+ and Al^{3+} are low.

B-horizon

The impact of the sodium bromide addition in the B-horizon lysimeters was very damped or nearly absent. The B-horizon was initially water saturated and only minor variations in the solution chemistry occurred during the application of the sodium bromide. A small drop in $[H^+]$ on the end of day 0 followed by a drop in $[Al^{3+}]$ on day 1 at cup 13 and 14 coincided with a rapid decline of the groundwater table. Remaining below its field capacity, from day 2 to day 11, $[H^+]$ declined as in the E-horizon. After 12 days the salt pulse had not reached the B-horizon. During the onset of the event on day 12 and 13 a small increase in concentration for all constituents, including bromide, in the Bhs-horizon was registered. The solute concentrations in the B-horizon declined when the horizon started discharging groundwater just prior to maximum discharge in the streams. The sample collected at Bhs-cup on day 27, after an additional 24 mm of rain, showed elevated amounts of all ions. Though remaining low the bromide reaches its maximum levels at this cup on day 35.

pH values ranged from only 4.35 to 5.05 and the pAl^{3+} remained within 4.55 and 4.65 (Fig. 11). Linear regression of pAl^{3+} against pH gave poor correlation for the cup 13 in the Bhs-horizon, improving slightly to a $r^2 = 0.31$ for cup 15 furthest down in the horizon.
Average pQ values are -9.19 in the Bhs layer and increases down in the profile to -8.95 and -8.85 for the Bs and Bs/C layers respectively (Fig. 12). Water sampled from the Bhs cup during unsaturated conditions exhibited decreasing pQ values with time, with the lowest pQ value registered (-10.33) after 12 days. A significant relationship is calculated between sodium and the square of calcium ($r^2 = 0.73$), and calcium and magnesium ($r^2 = 0.70$) both with a slope of 1.
The sulphate concentration drops during the day 12 and 13 event in cup 13. This lysimeter (i.e. # 13) is in the horizon where the humus carrying H^+ and Al_i is illuviated (Bhs), and exhibits the lowest TOC values (3.0 mg C/L) of the profile.

5.1.2 The Peat profile

Variations in concentrations of Br^- in time and depth for the peat profile are given in the 3-dimensional Fig. 13. Variations in time of TOC, $[Al^{3+}]$ and $[H^+]$ in cup lysimeter 21 to 23 are given in Figs. 14 to 16, respectively. Statistical chemical and physical relations are listed in Table 10b and c in Appendix A.

General remarks

Prior to the sodium bromide pulse, the peat profile had a shift towards lower $[H^+]$ and higher $[Al^{3+}]$ down through the soil layers, as in the podzol profile. General features in contrast to the podzol profile were its apparent lower permeability, causing significant correlations of bromide with depth, and higher ability to withhold the high ionic strength soil solution; after 27 days still 0.5 mM bromide was found in the highest peat lysimeter and in the lower cup the highest $[Br^-]$ was measured at the end of the monitoring period after 35 days. In the profile the Of-horizon therefore remained highest in $[H^+]$ and gained in addition the highest [Al] and [Tot-F] values after the salt addition.
The fluoride concentration has a good correlation to [Al] species and $[Br^-]$; Al^{3+} regression calculations with F-tot yield r^2 value of 0.92 for the Of and Oh horizons though r^2 value of only 0.61 was found in the C horizon. Calculated free fluoride is an insignificant part of [F-tot]. In average the fluoride complexes account for 36% of the $[Al_i]$ in the O/H horizon, and from 12 to 15 % in the other horizons.

The $[H^+]$ is positively correlated to all [Al] species, [Tot-F] and $[Br^-]$. Although the $[Na^+]$ correlation with $[H^+]$ was not good (< 99.9% level), it was better than the correlation with the $[Br^-]$. The total fluoride concentration followed $[H^+]$, $[Al^{3+}]$ and $[Br^-]$. [TOC] and $[SO_4^{2-}]$ decreased with depth and increased ionic loading. Nitrate remained generally below the detection limit (7.14 µeq/L). The sum of base cations was positively correlated to all other major constituents, although the correlations were poor.

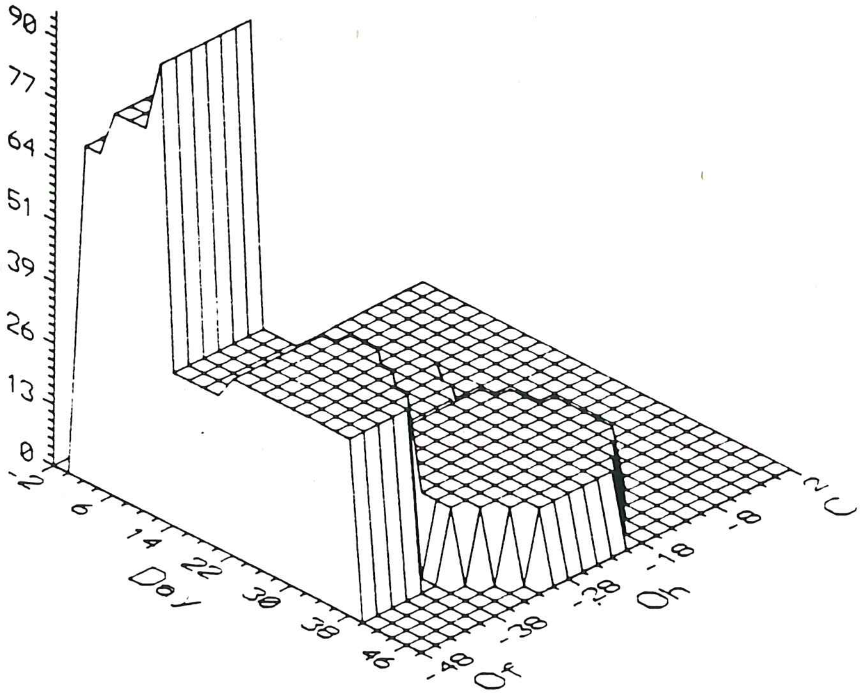

Figure 13. 3-dim. plot of soil water Br^- vs. time and the sampling location at the peat profile. The plot is based on 11 data points and smoothed slightly.

<u>Of-horizon</u>

In the upper lysimeter of the peat profile (5 cm below surface), the salt addition immediately produced an increase in bromide to 0.88 mM. Then, until the onset of the day 12 and 13 event, the bromide concentration increased with only 125 µM. During the day 12 and 13 event the $[Br^-]$ reached the maximum level of 1.19 mM; reflecting a dilution by 1:4 of the original salt solution. During maximum discharge on the day 13 the soil solution became diluted by an additional factor of 3 $[Br^-]$ decreased to 0.46 mM. 27 days after the sodium bromide addition, or after 54 mm of precipitation, the added bromide was diluted only by a factor of 10.

Following the immediate increase in bromide the hydrogen ion and Al^{3+} concentrations increased from 60 to 100 µM and from 18 to 60 µM respectively. During the dry period, prior to the day 12 and 13 event, the $[H^+]$ had a generally decreasing trend, while $[Al^{3+}]$ generally remained stable; Al^{3+} outliers on day 2 and on 7 are considered to caused by contamination or dilution errors due to limited volume.

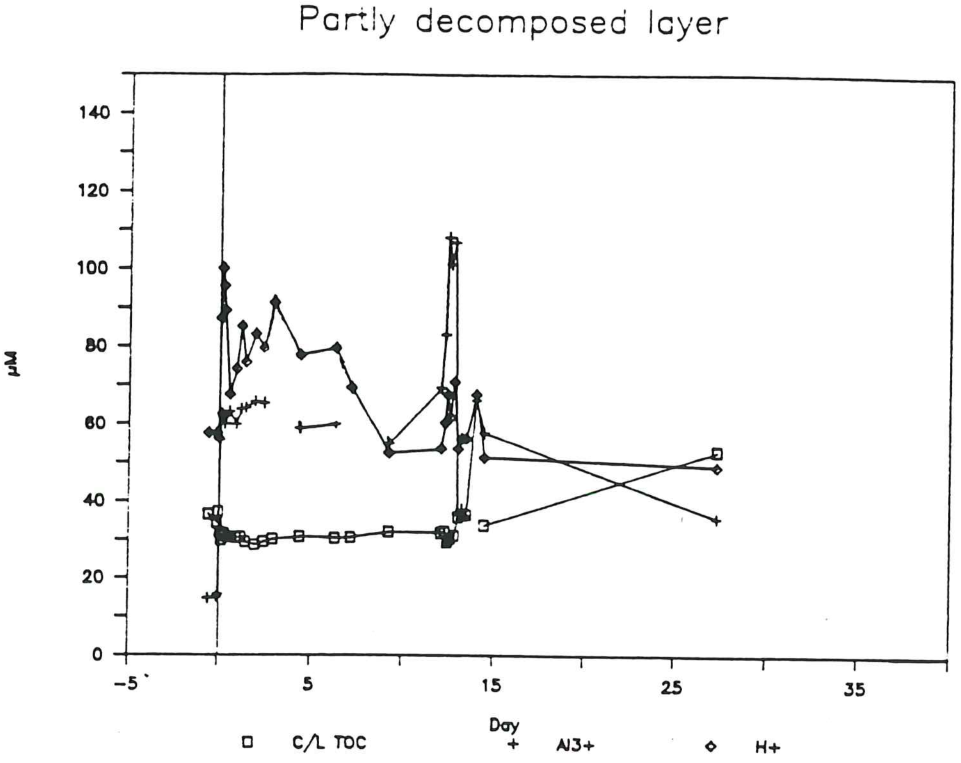

Figure 14. Total organic carbon, [Al^{3+}] and [H^+] vs. time at the cup lysimeter 21 in the Of-horizon of the peat profile. TOC is given as µM Carbon.

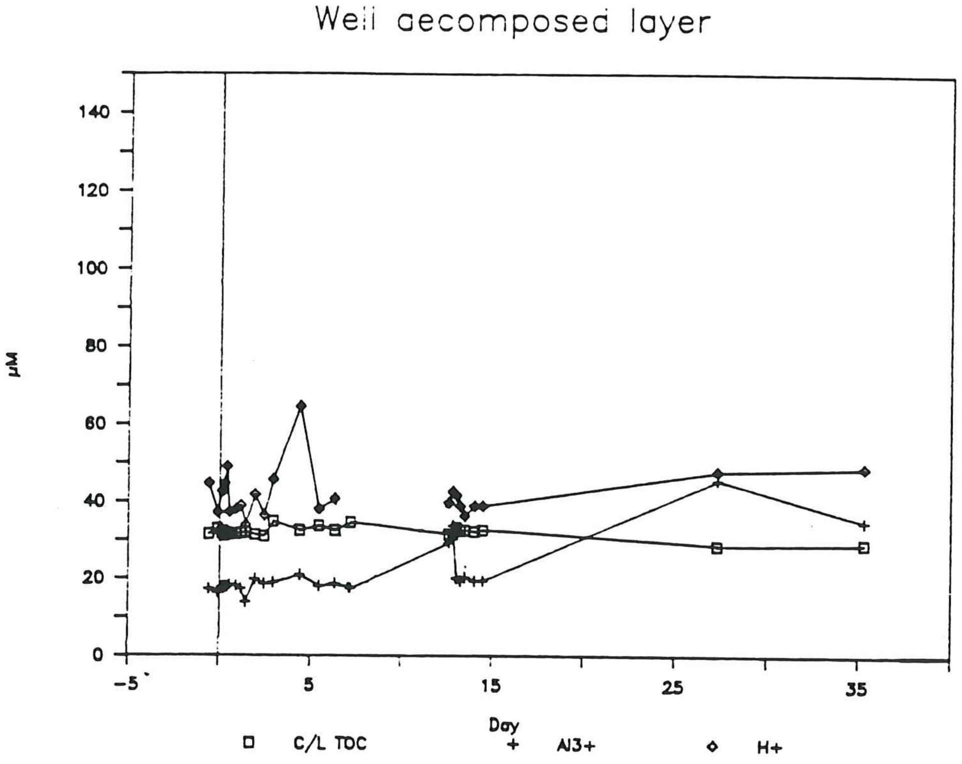

Figure 15. Total organic carbon, [Al^{3+}] and [H^+] vs. time at the cup lysimeter 22 in the Oh-horizon of the peat profile. TOC is given as µM Carbon.

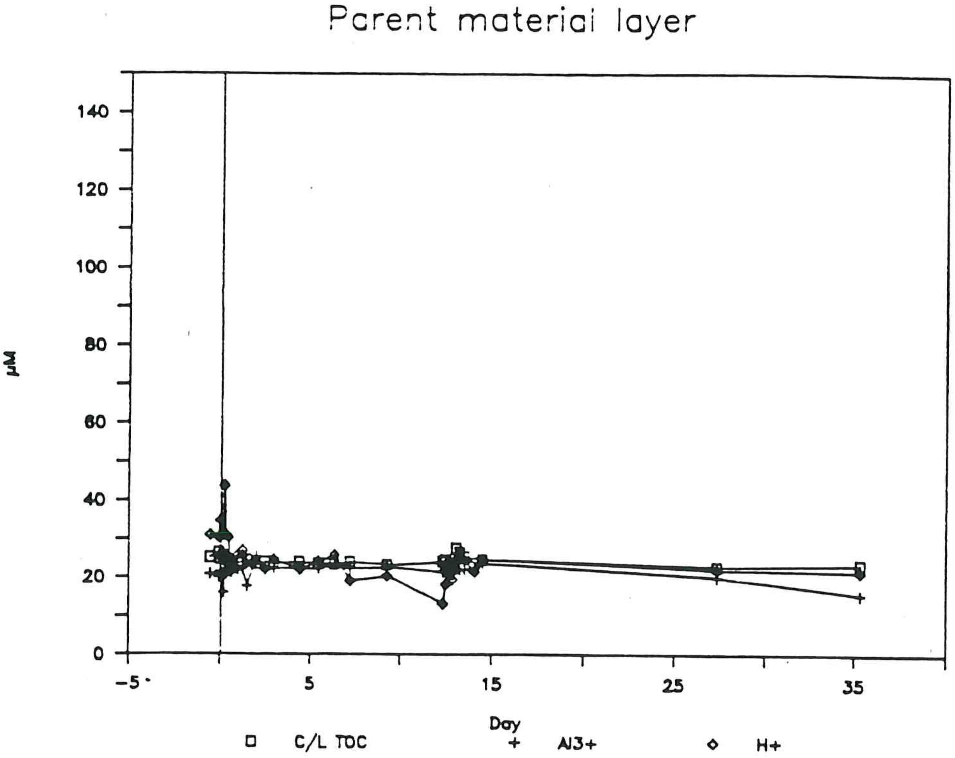

Figure 16. Total organic carbon, [Al^{3+}] and [H^+] vs. time at the cup lysimeter 23 in the C-horizon of the peat profile. TOC is given as µM Carbon.

At the day 12 and 13 event [H^+] increased only slightly both during the onset and decline of the storm, and was diluted during maximum runoff. [Al^{3+}] followed the same pattern though the initial increase was substantial (110 µM).
Samples collected during later episodes exhibit further dilution.

No immediate relation is clear between pH and pAl^{3+} (r^2= 0.13) (Fig. 17). Saturation indices show strong undersaturation for all Al-minerals (for synthetic gibbsite: SI=-1.65) except kaolinite (SI = 0.33). The pQ decreased during the hydrological stable period between day 2 and 11. During the salt addition and during the day 12 and 13 event pQ remained practically stable though at different values (cf. Fig. 18).
Following a decrease in TOC during the initial salt pulse the total organic carbon increased slowly until the electrolyte concentration became diluted during the peak discharge on the day 12 and 13 episode. Then the TOC increased rapidly to higher than background values (6.4 mg C/L) during the following event.

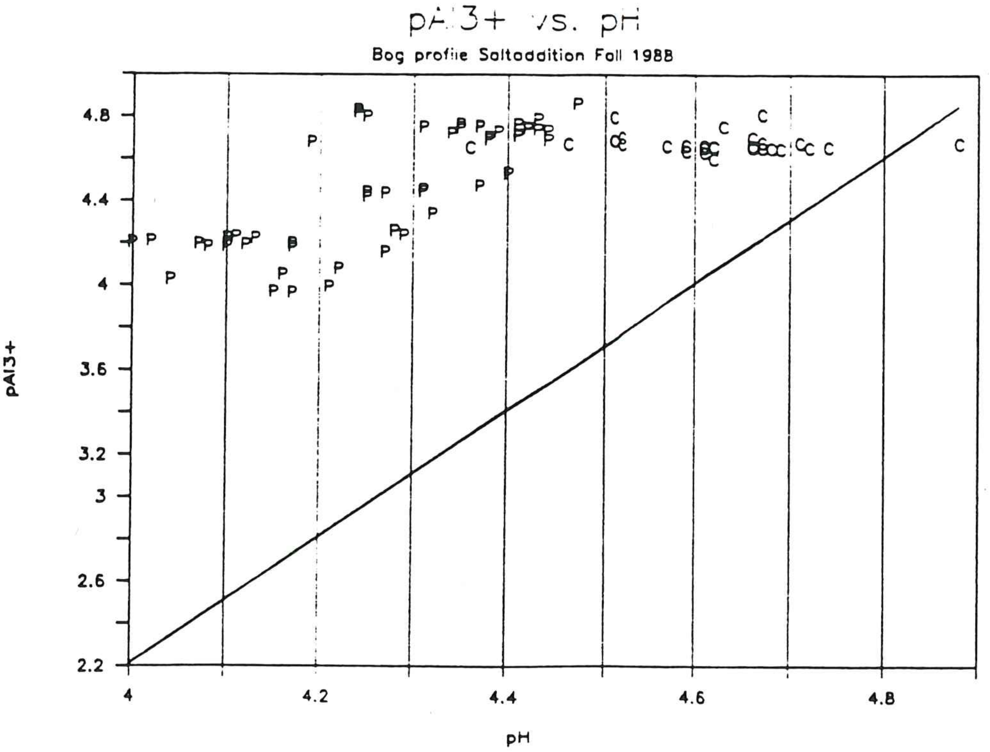

Figure 17. Plot of soil solution pH vs. pAl^{3+} at all sampling location in the peat profile. Natural Gibbsite solubility line using pK_s=-9.79 (temp. corrected to mean temp.=8.1°C) is indicated.

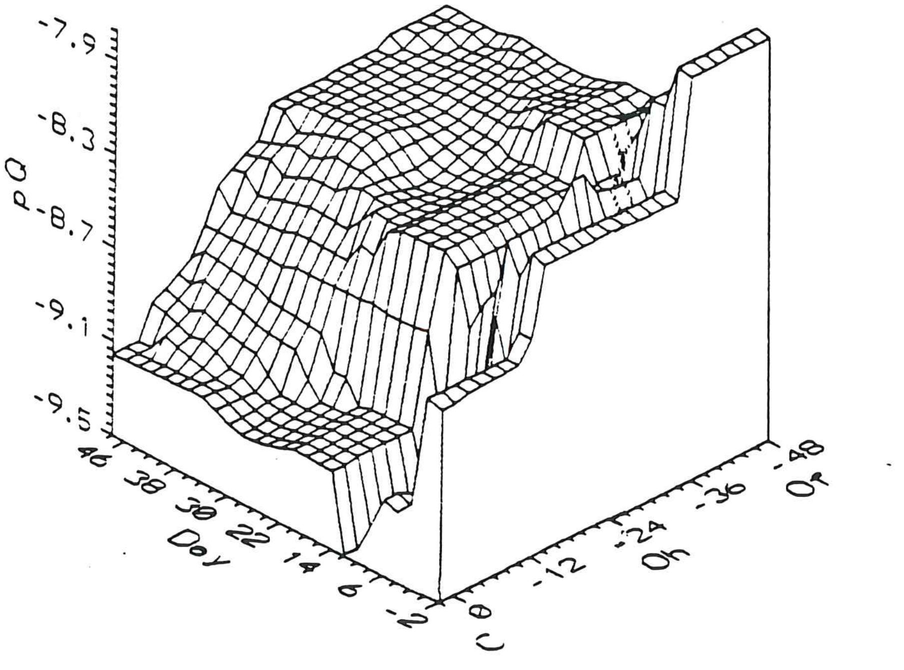

Figure 18. 3-dim. plot of soil solution pQ = pAl^{3+} - 3pH at all sampling location in the peat profile. The plot is based on 84 data points and smoothed slightly.

Oh-horizon

Five days were required for the NaBr pulse to reach the lysimeter located at 25 cm depth in the peat, causing a increase in conductivity of only 10 µS/cm. This occurred when the matrix became unsaturated. During the onset of day 12 and 13 event the bromide concentration increased 0.1 mM before the damped peak also became diluted when the soil became saturated. During later events the ion activity first increased further (i.e. day 27 event), then declined after the day 35. This may imply that the salt pulse maximum passed this lysimeter on day 27. The maximum bromide concentration at this depth in the profile was 0.2 mM. This value was found in the last sample collected and constitutes only 1/30 of the added sodium bromide solution.

When the groundwater table passes the horizon and dilute salt solution arrives, $[H^+]$ initially increases before it decreases to background values in the unsaturated soil. $[Al^{3+}]$ doubled in solution during the hydrological stable period prior to the day 12 and 13 event; a H^+ outlier on day 7 is probably due to analytical error on the small volume sample. During the event $[Al^{3+}]$ increased slightly further, though when the soil became water saturated the $[Al^{3+}]$ decreased to background levels. At the next event a new increase was observed.

No general relation between pH and pAl^{3+} is evident ($r^2=0.10$) (Fig. 17). pQ is relatively constant, and remained close to the level finally reached by the above lysimeter (Fig. 19) reflecting a greater loss in $[H^+]$ than increase in $[Al^{3+}]$ equivalents. Using both the Of- and Oh-horizon significant relationships are calculated between sodium and the square of calcium ($r^2=0.78$), and calcium and magnesium ($r^2=0.95$).

C-horizon

No sodium bromide pulse was experienced in the mineral layer, although an initial decrease in pH was measured approx. 11 hr. after the salt addition was initiated. During the stable conditions prior to the episode on day 12 and 13 the $[H^+]$ declined while $[Ca^{2+}]$ increased. The soil solution is chronically saturated with respect to synthetic gibbsite and oversaturated in regards to kaolinite (avg. SI for synthetic gibbsite = 0.03, and SI for kaolinite was 1.33) (cf. Fig. 18). No significant correlations between cations are found.

5.2 Acid addition

The acidification experiments conducted over only 5 meters of stream (experiment 3 and 4) proved too short to reveal any clear picture of Al release from the streambed. They are therefore not discussed further. Streamwater

chloride, nitrate, total-fluoride, sodium, potassium and magnesium did not respond significantly to the increased acidity. These constituents will therefore not be treated in the following. Sulphate increased according to added sulphuric acid and dilution.
The aluminium species of a grab sample from the mixing chamber, prior to any contact to streambed, has been subtracted from the respective values in the down-stream sample to obtain the "released" (RAl) concentrations of the Al-species. Minor equilibrium shifts within the different Al-species in the stream sample (caused by the increased acidity) are thereby eliminated.
Data from the acidification experiments are presented in Appendix C.

5.2.1 The autumn streambed

The site had experienced daily rain for approx. 2 months. Noteworthy here is also a major salt episode that occurred only 9 days prior to the experiment (Mulder et al., 1989). Frequent acid episodes must therefore have depleted any streambed Al-reservoir. We may therefore not expect any release of Al by the increased acidity. The added acid pulse can therefore be considered as an acid episode during wet conditions. The autumn study was originally a pilot attempt, where the main goal was to get acquainted with the equipment. In retrospect, the achieved data are valuable when used as a baseline reference.

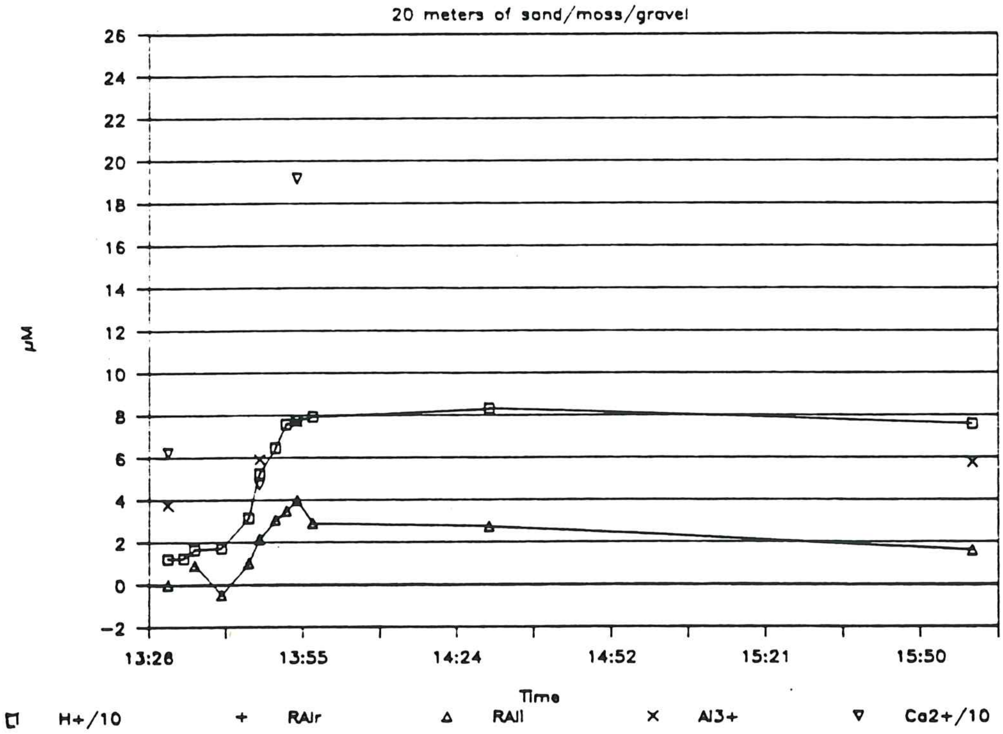

Figure 19. Chemical fluctuations during a autumn streambed acidification.

Chemical fluctuations during the autumn streambed acidification are depicted in Figure 19. Initial [H^+] and [Al_i] were 12.3 and 14.1 µM respectively. I depressed streamwater pH to 4.0 at the weir, nevertheless the pH never decreased below 4.1 at the sampling location 20 m downstream. Labile aluminium increased in soil solution from 14.1 to a maximum of 18.1 µM. Organically complexed aluminium decreased slightly from 4.0 to 3.5 µM; the correlation coefficient of [Al_o] to [H^+] was -0.9. Calcium increased from 125 to 384 µeq/L at the Al_i peak value; a large surplus in ion balance (+257) indicates that the high [Ca^{2+}] in the last sample is probably an analytical error. TOC was stable at 5.5 mg C/L. Al_r was not determined. SI for the gibbsite phases decreased with 2.22 units and even kaolinite became undersaturated.

5.2.2 The summer streambed

The summer study was conducted after 3 weeks of no significant precipitation. Water flow was down to 1 L/sec. Stream pH and [Al_i] was 4.8-4.9 and 6.4-7.8 µM respectively.

Chemical fluctuations during the summer streambed acidification are depicted in Figure 20. I depressed streamwater pH to the typical stormflow value of 4.2 at the weir, though the pH typically had increased again to 4.4 at the sampling location 20 m downstream. RAl_i and RAl_r increased to a stable maximum of 2 and 6 µM respectively. The RAl_i correlation coefficient with [H^+] was 0.9, while [Al_o] with [H^+] gave -0.7 . Calcium increased from 85 to 255 µeq/L just after start; a large surplus in ion balance at the two highest [Ca^{2+}], of +262 and +331 respectively, indicates that these are probably analytical errors. SI for the different gibbsite phases decreased with 1.18 units.

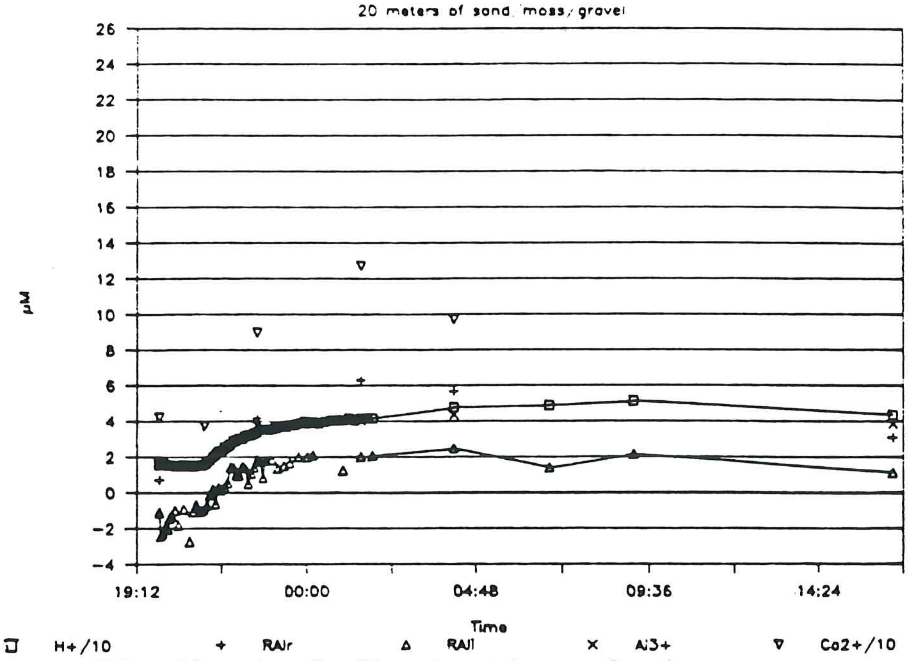

Figure 20. Chemical fluctuations during a summer streambed acidification.

6. DISCUSSION

> *Science itself has a two-sided*
> *one-sidedness*
>
> - Henry A. Bent -

6.1 Salt addition

I will here discuss the data in the light of the salt pulse movement through large and small pores in the soil, and suggested Al-controls in the various horizons.

6.1.1 Hydrology

By following the bromide tracer and other constituents through the soils I hope to verify if the surface flow (i.e. overland flow), sub surface lateral flowpath and the piston flow (i.e. release of soil water suction) are important postulated concepts in the selected soil profiles. Furthermore the discrimination of the large and small pore flowing water is helpful when discussing aluminium mobility controls in the next chapter.

Podzol profile

A direct response to the sodium bromide addition at the lysimeter 2 cm down in the partly decomposed organic horizon indicates a free seepage down in the O/H-horizon at this site. The dilution of the added bromide upon percolation through 2 cm of the O/H-horizon, from 5.0 to 3.75 mM is caused by water sampled prior to the salt reached the cup and by intrinsic soil water. Once the salt addition ceased, the high salt concentration in the podzol O/H-horizon decreased rapidly. This may be due to a surface water flow from higher elevated areas, though factors as further mixing with the solutions stored in smaller pores in the horizon, scattered showers, and/or transport to deeper horizons may be more important. A strong indication of surface flow is the moderate $[Al_i]$ recorded in the soil water and on the exchange complex of organic deposits. This is likely to be attributed to Al-adsorption by mosses and shrubs (Henriksen, et al., 1987) from deeper Al saturated soil solution, forced upward to the surface horizons due to uneven topography. Other factors as plant transpiration larger than precipitation causing an upwards flux in the profile during the growing season, or upwards capillary flow in small pores during dry conditions (Andersen, 1989) are not believed to be important during this study period.

The observed heterogeneity in response to the salt pulse in the E-horizon may indicate a large difference in pore size. The response to the salt pulse by the highest cup corresponds

to a flow rate of at least 3.5 cm/hr. This flow rate implies the use of large pore flow. In the lower lysimeter the added water probably caused a decline in soil water potential, allowing enhanced release of small pore bound water (i.e. piston flow), causing a shift to more neutralized water in the cup (cf. chap. 6.3.2.).
The shift towards typical O/H-horizon soil solution that occurred at E-horizon cups 11 and 12 after 14 and 30 hours respectively, coincides with the horizon becoming unsaturated, suggesting that this could be caused by soil solution in the O/H-horizon which is sucked down through large pores by the descending water columns. The increasing ion strength between day 1 and 11 is likely due to slow gravitational seepage of soil solution.
The poor sampling efficiency at the highest E-horizon cup after 7 days of practically no rain indicates that soil pores with d > 6 µm are drained. The day 12 and 13 precipitation and possibly some overland flow was then free to flush the salt further into the profile. The presence of large pores at the highest cup (suggested previously) then enhances a fast response. The dilution of bromide at this lysimeter was only by a factor of 2 with respect to peak values.
The precipitation gave a typical fast rise in the groundwater table, causing hydrologically supersaturated condition. Then presumably a high velocity flow of Br^- free groundwater through the large pores serves to dilute the soil solution, causing the concentrations to decline rapidly.
The cup situated deeper in the E-horizon appears to be more influenced by small pore transported water causing the salt pulse to be more diluted mainly due to mixing with the resident soil solution. It is also probably the finer soil texture and thereby smaller pores at this lysimeter that caused the delayed initial response and later the reduced ability for flushing.

The B-horizon was initially under saturated soil-water conditions, due to 15.9 mm rainfall on the day prior to the sodium bromide addition. The salt pulse may thereby initially have been inhibited from percolating into this horizon. The small variations observed during the addition of the sodium bromide, may be contributed to minute shifts in soil solution location caused by a piston type effect in the water-logged horizon.
The first hydrological response in the Bhs-horizon to the day 12 and 13 event, causing a minor increase in ion strength, was presumably a large pore flow from the above E-horizon. On the profile becoming saturated a high velocity lateral groundwater flow from the slope above the sodium bromide addition plot served to flush out the salt pulse. This was verified by water discharging out from the earlier dug profile ditch (cf. chap. 6.3.3).
When the groundwater table dropped past cup 13 (Bhs-horizon) the salt pulse followed, presumably by large pore flow from the E-horizon during the next event, causing a small increase of all ions in the sample collected on day 27. Considering the declining conductivity at the end of the monitoring period I

am inclined to believe that the salt pulse had passed this lysimeter at the Bhs-horizon after a total of 35 days. Bromide should have been recorded in the Bs-horizon on day 35 based on extrapolates of perclorating velocity in the E- and Bhs-horizon to the deeper soils. The explanation for this not occurring may be the lack of large pores due to (1) higher content of clay and organic precipitates, (2) more compact soil at deeper soil depth due to decreased biological activity, and (3) inhibited percloration due to a water clogged soil matrix.

The general loss of bromide from the profile without it moving through the B-horizons is a strong indication that soil water transport during high discharge periods mainly occurs through the upper horizons in the podzol profile. The large spatial variability in response and dilution emphasizes the importance of variable pore size flow.

Peat profile

It is evident by the high retention of the salt pulse that the peat is much less permeable for water than the podzol profile. In addition the peat soil has an ability to store larger amounts of water than the coarse mineral soil structure of the podzol profile, causing a initial higher dilution of the added salt.
The poor transport, but large capacity to store water permits the peat to capture the added sodium bromide solution and to restrain it from penetrating the profile. The soil pore size distribution is small, causing a more uniform transport of incoming water. A constant good sampling efficiency indicates that the bog water is slowly depleted by slow seepage during low flow conditions
The larger amounts of Al released to the solution of the Of-horizon than in the O/H-horizon of the podzol profile must have been translocated to this horizon by frequent surface water flow. This is reasonable since the soligenous bogs are formed where soil water flowpaths converge and the water is forced to the surface by a concave topography. Furthermore, due to the nature as a soligenous peat the surface is determined by the general groundwater table level. Surface water runoff is therefore common during high flow.

The hydrological properties of a peat soil may best be depicted as a sponge with high storage capacity and low permeability.

6.1.2 Aluminium chemistry

Previous studies on Al mobilization controls in the Birkenes catchment have concluded that the soil solution data are in general consistent with a cation exchange reactions determining the concentration of inorganic aluminium in the organic soils, while the concentrations may be calculated assuming equilibrium with gibbsite in the mineral soils (Mulder et al., 1989; Andersen, 1989). Furthermore Sullivan et

al. (1986) suggested that the water/soil contact time may play a role when residence time in the mineral soil for certain flowpaths during high flow is short.
I will here try to verify these Al-controls, in the different soil horizons, by use of the collected data obtained during highly varying chemical conditions.

Organic soils

$[H^+]$ is positively correlated to $[Na^+]$ in the organic soils, i.e. O/H-horizon of the podzol profile and the Of- and Oh-horizons of the peat. Coherent with the increase in acidity in the O/H-horizon a depletion of ≈ 1.2 mM Na^+ relative to Br^- has occurred. A minor (1.3 mm) rainfall with pH = 3.72 on the same day as the salt addition can only account for < 18 µM H^+ when mixed with the added solution and intrinsic soil water. Similar trends were found in the organic deposits of the peat. I therefore assume the $[H^+]$ increase in the soil solution with 240 µM in the O/H-horizon and 42 µM in the Of-horizon is due to release from mainly solid humic substances by interactions with the added Na^+. A H^+ exchange in organic soils by neutral salts is also found by several other authors (Rosenqvist, 1978; Krug & Frink, 1983; Bache, 1984; Reuss & Johnsen, 1986). The larger increase in $[H^+]$ in the O/H-horizon than in the peat horizons is explained by practically no consumption H^+ by dissolution of Al-bearing minerals and a relatively limited pool of exchangeable Al (see below).

The SI was negative with respect to all Al-containing minerals both in the O/H- and Of-horizon, except after the salt pulse. This implies that the Al solubility was probably not controlled by a Al-mineral. On the other hand the previous postulated interactions between dissolved species and organic matter, have been shown to give rise to pQ values lower than the pK_s for natural gibbsite (Tipping & Hurley, 1988; Krug & Frink, 1983; Bache, 1984). A cation exchange mechanism as a Al-solubility control is likely considering the high CEC of the organic soil.
The calculated less than cubic relationship between H^+ and Al^{3+}, expected where dissolved Al is controlled by equilibrium reactions with the solid phase, has been shown to be a typical property of acidified soils (Bloom, 1979; Bache, 1974; Richburg & Adams, 1970). Several suggestions for this deviation is found in the literature. These will be treated in Appendix D. Briefly I will here only state that in this data set the apparent increasing solubility with increasing pH may have been due two different factors:
(1) The constraint of cubic relationship in Eqn. 8 applies only to a solubility control with a constant pK_s value (J.Mulder pers. comm.) which is probably not the case for the organic complexity sites over the wide range of pH, pAl^{3+} and ion strength that we observe.
(2) Non equilibrium conditions during the day 12 and 13 event, due to external factors such as high velocity surface flow, and dilution by the precipitation (pH ≈ 5) (see previous chapter), may have caused a negative relationship at pH > 4.6

and even saturated conditions of synthetic gibbsite.
Further support for the cation exchange, controlling solute in the Birkenes organic horizons, follows from the linear relationships between Ca^{2+} and Mg^{2+}, and the squared relationship between Na^+ and Ca^{2+}.

Low $[SO_4^{2-}]$ corresponded generally to high conductivity readings. This may have been caused by SO_4 sorption onto soil sesquioxide surfaces which attain a positive charge (Bolt & Bruggenwert, 1978) at low pH, due to proton absorption. An Al-SO_4-mineral precipitation may be disregarded as a SO_4 activity control since soil solutions remain unsaturated with respect to alunite ($KAl_3(OH)_6(SO_4)_2$) and jurbanite ($Al(OH)SO_4$). Finally the apparent corresponding variations in [TOC] may have some relevance, due to the sulphate bound to the organics.
The peat layer is too thin, and the monitoring period is too short, for reduction and oxidation processes to be significant.

Mineral soil

In the mineral soil, where exchangeable aluminium, solid-phase organically complexed Al and aluminium minerals are present, the H^+ from the organic- and mineral exchange processes may partly be neutralized by the suggested Al-dissolution and/or by exchange again for $Al(OH)^{x+}_{3-x}$ at the cation exchange complexes.

The major salt effect on the eluvial horizon was a strong increase in $[Al^{3+}]$ up to 280 µM.
Although the pQ values vary considerably (STD = 0.66) the mean pQ_s value of -8.30 in the E-horizon suggests a general undersaturation with respect to all Al-hydroxide minerals (avg. SI = -0.78) except kaolinite. The large standard deviation of pQ and poor correlation between pAl^{3+} and pH (r^2 = 0.09) may have been caused both by non-equilibrium large pore flow upon the E-horizon becoming unsaturated (see chap. 6.1.1), and by a shift towards increased control by a slow Al-solubility equilibrium with increased residence time. A slow equilibria reaction was also observed by Bloom et al. (1979) who commented an increasing of the pH-pAl slope with time. Avoiding samples in the eluvial horizon where factors as long residence time or non-equilibrium flow are important (i.e. day 12 to 15) gives a close to cubic relationship between H^+ and Al^{3+} (r^2 = 0.70) with negative saturation indices with respect to $Al(OH)_3$ (pQ_s=-8.55, STD=0.17). The soil solution chemistry in the eluvial layer during this remaining period may primarily be explained by an ion exchange reactions as described by Eqn. 12.

Eqn. 12 $$pAl^{3+} - 2.8pH = - 8.6$$

Slow mineral dissolution reactions cause the pQ_s value to decrease during stable hydrological conditions prior to the day 12 event, giving rise to nearly saturated conditions with respect to natural gibbsite.

Ignoring the same samples as above the only clear relationships among other pairs of cations, indicative for cation exchange equilibrium, was a linearity between Ca^{2+} and Mg^{2+} (r^2 = 0.86, with a slope of ≈ 1).

High sulphate concentrations are only observed in the E-horizon when the concentrations of especially H^+ and Al^{3+} are low. This may be due to the precipitation of sulphate complexes due to the observed oversaturation of alunite ($KAl_3(OH)_6(SO_4)_2$) but a constant undersaturation of Jurbanite ($Al(OH)SO_4$) (average SI of -0.93).

Upon reaching field capacity large pore water from the E-horizon follows the declining groundwater table in to the B-horizon. As in the E-horizon, during the following stable hydrological conditions, a slow consumption of H^+ (shifting pH in the Bhs-horizon from 4.44 to 5.05), while pAl^{3+} remains constant, produces increased SI. In the B-horizon an oversaturated solution with respect to even monocrystalline gibbsite is observed (cf. Table 2 & 3 Appendix A). As described above this may be explained by a change of the Al-solubility control during stable conditions, from a fast ionexchange equilibrium in the initial soil solution from the E-horizon, to an increasing amount of a slower mineral dissolution with increasing resident time. On the other hand an indication for that cation exchange may be an important control for the cations follows from a significant relationships between sodium and the square of calcium (r^2 = 0.73), and calcium and magnesium (r^2 = 0.70) both with the slope of 1.

As for the organic soils the sulphate concentrations are low when $[H^+]$ and $[Al^{3+}]$ are high in all mineral layers. The precipitation of aluminium-sulphate complexes may be a more probable Al/SO_4 solubility control mechanism in the mineral soils since the soil solution was oversaturated for alunite ($KAl_3(OH)_6(SO_4)_2$) and basaluminite ($Al_4(OH)_{10}SO_4$).
An Al solubility control by Jurbanite was not found by Andersen (1989). Soils treated with chloric- and sulphuric acid showed no significant difference in Al-leaching.

In the mineral soil, below the peat, we observed increased pQ values during stable hydrologic periods with stagnant water. This was similar to the deep horizons in the podzol profile. No correlation between cations indicates that there is no support for a cation exchange process as a hydrochemical control. However it is likely that it was slow solubility reactions of Al-hydroxides that produced a saturation with respect to synthetic gibbsite (SI for synthetic gibbsite = 0.03). This indicates again that time may be an important factor.

The dissolved total fluoride concentration was always significantly correlated to Al^{3+} throughout the profiles. Aluminium is strongly complexed by F^- forming a number of soluble species (Table 4, Appendix A); aluminium speciation indicates that practically all fluoride was bound to aluminium. It is therefore possible that fluoride adsorbed on the soil was complexed by the solution Al^{3+} and thereby brought into solution. Considering the poor adsorption of fluoride to the soil it is more likely that it is the mobile fluoride that is complexing adsorbed aluminum. Once combined with Al^{3+} it may increase the mobility of the aluminium by decreasing the concentration of Al-species involved in equilibrium reactions with the soil matrix, and thereby causing a shift to more Al in solution.

6.1.3 Soluble organics

Recent studies (Driscoll et al., 1988; Tipping & Hurley, 1988; Andersen, 1989) have called the attention to the role of soluble organics in buffering the effect of reduced anthropogenic loadings. Important in this work is that the applied concepts are applicable in the different soil systems. I will here contemplate if the observed TOC variations can be explained by the generally accepted concepts.

The TOC was initially low in the O/H-horizon due to (1) flushing the O/H-horizon by a 40 mm storm on the previous day, (2) the biologically dormant period, and (3) a minor (1.3 mm) though acidic (pH = 3.72) precipitation just prior to the salt addition (see below). The initial low values and a further reduction during the salt pulse may be due to enhanced precipitation of the organic solutes. This would primarily be caused by protonation of the functional sites, adsorption to the DDL, and increased complexation by elevated activities of H^+, Na^+ and Al^{3+} respectively, serving to neutralize the net humic charge Z and thereby their repulsion (Hayes & Swift, 1978; Tipping & Hurlay, 1988). During the low ion strength and $[H^+]$ values, on day 12 and 13, TOC concentrations doubled, possibly because the precipitated organic complexes became water soluble again due to increase of the net humic charge by release of mainly Na^+ and some H^+.

The observed negative relation between $[H^+]$ and [TOC], during the salt pulse, were probably caused by the elevated amounts of sodium acting both as an exchange for H^+, increasing the $[H^+]$, and as an adsorbed cation, neutralizing the Z and their repulsion and thereby decreasing the [TOC] due to precipitation (see above) (Tipping & Hurlay, op cit.). During the event on day 12 and 13 the case is the opposite. The decrease in $[H^+]$ during the large increase in [TOC], though contradictory to the acidifying effect of soluble organic substances, is caused by the release of Na^+ instead of H^+.

In the Bhs-horizon the critical insoluble-metal / organic carbon ratio is frequently reached (Bolt & Bruggenwert, 1978). In this horizon the bulk TOC content of the soil solution is therefore illuviated and the water soluble [TOC] values typically drop to about 3 mg C/L.
Microbial oxidation further raises the metal/organic carbon

ratio and enhance this precipitation. Once started, the accumulation process tends to be self-perpetuating, since free oxides formed after oxidation of the organics tend to precipitate perclorating organics in the form of metal chelate Below the lysimeter in the Bhs-horizon I find a small increase in the amounts of TOC. This may be due to this lowered microbial activity in the chronically water saturated horizons (Bolt & Bruggenwert, op cit.).

As discussed for the podzol profile the TOC in the peat profile is to some extent dependent upon the amount of H^+, Na^+, and Al in the soil solution due their effect on the precipitation processes. During the salt pulse TOC amounts correlate negatively with the Al_i in the peat profiles. Correlation with H^+ is not as pronounced, but high [TOC] is generally found were the [H^+] is low. Within each horizon it is in the uppermost organic deposits where the correlation is most pronounced due to larger variation in H^+ and Al-concentrations.
That these correlations are only first approximations is illustrated by the TOC increases during the day 12 episode, even though [Al^{3+}] and [H^+] remain relatively constant. This is, as hypothesized for the podzol profile, probably due to the release of Na^+.

6.2 Acid addition

A contributing cause of the Al-concentration pattern in stream water during acidic episodes, could be mobilization of Al from a reservoir associated with streambed (Henriksen et al.1987, 1988). Norton et al. (1983) restricted the existence of such Al reservoirs to streams buffered by CO_2, and their buildup being mainly due to pH increases associated with CO_2 degassing. These streams must have pH values between 5 and 6, which is high enough for bicarbonate to acts as the main pH buffer, though low enough for significant amounts of Al to be in solution. A further constraint was that the ground water reservoirs must have pH < 5.5 to allow for significant amounts of dissolved Al.
The Birkenes streams are acidic, though during baseflow condition the pH may typically be above 5.0 . The base flow water reservoir is undefined, though recent research (Christophersen et al., 1989a) indicates that the deep bogs in the valley floor, with 5.5 < pH <7.0 (Table 7c), may be a significant source of high-pH seepage water. The qualifications that are needed to allow a buildup of an Al-reservoir in the streambed are therefore partially fulfilled. This causes uncertainty about the importance of such an Al-reservoir on the Birkenes streambeds.

6.2.1 Autumn streambed

Due to frequent high flow conditions prior to the autumn study the streambed is believed to have experienced frequent pH values < 4.2. Thus the streambed may be considered to be depleted of an easily mobilizable pool of aluminium. The 4 µM

increase in Al_i may primarily arise from organic Al-complexes already in the stream water (constant Al_r).
The calcium increase must be due to a fast regeneration of a streambed reservoir within one day. The Ca pool is presumably quickly exploited leaving low concentrations after few hours. A large Ca-pool was found by Henriksen et al. (1988) to be due to ion-exchange processes on mosses. Because of ion-exchange and other neutralization processes this Ca-reservoir will cause subdued acidic episode. Conversely, because these processes are controlled largely by ion-exchange, a large Ca-reservoir may delay recovery from a prolonged acidic episode, while the streambed (mosses and liverworts) re-equilibrate with higher Ca and higher pH waters.

6.2.2 Summer streambed

Prior to the summer acidification the low discharge, originating from deep soil water reservoirs, had caused the pH to increase (see below), but the stream pH was kept below 4.8 presumably due to the high in-stream bio-activity. The conditions were therefore not ideal for a buildup of an easily mobilizable streambed reservoir of aluminium and calcium (Henriksen et al., 1988).

The low observed acidification induced streambed release of 2 μM Al_i may nevertheless be interesting. This must be considered as an indication that we may expect a larger buildup of an Al-reservoir during low flow conditions with stream pH ≥ 5.0 .
The increase in $[Ca^{2+}]$ of 255 μeq/L is significant and forwards certain implications. With the existence of an easy mobilized base cation pool on the streambed one may expect subdued acid discharge episodes with increased $[Ca^{2+}]$ and reduced recovery as described in chapter 6.2.1. On the contrary, we find that the generally observed natural correlation is negative between base cations and discharge and H^+ (chapter 3.2.6). This is due to changes in flowpaths (cf. e.g. chap. 7.1). Though, an inspection of the calcium fluctuation during the three following natural episodes (unpublished data), reveal increased $[Ca^{2+}]$ during the first two minor (10 mm) episodes, and a negative correlation during the last large (30 mm) episode. The $[H^+]$ and $[Al_i]$ increased insignificantly throughout the study period in comparison to spring and autumn episodes.
It appears that streambed release of calcium may therefore be an important factor during minor episodes at least in biological active periods.
An explanation for the lack of Al-pool and occurrent Ca-pool is found in deep bog water as the postulated source of base flow seepage (Christophersen et al., 1989a). This water has experienced long residence time and contains 1 μM H^+, 5 μM Al_i and 92 μM Ca^{2+} μeq/L (Table 7b in Appendix A) (Christophersen et al., 1989b). Andersen (1989) collected water from the mineral soil below the bog and found high $[Ca^{2+}]$ (59-183 μeq/L) and low $[Al_i]$ (1-9 μM).
A pool of calcium as discussed above has implications on fish

mortality. Brown (1983) found that during otherwise constant conditions the fish mortality rate declined with increased calcium concentrations.

6.3 Method validation

6.3.1 Al/Fluoride experiment

The aluminium fractionation method used in this work (Barnes, 1975 and Driscoll, 1984) is constructed for the determination of bio-toxic amounts of aluminium. The speciation of Al_i is based on (1) the time allowed for reaction of $[Al^{3+}]$ with 8-hydroxyquinoline and (2) removal of inorganic charge species by their sorption on a cation exchange resin. The concentration of Al_i is therefore only methodically determined based on biological implications.
The use of this parameter as a measure for total inorganic aluminium present in the sample may therefore be somewhat arbitrary. Comparison with dialysis results indicates that the Al_i may be slightly (<10 %) overestimated (Backes & Tipping, 1987). An overestimation of Al_i is also found by Salbu et al. (pers. com.) using a hollow-fibre technique.
Here I have compared the 8-hydroxyquinoline method with a quantitatively sound analytical F-electrode technique which quantifies Al^{3+} concentration using equilibrium thermodynamic calculations and measured values of free-F concentration and total-F (Hodges, 1987) (see chap. 4.1 for total-F determination method). Stability constants are then used to calculate the speciation of inorganic forms of Al, and organically complexed forms are obtained by subtraction from total Al. See Table 13 in Appendix A for measured values, calculations and results.

The general conclusion is that we overestimate the Al_i fraction with a factor of 0.1 to 0.2, though reservations must be made due to restricted data material, with large variation in results, and no comparison with other water qualities. Differences in % deviation for different amounts of added fluoride is due to (a) uncertain determination of free-F for the lowest concentrations, and (b) a pH increase caused by the formation of hydrofluoric acid evolving increased organic complexation of Al in to polymer complexes.
This overestimation must be due to cracking of organically bound Al in the exchange column and a following sorption to the resin (Backes & Tipping, 1987). Andersen (1989) found that this may be caused by pH gradients within the exchange column, due to preparation procedures, though this is not found to have inflicted on our previous collected data.
The sample used for this analysis was generally rich in organic compounds (TOC = 8 mg C/L). We may assume that less deviations will occur in samples with less TOC. Experimental implications may therefore be restricted to data from the organic horizons. A possible decrease in the $[Al_i]$ of 20 % in the organic horizon has no influence on the main conclusions.

6.3.2 Soil solution sampling

There is no single devise that will perfectly sample soil solutions in all conditions encountered in the field (Litaor, 1988). This is not even the case for the applied cup lysimeters.
Differences in large and small pore solution chemistry, due to enhanced equilibrium in the latter (this study; Cozzarelli et al., 1987), rise an important complication concerning the use of tension lysimeters. The suction sampler does not discriminate between pore size, and will collect soil solution from soil pores of different sizes, depending on the soil water content and the applied pressure on the lysimeter.
In this study there is not found any significant correlation between the hydrological condition (soil solution sampling efficiency) and chemistry (Table 10a and b). On the contrary, by considering the hydrology I am able to account for the changes in sources of the collected soil solution (chap. 6.1.1.).
Spatial variability due to the inherent soil heterogeneity is evident by considering the two E-horizon lysimeters used in the podzol profile. Comparing results obtained from these locations with results from a large number of other plots in the Birkenes catchment, shows that the selected locations are characteristic for their soil horizons.

6.3.3 Hydrological deviations

Reservations regarding the quality of my data on water movement must be made due to two important, though necessary, methodical impacts:
1. The plot D(1) ditch: To install lysimeters at the correct depth it has been necessary to dig a ditch down to the bedrock approx. 30-40 cm down-slope of plot D(1). This ditch will attract soil water flowing under over-pressure (>1 atm.) e.g. supersaturated flow. This re-routing is caused by physical power vectors that forces the water towards lower pressure and easy escape. This restriction will only be important during supersaturated flow conditions, such as after the event on day 13. This may nevertheless have lead to an enhanced washout of the added sodium bromide and hence low observed infiltration in the lower B- and B/C-horizons.

2. The local precipitation: The NaBr-solution was added during wet hydrological conditions, within an area of 4 sq. meters. A local increase in the water table with subsequent lateral flow out from the test area may therefore be induced by the addition of 11 mm of precipitation. Such flow would cause an induced increase in lateral transport of NaBr from the cup lysimeters. This increased lateral transport may in the podzol horizon cause additional removal of added salt prior to reaching lower horizons. In the peat profile this lateral transport only serves to further document the low removal of added salts.

7. CONCLUSIONS

Man is a rational animal who always loses his temper when he is called upon to act in accord with dictates of reason.

\- Oscar Wilde -

7.1 Hydrologic controls; A flowpath model

The data imply that the concepts of surface flow, sub surface lateral flowpath and the piston flow as well as large- and small-pore flow are necessary to account for the water movements found by tracing the salt pulse through the soil profiles. A hypothesized picture of the contributing soil water reservoirs, and the active flowpaths during different conditions, is presented below:

During dry conditions the groundwater table is low. Then the main source of base flow is the water stored in deep soils and especially in organic deposits (bogs) in the valley bottom (VB). This water has long residence time and is in equilibrium with gibbsite.

The primary response to a precipitation event is percolation of soil solution through large pores down to the bedrock or groundwater table. At deep profiles (> about 20 cm) this water becomes neutralized and mixed with ground water. The water table rises and a flow of B-horizon water to the stream may occur. This groundwater flow causes the discharge in the brook to respond within a few hours by forcing old down-slope water out in the stream, e.g. piston flow. The opening of this flowpath causes a shift from baseflow conditions with pH = 5.2 and $[Al^{3+}] \leq 2$ µM to pH = 4.5 and $[Al^{3+}]$ from 5 to 11 µM. When the water table intercepts the E-horizon, the water from the lower O/H- and E-horizons may be short-circuited as lateral flow through large pores in these horizons (Joslin et al., 1987) and reach the surface waters directly.
The Cl budget of the salt episode studied by Mulder et al. (1989), indicated that under the prevailing conditions 20-30% of the water at Birkenes reached the stream so quickly that it had probably not passed the B-horizon. This water was thereby not neutralized in the deeper layers, and negative saturation indices with respect to synthetic gibbsite in surface waters were therefore observed.
Seip et al. (1989) showed that the soil solutions from the humic/organic horizons are more acid, and soil solution from the E-horizon is more aluminium rich, than water in the deeper mineral soil, resulting in further increase in acidity to pH = 4.3 and $[Al^{3+}]$ up to 11 µM commonly observed in the stream during wet conditions.

A contributing factor is that the shallow soils are mainly situated at the higher elevations farthest away from the streams. The precipitation that reaches these regions drains rapidly into the deeper soil profiles at lower elevations. This large flux of groundwater causes a billow on the groundwater table that moves rapidly down the hillslope. This wave sweeps the organic deposits on its journey and accumulates aluminium and hydrogen ions. The wave peak reaches the brook and causes maximum discharge 2 to 6 hours after the peak in precipitation.

During dry conditions a pool of easily mobilized salts will accumulate in the upper soils (especially peat) and on the vegetation due to dry deposition and small rainfall events followed by evapotranspiration. This pool will be mobilized by the first large rain event. Episodes high in salts will also occur in the beginning of snowmelt. During the winter months all deposited salts are stored in the snowpack.

The NaBr addition shows that such a pool of salts when mobilized may lead to dramatically elevated aluminium and hydrogen ion concentrations in the upper soil horizons. The observed lateral water flowpath may result in discharge from the organic and E-horizons directly to the stream. The resulting stream water concentrations will depend on the relative amounts of water from these horizons. (The soil solution in the H-horizon has the highest $[H^+]$, the soil solution in E the highest $[Al^{3+}]$). This mechanism may explain the minimum pH values (about 4.1) and/or maximum $[Al^{3+}] \geq 11$ µM observed during the first event after antecedent dry conditions or in the beginning of snowmelt.

During periods of frequent precipitation (and thus saturated hydrological conditions), $[H^+]$ generally shows maxima at all discharge peaks. $[Al^{3+}]$, however, has only one clear maximum corresponding to the first storm event after a dry period. During later events $[Al^{3+}]$ may even show a minimum. This may be explained by an additional increase in the water table into the organic deposits and discharge from the humic horizons with elevated $[H^+]$ without contact with mineral soil (Sullivan et al., 1987c). After the first heavy episode the salt pool is of little importance and organic leachate will only dilute the surface waters; minimum pH values are therefore about 4.3. The E-horizon soil solution becomes more and more mixed with new precipitation and old groundwater and will to a lesser extent contribute to elevated aluminium and hydrogen ion concentrations in the surface waters. The succeeding events may therefore result in lower Al-concentrations in stream water.

7.2 Aluminium controls

The results are consistent with the hypothesis that a fixed potential organic ion exchanger controls $[Al^{3+}]$ and $[H^+]$ in the soil solution in both humic and peat organic soils. In the humic layer the pK_{sel} of the exchanger increases with decreasing pH possibly due to protonation of the functional sites, and a shift to only strongly complexed Al left on the exchanger. In the peat the ion exchanger adjusts to stable decreases in the ionic levels by a decrease in pK_{sel} presumably

due to slow reorganization of exchangeable and complexed Na, H and Al on the functional sites and the DDL, creating a new equilibrium at a lower pK_{sel} value when the salt pulse is washed away.
The soil solution chemistry in the eluvial layer is primarily controlled by ion exchange reactions, though during stable hydrological conditions mineral dissolution may prevail.
In the illuvial and parent material layers of the mineral soils the most probable Al-control system is a change of the Al-release mechanisms during stable conditions, from a fast ionexchange equilibrium in the initial water entering the horizon, to an increasing amount of a slower mineral dissolution/precipitation with increasing resident time. This is evident by the lack of exchange relations in the water stagnant C-horizon below the peat.
Due to the generally high residence time prior to entering the stream, one can postulate that a simple gibbsite mineral dissolution (Eqn. 7) determines $[H^+]$ and $[Al^{3+}]$ in the water from the B and C layers.

A very good correlation between Al and tot-fluoride is caused by strong fluoride complexes with aluminium. These water soluble complexes serve to increase the mobility of aluminium through the soils.
Sulphate retention in the organic horizons during the salt addition study is probably caused by adsorption on soil surfaces, while the precipitation of sulphate-aluminium minerals may be the controlling mechanism of sulphate retention in the mineral soils.

This data set suggests further that the reaction rate is important when contact time was short and large concentration gradients are experienced. This was specially evident in the E- and Bhs-horizon where slow shifts in time of $[H^+]$ and $[Al^{3+}]$ during hydrological stable conditions were observed.

7.3 Soluble organic controls

Variations in the [TOC] caused by the salt pulse may be accounted for using previous postulations.
The salt addition illustrates further that the ability of the TOC to stay in solution is reduced during exceptionally high salt or anthropogenic loadings. Thus, one consequence of increased rain acidity might be an antagonistic decrease in the soluble organic acids, cf. Krug & Fink (1983). Though the salt addition shows further that an increased [TOC] not necessarily causes an increased acidity.

Due to their function as complexing agents and mobile anions TOC permit accelerated rate of Al mobilization in the eluvial horizon. By escaping the Bhs-horizon, through the postulated lateral flow, these organic acids may considerably enhance preferential dissolution and migration of aluminium out into the surface waters.

7.4 Streambed controls

The acidification of the Birkenes streambed indicates that we may expect minor buildup of an Al-reservoir during low flow conditions with stream pH ≥ 5.0 .
The data further suggest that streambed release of calcium as a response to increased acidity may therefore be an important factor during episodes in at least biologically active periods.

7.5 Model implications

Birkenes model

The potential of an easily mobilized pool of ions coincides with the conditions where the "Birkenes Model" (Christophersen et al., 1982; Stone & Seip, 1989a) fails to describe Al-concentrations in stream water satisfactorily. The model takes care of accumulation of chloride and sulphate during dry summer periods and the salt pulse in the beginning of snowmelt. However, the different Al-solubility controls in the various soil water reservoirs and the salt effect suggests that improvement may be made with the use of a 3-box model with the following characteristics;
A box : Organic soil layer reservoirs controlled by fast ion exchange. Contributes water to the stream with a variable composition depending on salt loadings.
B box : Mineral soil controlled by both fast ion exchange and slow mineral solubility depending on residence time of the soil solution.
C box : Deep valley bottom groundwater reservoirs which are neutralized by base cations and may be considered as constant.

Emma model

Pulses of high ionic strength occur naturally for example due to large deposition of sea salts. The salt pulse study shows that we may thereby expect considerable temporal variations in acidity and Al concentrations in soil solution in the upper soil horizons (O/H, E). This implies that the assumption of constant chemical composition of the soil solutions in selected soil water classes as claimed in the EMMA model, is only a rough first approximation. The EMMA-model may be useful in determining water pathways, but for the use of the EMMA model in scenario predications the composition of the endmember corresponding to the O-horizons must be considered. Furthermore the observed sub surface lateral flowpath stresses the importance of the E-horizon on surface water quality. This horizon may therefore not be excluded.

Finally the observed streambed reservoir of Ca^{2+}, which is not accounted for in the model, may have caused the higher observed level of calcium during events than what the model can produce.

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Table 7b.

Soil solution chemical characteristics of the various soil horizons of the Birkenes Catchment. The values are based on data from cup lysimeter samples, collected during the summer of 1988 episode study, where we followed the soil solutions from dry to wet conditions (Vogt et al., 1989).

Site	Hor	H^+	AL_a	Al_i	Cl^-	NO^-	SO^{--}	Na^+	Mg^{++}	Ca^{++}	K^+	F-to	Cond	TOC
		µM	µM	µM	µM	µM	µM	µM	µM	µM	µM	µM	µS/cm	mgC/L
AVG	H/O	54	15	6	88	25	217	69	60	96	44	2	76	19
MIN	H/O	18	6	0	56	7	137	38	41	45	11	1	40	6
MAX	H/O	83	26	13	113	93	449	102	132	279	153	2	270	70
STD	H/O	19	5	4	16	30	99	21	30	77	47	0	60	16
#	H/O	20	15	15	7	7	14	7	14	14	7	7	20	19
AVG	E	57	29	19	115	60	241	120	57	81	24	1	54	10
MIN	E	18	14	5	113	7	150	100	35	43	13	0	35	4
MAX	E	93	46	32	118	146	299	138	86	104	35	2	94	25
STD	E	18	6	6	3	61	65	16	21	27	9	1	13	4
#	E	34	29	29	3	3	6	3	6	6	3	3	34	31
AVG	B	30	34	27	118	12	284	111	66	79	25	4	46	5
MIN	B	19	24	20	56	7	200	61	40	53	2	1	35	3
MAX	B	52	60	51	254	83	499	143	155	319	118	6	86	10
STD	B	7	6	5	37	14	88	15	26	50	35	1	9	2
#	B	52	44	44	30	30	60	30	60	60	30	31	52	48
AVG	C	20	28	23	92	16	261	98	55	57	40	3	41	4
MIN	C	4	14	9	34	7	50	33	20	27	2	1	28	2
MAX	C	33	48	41	197	71	499	130	91	130	182	4	65	7
STD	C	5	7	6	37	17	92	22	17	23	51	1	8	1
#	C	35	28	28	24	24	48	24	48	48	24	23	35	34
AVG	P	52	25	19	124	69	258	94	82	115	59	3	64	6
MIN	P	1	9	4	28	7	75	30	20	37	7	0	33	3
MAX	P	513	53	46	491	600	649	248	217	798	253	7	525	21
STD	P	65	8	9	99	101	109	41	47	156	61	1	66	4
#	P	60	58	58	37	37	74	37	74	74	37	36	60	52
AVG	M	23	19	14	109	43	168	113	48	75	6	3	41	6
MIN	M	11	10	5	85	9	50	100	33	45	3	2	29	2
MAX	M	59	31	28	141	107	349	130	69	110	18	6	55	13
STD	M	9	6	7	13	24	88	9	12	15	4	1	5	3
#	M	52	50	50	20	20	40	20	40	40	20	20	52	46
AVG	DM	0	5	4	140	9	60	126	69	134	4	7	68	8
MIN	DM	0	1	0	127	1	25	112	61	120	2	3	49	3
MAX	DM	1	18	17	158	23	237	143	81	165	10	8	81	14
STD	DM	0	3	3	9	6	69	9	6	11	2	2	8	3
#	DM	25	25	25	13	13	26	14	28	28	14	15	25	22
AVG	DC	1	6	5	140	5	644	110	92	215	5	9	65	4
MIN	DC	0	1	0	127	0	62	29	23	77	1	5	43	1
MAX	DC	2	10	8	172	22	861	139	127	334	8	13	93	9
STD	DC	0	2	2	16	8	263	28	29	95	2	3	15	2
#	DC	42	38	38	8	7	16	11	22	22	11	10	39	39

P, M, DM, DC denotes peat, mud, deep mud and deep C respectively.

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APPENDIX A

Table 1.

The carbon dioxide degassing and carbonic acid dissociation constants. Data are collected from Sillen and Martell (1964).

$\log(H_2CO_3)^* - \log P_{co2(g)} = -1.46$

$\log(HCO_3^-) - \log P_{co2(g)} - pH = -7.81$

$\log(CO_3^{2-}) - \log P_{co2(g)} - 2pH = -18.14$

Table 2.

Solubility and enthalpy values for different gibbsite forms. Values are collected from May et al., (1979), Hem et al., (1973), Stumm & Morgan (1981), Ball et al., (1980).

Synthetic gibbsite	$pK^\circ_s = -8.11$	
Natural gibbsite	$pK^\circ_s = -8.77$	$\Delta Hr = -23.2$ kcal/mole
Monocrystalline gibbsite	$pK^\circ_s = -9.35$	$\Delta Hr = -22.8$ kcal/mole
Amorphous $Al(OH)_3$	$pK^\circ_s = -10.80$	$\Delta Hr = -25.5$ kcal/mole

Table 3.

Temperature corrected pK_s values for gibbsite to match ambient catchment temperature.

Temperature	2.5 °C Minimum	8.1 °C Middle	12.5 °C Maximum
Natural gibbsite	$pK_s = -10.16$	$pK_s = -9.79$	$pK_s = -9.55$
Monocrystalline gibbsite	$pK_s = -10.71$	$pK_s = -10.35$	$pK_s = -10.11$
Amorphous $Al(OH)_3$	$pK_s = -12.33$	$pK_s = -11.92$	$pK_s = -11.65$

Table 4.

The significant mononuclear ion species at equilibrium with aluminum in acid waters. Values are collected from Ball et al., (1980), Baes and Mesmer (1976) and Nordstrom and Ball (1986).

$Al^{3+} + H_2O \leftrightarrow Al(OH)^{2+} + H^+$	$pK^0 = -4.99$	$\Delta Hr = 11.9$kcal/mole
$Al^{3+} + 2H_2O \leftrightarrow Al(OH)_2^+ + 2H^+$	$pK^0 = -10.00$	$\Delta Hr = 22.0$kcal/mole
$Al^{3+} + 3H_2O \leftrightarrow Al(OH)_3 + 3H^+$	$pK^0 = -16.76$	$\Delta Hr = 33.0$kcal/mole
$Al^{3+} + 4H_2O \leftrightarrow Al(OH)_4^- + 4H^+$	$pK^0 = -23.00$	$\Delta Hr = 44.1$kcal/mole
$Al^{3+} + F^- \leftrightarrow AlF$	$pK^0 = 7.02$	$\Delta Hr = 1.1$kcal/mole
$Al^{3+} + 2F^- \leftrightarrow AlF_2$	$pK^0 = 12.76$	$\Delta Hr = 2.0$kcal/mole
$Al^{3+} + 3F^- \leftrightarrow AlF_3$	$pK^0 = 17.03$	$\Delta Hr = 2.5$kcal/mole
$Al^{3+} + 4F^- \leftrightarrow AlF_4$	$pK^0 = 19.73$	$\Delta Hr = 2.2$kcal/mole
$Al^{3+} + 5F^- \leftrightarrow AlF_5$	$pK^0 = 20.92$	$\Delta Hr = 1.8$kcal/mole
$Al^{3+} + SO_4 \leftrightarrow AlSO_4$	$pK^0 = 3.02$	$\Delta Hr = 2.2$kcal/mole
$Al^{3+} + 2SO_4 \leftrightarrow Al(SO_4)_2$	$pK^0 = 4.92$	$\Delta Hr = 2.8$kcal/mole

Table 5.

Solubility and enthalpy values for likely aluminium sulphates controlling sulphate (and aluminum) retention in acid environments. Values are collected from Nordstrom (1982), Singh and Brydon (1970) and Adams and Rawajfih (1977), respectively.

Jurbanite($Al(OH)SO_4$)	pK°_{s}= 3.80
Basaluminite($Al_4(OH)_{10}$SO24)	pK°_{s}= 22.50
Alunite($KAl_3(OH)_6SO_4$)	pK°_{s}= 1.40

Table 6

Average volume-weighted concentrations of major ions in precipitation and streamwater at Birkenes (1973-1978, 1981-1983 and 1985-1987) (SFT, 1988).

		Precipitation BIN01	Stream BIE01
Water	mm	1370	1067
H^+	µeq L^{-1}	54	30
Na	µeq L^{-1}	52	114
K	µeq L^{-1}	4	6
Ca	µeq L^{-1}	9	58
Mg	µeq L^{-1}	13	36
Tot-Al	µM		21
NH_4	µeq L^{-1}	40	
SO_4	µeq L^{-1}	68	145
Cl	µeq L^{-1}	56	125
NO_3	µeq L^{-1}	38	8

Table 7a.

Soil chemical characteristics of the various horizons of the 2 major soil types in the Birkenes catchment (Mulder et al., 1989 and * asterisks denote data from Frank, 1980).

		Podzolized brown earth				Bog		
Horizons		O/H	E	Bhs	Bs	Of	Oh	C
pH(1:1.25H_2O)		3.7*	4.2	4.7	4.8	3.7	4.2	5.1
Loss on ignition	%w/w	69.5*	3.0*	9.6*	0.8*	93.2*	64.9*	-
Ca(ex)	%CEC	-	4.1	3.7	2.8	1.2	5.2	33.4
Mg(ex)	%CEC	-	2.1	1.5	1.2	0.4	0.5	6.1
Na(ex)	%CEC	-	<2.2	<1.8	<1.8	<0.4	<0.5	<8.4
K(ex)	%CEC	-	<2.2	<1.8	<1.8	<0.4	<0.5	<8.4
Al(ex)	%CEC	-	49.0	63.4	63.2	78.8	70.6	8.8
H(ex)	%CEC	-	43.9	29.9	32.1	19.6	23.7	49.4
CEC	mmol/kg	-	47	59	61	245	194	15

Exchangeable base cations were determined in Li-EDTA at pH 7.0 and exchangeable H and Al in 1N KCl extracts.

Table 8

Dilution scheme used prior to aluminum fractionation.

Sample volume	Dilution factor
< 25 ml	20
25 ml → 50 ml	10
50 ml → 100 ml	8
100 ml → 200 ml	4
200 ml → 300 ml	2
300 ml >	1

Table 9.

Lysimeter depth and soil horizon in podzol- and peat plot.

Lysimeter	Plot	Horizon	Depth cm	Hight cm
Cup lysimeter 10	D (1)	Organic (O/H)	- 8	48
Cup lysimeter 11	D (1)	Eluvial (Ea)	5	35
Cup lysimeter 12	D (1)	Eluvial (Ea)	4	36
Cup lysimeter 13	D (1)	Illuvial humus (Bhs)	17	23
Cup lysimeter 14	D (1)	Illuvial iron (Bs)	23	17
Cup lysimeter 15	D (1)	Parent material (Bs/C)	32	8
Cup lysimeter 21	D (3)	Partly decomposed (Of)	-45	48
Cup lysimeter 22	D (3)	Well decomposed (Oh)	-25	28
Cup lysimeter 23	D (3)	Parent material (C)	1	1

Table 10a

Correlation coefficients between chemical components in the podzol profile.
Good correlations (absolute coefficient > 0.6, with significance > 99.9%) are high-lighted.
Top: Correlation coefficient,
Middle: Number of samples,
Bottom: Significance level; possibility of mistaking.

	S.ef ml/h	H^+ µM	Temp °C	Cond µS/cm	TOC mgC/L	Al_a µM	Al_o µM	Al^{3+} µM	F-tot µM	NO^{3-} µe/L	SO^{4--} µe/L	Na^+ µe/L	Σ BC µe/L	Br^- mg/L
Depth	0.4	-0.5	-0.1	**-0.6**	**-0.6**	-0.2	-0.2	-0.2	-0.2	-0.5	0.3	-0.4	-0.4	-0.5
cm	138	138	137	137	132	129	128	128	61	21	21	21	21	95
	0	0	0.3	0	0	0.0	0.0	0.0	0.1	0.0	0.2	0.1	0.1	0
Sampling		-0.1	0.0	-0.2	-0.2	-0.2	-0.0	-0.2	-0.2	-0.2	0.2	-0.1	-0.2	-0.1
Efficiency		38	137	137	132	129	128	128	61	21	21	21	21	95
ml/hour		0.1	0.8	0.0	0.0	0.1	0	0.0	0.1	0.4	0.4	0.7	0.4	0.2
H+			0.1	**0.9**	0.2	0.2	0.3	0.2	0.4	-0.0	-0.3	**0.8**	**0.8**	**0.9**
µM			137	137	132	129	128	128	61	21	21	21	21	95
			0.4	0	0.0	0.1	0.0	0.1	0.0	0	0.1	0	0	0
Temp				0.0	0.0	-0.1	0.0	-0.1	-0.2	0.1	0.4	0.1	0.2	0.0
°C				137	131	129	128	128	61	21	21	21	21	95
				0.8	0	0.2	0.9	0.2	0.1	0.6	0.1	0.7	0.5	0.7
Cond					0.2	0.5	0.5	0.5	**0.7**	-0.0	-0.5	0.7	**0.9**	**1.0**
µS/cm					131	129	128	128	61	21	21	21	21	95
					0.1	0	0	0	0	0.9	0.0	0.0	0	0
TOC						-0.1	-0.1	-0.1	-0.2	0.5	-0.1	-0.1	-0.2	0.2
mg C/L						125	124	124	60	21	21	21	21	93
						0.2	0.5	0.2	0.2	0.0	0.8	0.6	0.4	0.0
Ala							**0.8**	**1.0**	**0.9**	-0.3	-0.4	0.1	0.4	0.4
µM							128	128	57	18	18	19	19	93
							0	0	0	0.3	0.1	0.8	0.1	0
Alo								**0.8**	**0.8**	-0.4	-0.4	0.2	0.5	0.4
µM								128	57	18	18	19	19	92
								0	0	0.1	0.1	0.5	0.0	0
Al3+									**0.9**	-0.3	-0.5	0.1	0.4	0.4
µM									57	18	18	19	19	92
									0	0.3	0.1	0.8	0.1	0
F-tot										-0.3	-0.5	0.1	0.7	**1.0**
µM										17	17	15	15	24
										0.2	0.1	0.6	0.0	0
NO3-											0.1	0.0	-0.1	0.4
µeq/L											21	19	19	11
											0.8	0	0.8	0.2
SO4--												-0.5	-0.6	-0.7
µeq/L												19	19	11
												0.0	0.0	0.0
Na+													**0.8**	0.8
µeq/L													21	13
													0	0.0
Σ Base cations														**0.9**
µeq/L														13
														0

Table 10b

Correlation coefficients between chemical components in the peat profile.
Good correlations (absolute coefficient > 0.6, with significance > 99.9%) are high lighted.
Top: Correlation coefficient,
Middle: Number of samples,
Bottom: Significance level; possibility of mistaking.

	S.ef ml/h	H^+ µM	Temp °C	Cond µS/cm	TOC mgC/L	Al_a µM	Al_o µM	Al^{3+} µM	F-tot µM	NO^{3-} µe/L	SO^{4--} µe/L	Na^+ µe/L	Σ BC µe/L	Br^- mg/L
Depth-	0.1	**-0.9**	0.0	**-0.8**	**-0.8**	**-0.7**	**-0.8**	**-0.7**	**-0.6**	-0.3	-0.4	-0.6	-0.5	**-0.7**
cm	85	85	85	85	84	85	85	85	85	12	12	14	14	41
	0.6	0	0.7	0	0	0	0	0	0	0.4	0.2	0.0	0.1	0
Sampling		0.2	0.2	-0.1	0.1	-0.1	0.2	-0.1	-0.1	-0.2	0.1	0.2	0.1	0.0
efficiency		85	85	85	84	85	85	85	85	12	12	14	14	41
ml/hour		0.1	0.1	0.4	0.5	0.3	0.0	0.3	0.3	0.5	0.8	0.6	0.8	0.9
H+			0.0	**0.8**	0.5	**0.7**	**0.8**	**0.7**	**0.8**	0.0	0.0	0.6	0.6	**0.7**
µM			85	85	84	85	85	85	85	12	12	14	14	41
			0.7	0	0	0	0	0	0	0	0.9	0.0	0.0	0
Temp				-0.1	0.0	-0.1	-0.1	-0.1	-0.0	0.2	-0.4	-0.0	-0.0	0.0
°C				85	84	85	85	85	85	12	12	14	14	41
				0.3	0.7	0.4	0.2	0.2	0.7	0.5	0.2	0.9	0	0.8
Cond					0.3	**1.0**	**0.8**	**1.0**	**1.0**	0.1	-0.2	0.4	0.3	**1.0**
µS/cm					84	85	85	85	85	12	12	14	14	41
					0.0	0	0	0	0	0.9	0.6	0.2	0.3	0
TOC						0.2	0.5	0.2	0.1	0.9	0.5	0.2	0.3	0.5
mg C/L						84	84	84	84	12	12	14	14	41
						0.1	0	0.1	0.3	0.0	0.1	0.6	0.2	0.0
Ala							**0.8**	**1.0**	**1.0**	-0.0	-0.4	0.3	0.3	**0.9**
µM							85	85	85	12	12	14	14	41
							0	0	0	0	0.3	0.3	0.4	0
Alo								**0.8**	**0.8**	0.2	0.3	0.4	0.3	**0.8**
µM								85	85	12	12	14	14	41
								0	0	0.6	0.4	0.2	0.3	0
Al3+									**1.0**	-0.0	-0.4	0.3	0.3	**0.9**
µM									85	12	12	14	14	41
									0	0.9	0.3	0.3	0.3	0
F-tot										-0.0	-0.5	0.3	0.2	**0.9**
µM										12	12	14	14	41
										0.9	0.1	0.4	0.5	0
NO3-											0.1	-0.2	0.1	0.0
µeq/L											12	12	12	10
											0.7	0.5	0.6	0.9
SO4--												0.2	0.2	-0.0
µeq/L												12	12	10
												0.5	0.6	0.9
Na+													0.8	0.2
µeq/L													14	12
													0.0	0.5
Σ Base Cations														0.2
µeq/L														12
														0.6

Table 10c.

Soil solution Al^{3+} and H^+ relationships calculated from the salt addition experiment

Lysimeter	Horizon	Avg. pQ	Stand.div	Regress pAl^{3+}=	r^2	n
Podzol:						
Cup 10	Of	-7.11	1.19	0.66pH+ 2.85	0.53	10
Cup 11	Ea	-8.20	0.95	0.65pH+ 2.02	0.01	14
Cup 12	Ea	-8.38	0.29	1.76pH- 3.10	0.23	19
Cup 13	Bhs	-9.19	0.41	0.07pH+ 4.34	0.02	27
Cup 14	Bs	-8.95	0.20	0.12pH+ 4.20	0.08	29
Cup 15	Bs/C	-8.85	0.22	-0.11pH+ 5.20	0.31	29
Cup 11+12	Ea	-8.30	0.66	1.66pH- 2.57	0.09	33
Cup 13+14+15	B	-8.99	0.32	-0.01pH+ 4.74	0.00	85
Peat:						
Cup 21	Of	-8.06	0.27	1.03pH- 0.13	0.18	29
Cup 22	Oh	-8.38	0.30	0.32pH+ 3.41	0.10	26
Cup 23	C	-9.07	0.29	-0.03pH+ 4.95	0.01	30
Cup 21+22	O	-8.21	0.32	1.23pH- 0.64	0.52	55

Table 11.
Selected parameters of precipitation water chemistry during the salt addition experiment (from NILU/Joranger, pers. com.). Days devoid of precipitation are omitted. Samples were collected at 8 a.m. the following day.

Day	Pre. mm	pH	$[Cl^-]$ µe/L	$[NO_3^-]$ µe/L	$[SO_4^{2+}]$ µe/L	$[Na^+]$ µe/L	$[Mg^{2+}]$ µe/L	$[Ca^{2+}]$ µe/L	$[K^+]$ µe/L	$[NH_4+]$ µe/L
-2	35.7	4.58	17.2	6.4	26.2	19.1	4.9	3.5	2.0	7.1
-1	15.9	4.46	11.6	7.1	37.4	9.6	2.9	2.5	2.8	10.0
0	1.3	3.72	50.8	208	71.1	45.7	10.3	15.5	21.0	53.6
8	0.7	3.60	NA	227	231	295	61.7	92.8	NA	55.0
12	22.1	4.46	35.3	32.1	37.4	32.2	10.3	6.5	4.3	37.1
13	6.0	4.95	147	29.3	30.6	127	29.6	12.5	18.9	43.6
14	1.5	5.10	279	10.7	8.1	282	62.5	16.5	16.1	27.1
26	7.8	4.13	155	97.9	101	123	30.5	16.0	6.9	117
27	14.3	3.98	36.7	113	120	26.1	6.6	6.5	4.9	227
29	1.2	4.42	141	53.6	36.2	111	21.4	9.5	16.4	47.9
34	1.9	3.54	147	319	150	89.1	22.2	19.0	28.4	149

Table 12.

Site description of acidified stream localities.

Exp.	Site	Length	Substrate	Characteristics
1	Trib.BIE01	20 m	Moss/sand/gravel	High flow
2	BIE01	20 m	Sand/gravel	Flat, water basins
3	BIE01	5 m	Moss/bedrock	Good moss/water contact
4	BIE01	5 m	Moss/sand/gravel	Highly divers

Table 13

Results from the comparison of F-electrode and 8-hydroxyquinoline method for the determination of [Al_i].

Measured concentrations:

Sample	pH	Al_o µM	Al_i µM	F-tot µM	F^- µM
Natural sample	4.57	4.21	11.94	4.54	NA
+ 2µM F^-	4.57	3.28	12.96	7.11	0.16
+ 4µM F^-	4.60	2.79	13.58	9.36	0.37
+ 8µM F^-	4.66	3.18	12.95	13.85	1.05
+12µM F^-	4.72	2.94	12.80	18.59	2.16
+16µM F^-	4.74	2.76	12.76	23.27	3.58

Calculations (20 °C):

Sample	Al^{3+} µM	$Al(OH)^{2+}$ µM	$Al(OH)^{+}$ µM	AlF^{2+} µM	AlF_2^{+} µM	AlF_3 µM
Natural sample	NA	NA	NA	NA	NA	NA
+ 2µM F^-	3.67	1.00	0.20	5.87	0.54	0.00
+ 4µM F^-	1.70	0.50	0.11	6.29	1.34	0.01
+ 8µM F^-	0.54	0.18	0.05	5.70	3.45	0.07
+12µM F^-	0.21	0.08	0.02	4.52	5.62	0.23
+16µM F^-	0.10	0.04	0.01	3.56	7.33	0.49

Results:

Sample	Sum cal.Al_i µM	Deviation µM	Diff.% from meas.Al_i %
Natural sample	NA	NA	NA
+ 2µM F^-	11.27	1.68	13.0
+ 4µM F^-	9.93	3.64	26.8
+ 8µM F^-	9.99	2.96	22.9
+12µM F^-	10.67	2.12	16.6
+16µM F^-	11.53	1.23	9.6

APPENDIX B

Soil solution chemical data from the salt addition experiment. The time denotion is set to when the suction was initiated.

Cup lysometer 10, Podzol profile O/H-horizon, -8 cm

Time Day	Smp.In ml/day	pH	Temp. deg.C	Cond µS/cm	F-tot µM	TOC mgC/L	ALa µM	Alo µM	Ali µM	Al3+ µM
-0.55	43	4.38	11.1	36.4	NA	NA	8.4	4.8	3.5	0.6
0.00	744	3.68	11.4	384.0	4.21	7.4	24.2	9.3	14.9	10.4
0.08	228	3.55	11.0	519.0	NA	4.9	29.3	7.0	22.3	18.5
0.25	57	3.75	11.0	377.0	NA	NA	NA	NA	NA	NA
0.58	17	3.77	10.2	335.0	NA	NA	12.4	4.2	8.1	5.3
1.46	9	3.92	9.5	286.0	NA	NA	30.9	7.4	23.5	20.5
2.96	4	3.94	10.5	240.0	NA	NA	NA	NA	NA	NA
5.46	6	3.90	NA	NA	NA	7.6	NA	NA	NA	NA
7.20	12	4.43	9.0	85.3	1.58	9.1	7.4	3.4	3.9	2.2
12.61	149	5.01	8.7	47.6	NA	8.8	6.2	2.3	3.9	1.8
13.05	87	4.91	7.8	35.1	1.47	13.8	7.4	3.8	3.6	1.8
13.51	56	4.68	5.7	49.8	2.21	17.2	8.2	5.0	3.1	1.1
27.32	201	4.20	14.8	77.2	1.37	8.8	7.9	4.3	3.6	2.1

Cup lysometer 10, Podzol profile O/H-horizon, -8 cm

Time Day	NO- µeq/L	SO-- µeq/L	Na+ µeq/L	Mg++ µeq/L	Ca++ µeq/L	K+ µeq/L	Br- mg/L	Dilution Factor
-0.55	NA	NA	NA	NA	NA	NA	NA	20
0.00	NA	NA	NA	NA	NA	NA	NA	10
0.08	28.6	25.0	2504.4	154.7	261.5	32.7	300.0	10
0.25	NA	NA	NA	NA	NA	NA	NA	NA
0.58	NA	NA	NA	NA	NA	NA	NA	10
1.46	NA	NA	NA	NA	NA	NA	NA	10
2.96	NA	NA	NA	NA	NA	NA	NA	NA
5.46	NA	NA	NA	NA	NA	NA	NA	NA
7.20	228.6	62.4	370.4	26.3	66.9	14.8	NA	10
12.61	NA	NA	NA	NA	NA	NA	11.6	10
13.05	28.6	25.0	NA	NA	NA	NA	NA	10
13.51	NA	NA	NA	NA	NA	NA	NA	10
27.32	121.4	218.3	84.4	23.9	17.5	0.8	NA	4

Cup lysometer 11, Podzol profile E-Horizon, 5 cm

Time Day	Samp.In ml/day	pH	Temp. deg.C	Cond µS/cm	F-tot µM	TOC mgC/L	ALa µM	Alo µM	Ali µM	Al3+ µM
-0.55	733	4.26	11.0	51.2	3.42	5.1	31.9	8.2	23.6	18.3
0.00	540	4.24	11.4	67.7	3.47	5.2	NA	NA	NA	NA
0.08	366	4.25	11.7	54.3	3.63	5.5	24.6	10.9	13.7	9.3
0.25	258	4.46	10.8	46.2	3.16	5.9	32.4	8.9	23.5	17.9
0.58	66	4.37	6.8	53.1	3.68	5.9	5.4	4.2	1.2	0.0
1.46	158	4.36	5.5	54.6	6.11	5.5	12.8	6.6	6.2	1.2
1.96	67	4.43	6.7	60.2	4.74	5.4	46.3	8.9	37.4	29.9
2.96	14	4.37	8.1	72.9	5.89	5.0	47.5	8.2	39.4	30.7
6.34	70	4.33	8.1	79.4	6.53	4.7	70.5	7.4	63.1	52.1
7.20	3	4.52	4.9	76.9	7.16	4.8	NA	NA	NA	NA
12.13	78	4.70	9.0	84.2	NA	4.7	74.0	6.5	67.5	51.6
12.61	137	4.31	7.6	119.0	9.79	4.7	128.6	8.9	119.6	102.4
13.01	273	4.45	7.4	128.2	10.42	4.3	143.0	10.9	132.1	111.0
13.51	179	4.15	5.4	145.0	NA	4.3	135.0	10.2	124.8	111.1
14.49	166	4.17	3.5	145.6	10.74	4.2	136.0	7.7	128.3	111.9
27.32	179	4.23	16.2	105.5	NA	5.2	84.9	8.1	76.8	62.8
35.32	28	4.59	24.6	85.5	6.74	4.5	NA	NA	NA	NA

Cup lysometer 11, Podzol profile E-Horizon, 5 cm

Time Day	NO- µeq/L	SO-- µeq/L	Na+ µeq/L	Mg++ µeq/L	Ca++ µeq/L	K+ µeq/L	Br- mg/L	Dilution Factor
-0.55	7.1	137.2	215.2	23.0	39.9	15.1	NA	1
0.00	NA	NA	NA	NA	NA	NA	NA	NA
0.08	NA	NA	NA	NA	NA	NA	NA	10
0.25	14.3	124.8	195.7	54.3	42.9	13.3	NA	10
0.58	7.1	62.4	53.0	14.0	21.0	3.6	0.9	10
1.46	NA	NA	NA	NA	NA	NA	NA	10
1.96	NA	NA	NA	NA	NA	NA	NA	8
2.96	NA	NA	NA	NA	NA	NA	NA	2
6.34	NA	NA	NA	NA	NA	NA	NA	10
7.20	28.6	49.9	NA	NA	NA	NA	NA	1
12.13	NA	NA	NA	NA	NA	NA	21.6	10
12.61	NA	NA	NA	NA	NA	NA	NA	10
13.01	NA	NA	NA	NA	NA	NA	NA	8
13.51	14.3	37.4	356.5	101.7	77.0	16.6	52.0	2
14.49	NA	NA	NA	NA	NA	NA	NA	8
27.32	NA	NA	316.1	76.3	60.3	29.1	26.5	4
35.32	28.6	99.8	229.6	62.5	65.9	23.5	NA	NA

Cup lysometer 12, Podzol profile E-Horizon, 4 cm

Time Day	Samp.In ml/day	pH	Temp. deg.C	Cond µS/cm	F-tot µM	TOC mgC/L	ALa µM	Alo µM	Ali µM	Al3+ µM
-0.55	487	4.34	11.3	48.4	3.42	4.7	33.7	7.9	25.8	20.1
0.00	792	4.34	11.4	59.1	3.79	5.0	33.6	8.2	25.4	19.7
0.08	702	4.29	11.1	59.5	4.11	4.8	29.7	9.6	20.0	14.6
0.25	456	4.20	10.5	102.1	7.58	3.9	96.7	10.5	86.2	73.3
0.46	368	4.20	11.2	124.2	NA	4.0	121.1	11.7	109.4	94.7
0.58	405	4.15	9.1	123.7	8.21	3.8	115.8	8.1	107.7	94.3
0.96	272	4.21	8.2	121.7	8.53	4.2	108.8	9.3	99.5	85.7
1.21	204	4.22	6.7	116.9	8.21	4.1	59.9	7.4	52.6	41.9
1.46	286	4.17	5.7	113.4	7.05	7.2	57.0	7.4	49.5	40.1
1.96	111	4.27	6.7	109.5	6.79	4.4	92.1	8.7	83.5	72.0
2.96	61	4.28	11.0	103.0	6.47	4.6	85.8	10.2	75.6	63.6
4.41	23	4.24	7.8	117.2	7.89	4.3	99.5	7.0	92.5	79.4
6.34	70	4.24	7.9	111.2	7.74	4.4	93.6	7.0	86.6	73.9
7.20	12	4.48	8.8	139.4	NA	4.1	138.0	8.2	129.8	108.8
12.61	286	4.13	8.0	323.0	17.89	3.9	325.8	19.6	306.2	278.2
13.05	284	4.15	7.6	276.0	13.37	4.2	221.7	14.5	207.2	184.2
13.51	163	4.19	5.0	213.0	9.53	4.7	157.5	11.8	145.7	130.2
14.49	215	4.23	3.5	187.0	8.63	4.8	137.9	10.6	127.3	112.2
27.32	123	4.34	16.0	91.2	NA	6.8	44.7	8.7	36.0	27.8
35.32	56	4.55	24.4	75.4	3.47	6.5	30.0	NA	NA	NA

Cup lysometer 12, Podzol profile E-Horizon, 4 cm

Time Day	NO- µeq/L	SO-- µeq/L	Na+ µeq/L	Mg++ µeq/L	Ca++ µeq/L	K+ µeq/L	Br- mg/L	Dilution Factor
-0.55	7.1	112.3	756.6	56.8	71.9	5.9	NA	2
0.00	NA	NA	NA	NA	NA	NA	NA	10
0.08	NA	NA	NA	NA	NA	NA	NA	8
0.25	NA	NA	NA	NA	NA	NA	NA	10
0.46	28.6	25.0	1721.8	138.3	95.8	9.2	44.0	10
0.58	NA	NA	NA	NA	NA	NA	NA	4
0.96	NA	NA	NA	NA	NA	NA	NA	10
1.21	NA	NA	NA	NA	NA	NA	NA	10
1.46	7.1	99.8	57.4	15.6	29.9	14.8	NA	8
1.96	NA	NA	NA	NA	NA	NA	NA	8
2.96	NA	NA	NA	NA	NA	NA	NA	8
4.41	NA	NA	NA	NA	NA	NA	NA	10
6.34	NA	NA	NA	NA	NA	NA	NA	10
7.20	NA	NA	NA	NA	NA	NA	49.0	10
12.61	7.1	12.5	417.4	138.0	135.5	25.8	145.0	8
13.05	NA	NA	NA	NA	NA	NA	NA	4
13.51	NA	NA	NA	NA	NA	NA	NA	4
14.49	7.1	99.8	99.6	27.2	25.9	2.6	NA	8
27.32	NA	NA	417.4	34.6	27.7	11.5	17.0	8
35.32	21.4	168.4	203.5	64.2	70.4	6.9	NA	10

Cup lysometer 13, Podzol profile Bhs-Horizon, 17 cm

Time Day	Samp.In ml/day	pH	Temp. deg.C	Cond µS/cm	F-tot µM	TOC mgC/L	ALa µM	Alo µM	Ali µM	Al3+ µM
-0.55	656	4.56	11.1	43.5	3.58	2.9	41.0	6.4	34.6	26.3
0.00	4776	4.53	11.2	44.7	3.63	3.0	40.5	6.1	34.3	26.2
0.08	2196	4.45	11.5	44.5	3.63	2.9	36.3	7.0	29.3	22.4
0.17	3000	4.51	10.9	44.1	3.53	3.0	39.4	6.3	33.1	25.5
0.25	3192	4.44	11.2	45.5	3.53	3.0	41.2	6.4	34.9	27.5
0.33	1240	4.54	10.3	44.5	3.42	3.0	41.2	7.0	34.2	26.5
0.46	1928	4.52	10.4	45.0	3.47	2.9	41.2	6.3	35.0	27.2
0.58	592	4.72	8.6	43.2	3.47	2.9	40.8	5.2	35.5	26.5
0.96	736	4.61	8.2	43.3	3.53	2.9	42.1	5.1	37.0	28.8
1.21	400	4.6	7.2	43.4	3.68	2.9	26.6	4.9	21.6	15.6
1.46	424	4.56	5.9	44.4	3.47	2.9	36.0	5.3	30.7	24.2
1.96	208	4.61	8.0	42.9	3.63	2.9	42.3	5.1	37.2	28.9
2.46	172	4.63	6.9	42.9	3.68	2.9	58.6	7.8	50.8	40.8
2.96	83	4.62	8.6	42.5	3.53	3.0	40.5	5.9	34.6	26.6
4.41	45	4.38	10.1	52.3	NA	3.1	41.6	5.5	36.1	28.3
5.46	128	4.67	7.7	42.0	3.53	NA	40.7	4.9	35.8	27.4
6.34	152	4.63	8.0	43.0	3.53	3.0	40.4	5.1	35.3	27.2
7.20	11	4.75	4.2	40.0	3.79	3.0	40.7	4.6	36.0	27.7
12.13	449	5.05	8.6	39.4	3.68	3.2	38.2	5.4	32.8	20.0
12.61	594	4.86	7.6	40.2	3.63	3.1	40.7	5.5	35.2	25.0
13.05	1454	4.64	7.8	46.2	4.11	2.9	48.1	5.6	42.5	32.9
13.26	380	4.72	7.5	48.5	NA	3.0	53.6	5.2	48.4	36.4
13.51	480	4.79	8.2	44.1	3.79	3.1	44.7	6.3	38.4	28.0
14.03	480	4.78	5.5	41.9	3.74	3.1	42.0	5.2	36.8	27.8
14.49	257	4.66	3.5	44.1	3.89	2.9	42.4	4.8	37.6	29.9
27.32	45	4.52	20.3	59.3	NA	2.7	67.4	5.9	61.5	42.8
35.32	182	4.54	24.4	51.9	NA	3.0	46.4	4.7	41.6	25.9

Cup lysometer 13, Podzol profile Bhs-Horizon, 17 cm

Time Day	NO- µeq/L	SO-- µeq/L	Na+ µeq/L	Mg++ µeq/L	Ca++ µeq/L	K+ µeq/L	Br- mg/L	Dilution Factor
-0.55	NA	NA	NA	NA	NA	NA	NA	1
0.00	NA	NA	NA	NA	NA	NA	NA	1
0.08	NA	NA	NA	NA	NA	NA	NA	4
0.17	NA	NA	NA	NA	NA	NA	NA	2
0.25	NA	NA	NA	NA	NA	NA	NA	2
0.33	NA	NA	NA	NA	NA	NA	NA	4
0.46	NA	NA	NA	NA	NA	NA	NA	2
0.58	NA	NA	NA	NA	NA	NA	NA	2
0.96	NA	NA	NA	NA	NA	NA	NA	4
1.21	NA	NA	NA	NA	NA	NA	NA	4
1.46	NA	NA	NA	NA	NA	NA	NA	2
1.96	NA	NA	NA	NA	NA	NA	NA	4
2.46	NA	NA	NA	NA	NA	NA	NA	8
2.96	NA	NA	NA	NA	NA	NA	NA	4
4.41	NA	NA	NA	NA	NA	NA	0.2	8
5.46	NA	NA	NA	NA	NA	NA	NA	8
6.34	NA	NA	NA	NA	NA	NA	NA	4
7.20	NA	NA	NA	NA	NA	NA	NA	10
12.13	7.1	143.5	282.6	65.0	52.9	6.7	0.2	2
12.61	NA	NA	NA	NA	NA	NA	NA	2
13.05	NA	NA	NA	NA	NA	NA	NA	1
13.26	21.4	112.3	140.5	32.9	31.2	1.4	3.3	8
13.51	NA	NA	NA	NA	NA	NA	NA	1
14.03	NA	NA	NA	NA	NA	NA	NA	2
14.49	7.1	112.3	87.4	23.9	16.5	1.5	NA	4
27.32	NA	NA	NA	NA	NA	NA	3.1	20
35.32	NA	NA	NA	NA	NA	NA	4.2	3

Cup lysometer 14, Podzol profile Bs-Horizon, 23 cm

Time Day	Samp.In ml/day	pH	Temp. deg.C	Cond µS/cm	F-tot µM	TOC mgC/L	ALa µM	Alo µM	Ali µM	Al3+ µM
-0.55	590	4.52	10.8	44.7	NA	3.6	39.5	7.2	32.3	24.3
0.00	5508	4.49	11.0	47.8	NA	3.6	39.8	7.2	32.6	24.7
0.08	3000	4.46	11.1	45.1	NA	3.7	39.3	7.4	31.8	24.2
0.17	4968	4.45	10.9	46.1	NA	3.7	39.8	7.1	32.7	25.1
0.25	5676	4.46	10.5	46.8	NA	3.7	39.6	7.5	32.1	24.6
0.33	3104	4.48	10.1	46.2	NA	3.6	40.0	7.4	32.6	25.0
0.46	3344	4.48	9.2	46.2	NA	3.5	40.0	7.4	32.6	25.1
0.58	1293	4.57	8.5	45.1	NA	3.6	38.7	6.0	32.7	24.8
0.96	1972	4.53	8.5	45.5	NA	3.6	39.0	6.0	33.0	25.3
1.21	904	4.55	6.8	44.6	NA	3.7	33.9	6.0	27.8	21.2
1.46	838	4.59	6.4	44.9	NA	3.5	39.1	6.2	32.9	25.3
1.96	132	4.55	8.0	45.9	NA	3.6	41.9	5.4	36.5	28.2
2.46	872	4.56	6.7	45.2	NA	3.6	39.0	6.7	32.2	24.8
2.96	218	4.53	8.7	45.5	NA	3.7	39.1	6.2	32.9	25.2
4.41	126	4.78	9.7	41.6	NA	3.7	37.9	6.5	31.4	21.8
5.46	357	4.54	8.2	44.5	NA	3.6	39.6	6.5	33.1	25.4
6.34	152	4.58	7.9	44.5	NA	3.6	39.6	6.0	33.6	25.6
7.20	120	4.55	3.7	45.2	NA	3.7	35.0	6.7	28.3	22.1
9.28	64	4.58	5.3	44.7	NA	3.7	39.7	6.3	33.4	26.0
12.32	1495	4.67	6.8	42.4	NA	4.0	33.7	5.1	28.6	21.2
12.47	1989	4.58	7.4	44.3	4.11	3.6	40.9	6.5	34.4	26.7
12.61	1898	4.66	6.1	43.1	NA	3.6	39.8	6.9	32.9	24.9
12.84	2208	4.60	7.0	44.9	NA	3.7	40.2	6.7	33.5	25.6
13.05	2064	4.55	7.8	44.9	NA	3.7	40.9	6.8	34.1	26.3
13.26	1720	4.54	6.9	45.3	NA	3.7	40.7	6.6	34.0	26.4
13.51	893	4.57	8.2	45.3	NA	3.7	40.8	6.9	33.8	25.8
14.03	1091	4.56	5.1	45.2	NA	3.7	40.0	7.0	32.9	25.7
14.49	513	4.62	3.0	43.5	NA	3.6	40.0	6.8	33.2	26.0
27.32	357	4.56	17.0	43.9	NA	3.6	38.1	5.9	32.2	22.3
35.32	28	4.60	24.5	41.6	NA	3.3	NA	NA	NA	NA

Cup lysometer 14, Podzol profile Bs-Horizon, 23 cm

Time Day	NO- µeq/L	SO-- µeq/L	Na+ µeq/L	Mg++ µeq/L	Ca++ µeq/L	K+ µeq/L	Br- mg/L	Dilution Factor
-0.55	NA	NA	NA	NA	NA	NA	NA	1
0.00	NA	NA	NA	NA	NA	NA	NA	1
0.08	NA	NA	NA	NA	NA	NA	NA	2
0.17	NA	NA	NA	NA	NA	NA	NA	1
0.25	NA	NA	NA	NA	NA	NA	NA	1
0.33	NA	NA	NA	NA	NA	NA	NA	1
0.46	NA	NA	NA	NA	NA	NA	NA	1
0.58	NA	NA	NA	NA	NA	NA	NA	1
0.96	NA	NA	NA	NA	NA	NA	NA	1
1.21	NA	NA	NA	NA	NA	NA	NA	2
1.46	NA	NA	NA	NA	NA	NA	NA	1
1.96	NA	NA	NA	NA	NA	NA	NA	10
2.46	NA	NA	NA	NA	NA	NA	NA	1
2.96	NA	NA	NA	NA	NA	NA	NA	1
4.41	NA	NA	NA	NA	NA	NA	NA	4
5.46	NA	NA	NA	NA	NA	NA	NA	1
6.34	NA	NA	NA	NA	NA	NA	NA	4
7.20	NA	NA	NA	NA	NA	NA	NA	2
9.28	NA	NA	NA	NA	NA	NA	NA	2
12.32	NA	NA	NA	NA	NA	NA	NA	2
12.47	21.4	93.6	128.4	26.0	25.2	2.1	0.2	1
12.61	NA	NA	NA	NA	NA	NA	NA	1
12.84	NA	NA	NA	NA	NA	NA	NA	1
13.05	NA	NA	NA	NA	NA	NA	NA	1
13.26	NA	NA	NA	NA	NA	NA	NA	1
13.51	NA	NA	NA	NA	NA	NA	NA	1
14.03	NA	NA	NA	NA	NA	NA	NA	1
14.49	NA	NA	NA	NA	NA	NA	NA	1
27.32	NA	NA	NA	NA	NA	NA	NA	1
35.32	NA	NA	NA	NA	NA	NA	0.2	NA

Cup lysometer 15, Podzol profile B/C-Horizon, 32 cm

Time Day	Samp.In ml/day	pH	Temp. deg.C	Cond µS/cm	F-tot µM	TOC mgC/L	ALa µM	Alo µM	Ali µM	Al3+ µM
-0.55	831	4.43	11.0	46.9	NA	3.5	39.6	7.3	32.3	24.8
-0.07	5733	4.47	10.5	45.3	NA	3.7	38.7	7.6	31.1	23.7
0.00	6480	4.43	11.0	46.7	NA	3.6	39.3	7.4	31.8	24.4
0.08	5160	4.42	10.9	46.4	NA	3.6	38.8	7.0	31.8	24.5
0.17	5040	4.41	10.4	47.6	NA	3.6	39.1	7.2	31.9	24.7
0.25	5076	4.44	10.2	47.1	NA	3.6	39.8	7.2	32.5	25.1
0.33	3296	4.47	10.2	45.7	NA	3.6	39.6	7.4	32.1	24.6
0.46	3400	4.37	9.4	50.1	NA	3.6	39.2	7.3	31.9	25.0
0.58	776	4.49	8.4	46.6	NA	3.5	38.8	6.2	32.6	25.2
0.96	1872	4.52	8.0	45.8	NA	3.6	38.0	5.9	32.1	24.7
1.21	1968	4.51	6.7	45.8	NA	3.6	38.1	6.0	32.1	25.0
1.46	852	4.53	6.2	45.3	NA	3.6	38.6	6.4	32.2	25.1
1.96	178	4.52	7.7	45.8	NA	3.6	40.7	5.3	35.5	27.6
2.46	570	4.57	6.9	45.3	NA	3.6	39.3	6.4	32.9	25.3
2.96	336	4.55	8.7	45.5	NA	3.7	39.1	6.2	32.9	25.1
4.41	231	4.56	9.2	44.9	NA	3.6	40.8	6.3	34.5	26.2
5.56	466	4.51	8.0	45.0	NA	3.6	39.4	6.4	33.1	25.6
6.34	468	4.52	7.7	45.2	NA	3.6	39.0	6.5	32.5	25.1
7.20	178	4.55	3.0	45.9	NA	3.7	39.2	6.9	32.3	25.6
9.28	141	4.58	6.1	45.5	NA	3.7	39.2	6.5	32.8	25.3
12.13	1011	4.57	6.1	44.4	NA	3.6	39.5	6.0	33.5	26.0
12.32	1440	4.58	6.3	44.2	NA	3.8	39.5	6.3	33.2	25.6
12.47	960	4.71	7.6	42.6	4.00	3.8	44.1	6.5	37.6	28.0
12.61	1759	4.58	6.3	45.0	NA	3.6	40.4	6.7	33.7	26.1
12.84	2208	4.58	7.7	45.7	NA	3.6	40.7	6.7	34.0	26.0
13.05	2544	4.53	7.8	45.7	NA	3.8	41.0	6.5	34.5	26.7
13.26	694	4.55	8.3	45.6	NA	3.7	40.6	6.5	34.1	26.2
14.03	720	4.63	4.9	43.8	NA	3.8	39.0	6.9	32.1	24.7
14.49	712	4.58	2.6	44.3	NA	3.7	38.9	7.0	31.9	25.2
27.32	17	4.67	25.0	38.8	NA	3.3	NA	NA	NA	NA
35.32	35	4.59	24.4	43.4	NA	3.4	34.8	NA	NA	NA

Cup lysometer 15, Podzol profile B/C-Horizon, 32 cm

Time Day	NO- µeq/L	SO-- µeq/L	Na+ µeq/L	Mg++ µeq/L	Ca++ µeq/L	K+ µeq/L	Br- mg/L	Dilution Factor
-0.55	NA	NA	NA	NA	NA	NA	NA	1
-0.07	NA	NA	NA	NA	NA	NA	NA	1
0.00	NA	NA	NA	NA	NA	NA	NA	1
0.08	NA	NA	NA	NA	NA	NA	NA	1
0.17	NA	NA	NA	NA	NA	NA	NA	1
0.25	NA	NA	NA	NA	NA	NA	NA	1
0.33	NA	NA	NA	NA	NA	NA	NA	1
0.46	NA	NA	NA	NA	NA	NA	NA	1
0.58	NA	NA	NA	NA	NA	NA	NA	2
0.96	NA	NA	NA	NA	NA	NA	NA	1
1.21	NA	NA	NA	NA	NA	NA	NA	1
1.46	NA	NA	NA	NA	NA	NA	NA	1
1.96	NA	NA	NA	NA	NA	NA	NA	8
2.46	NA	NA	NA	NA	NA	NA	NA	1
2.96	NA	NA	NA	NA	NA	NA	NA	1
4.41	NA	NA	NA	NA	NA	NA	NA	2
5.46	NA	NA	NA	NA	NA	NA	NA	1
6.34	NA	NA	NA	NA	NA	NA	NA	1
7.20	NA	NA	NA	NA	NA	NA	NA	1
9.28	NA	NA	NA	NA	NA	NA	NA	1
12.13	NA	NA	NA	NA	NA	NA	NA	2
12.32	NA	NA	NA	NA	NA	NA	NA	2
12.47	14.3	162.2	125.9	26.5	39.4	4.5	0.2	4
12.61	NA	NA	NA	NA	NA	NA	NA	1
12.84	NA	NA	NA	NA	NA	NA	NA	1
13.05	NA	NA	NA	NA	NA	NA	NA	1
13.26	NA	NA	NA	NA	NA	NA	NA	1
14.03	NA	NA	NA	NA	NA	NA	NA	1
14.49	NA	NA	NA	NA	NA	NA	NA	1
27.32	NA	NA	NA	NA	NA	NA	NA	NA
35.32	NA	NA	NA	NA	NA	NA	0.2	10

Cup lysometer 21, Peat profile Of-Horizon, -45 cm

Time Day	Samp.In ml/day	pH	Temp. deg.C	Cond µS/cm	F-tot µM	TOC mgC/L	ALa µM	Alo µM	Ali µM	Al3+ µM
-0.55	776	4.24	10.7	47.8	3.05	4.4	25.8	6.7	19.1	14.7
-0.07	5431	4.24	11.0	47.1	3.21	4.1	26.3	6.7	19.6	15.1
0.00	3672	4.25	11.0	48.5	3.21	4.5	27.2	6.8	20.4	15.8
0.08	6072	4.06	11.0	116.4	6.84	3.8	75.8	9.5	66.3	55.8
0.17	4368	4.00	10.5	161.6	7.84	3.6	85.4	11.6	73.8	62.5
0.25	4248	4.02	10.9	170.2	7.68	3.7	84.6	11.6	73.0	61.7
0.33	1620	4.05	9.8	162.9	7.26	3.8	81.4	10.7	70.7	59.9
0.58	1128	4.17	8.6	164.3	7.32	3.7	82.1	7.4	74.7	63.1
0.96	1724	4.13	8.2	152.1	7.00	3.7	77.5	6.9	70.5	59.8
1.21	1700	4.07	5.8	172.8	7.26	3.7	81.8	7.7	74.1	63.8
1.46	726	4.12	7.0	172.9	7.95	3.5	83.8	8.2	75.6	64.1
1.96	584	4.08	7.5	174.4	8.16	3.4	85.4	7.9	77.4	65.7
2.46	744	4.10	6.8	190.8	8.47	3.5	86.2	9.1	77.1	65.2
2.96	97	4.04	8.5	186.6	8.42	3.6	114.9	8.1	106.8	(93.7)
4.41	365	4.11	9.0	159.4	7.21	3.7	77.6	8.0	69.6	58.7
5.46	351	4.10	8.0	178.5	7.68	3.6	79.1	8.0	71.1	59.9
7.20	53	4.16	4.4	190.8	7.89	3.7	111.0	10.3	100.7	(88.7)
9.28	127	4.28	6.9	167.1	7.21	3.8	75.1	9.1	66.0	54.9
12.13	611	4.27	7.2	161.3	7.37	3.8	88.7	7.1	81.5	69.3
12.32	1241	4.22	6.2	192.8	8.05	3.9	106.2	10.0	96.2	83.1
12.47	651	4.17	9.0	224.0	8.95	3.5	133.6	9.3	124.2	108.1
12.61	1047	4.21	6.1	235.0	8.95	3.6	127.2	10.7	116.5	101.1
12.84	744	4.15	8.2	238.0	9.89	3.7	131.4	9.7	121.7	106.8
13.05	1824	4.27	8.4	102.3	5.05	4.3	52.3	7.6	44.7	36.6
13.26	900	4.25	7.6	107.2	4.63	4.4	52.7	7.4	45.3	37.9
13.51	778	4.25	8.4	112.3	4.95	4.4	51.5	7.7	43.8	36.1
14.03	120	4.17	5.9	140.5	6.71	NA	83.5	7.0	76.5	66.1
14.49	372	4.29	5.9	129.7	7.21	4.0	77.5	8.5	68.9	57.7
27.32	474	4.31	13.3	106.3	5.11	6.4	53.1	8.4	44.7	35.6

Cup lysometer 21, Peat profile Of-Horizon, -45 cm

Time Day	NO- µeq/L	SO-- µeq/L	Na+ µeq/L	Mg++ µeq/L	Ca++ µeq/L	K+ µeq/L	Br- mg/L	Dilution Factor
-0.55	7.1	112.3	695.7	87.2	70.4	14.8	NA	1
-0.07	NA	NA	NA	NA	NA	NA	NA	1
0.00	NA	NA	NA	NA	NA	NA	NA	1
0.08	NA	NA	NA	NA	NA	NA	NA	1
0.17	NA	NA	NA	NA	NA	NA	NA	1
0.25	7.1	87.3	406.1	66.5	46.6	4.6	70.0	1
0.33	NA	NA	NA	NA	NA	NA	NA	1
0.58	NA	NA	NA	NA	NA	NA	NA	1
0.96	NA	NA	NA	NA	NA	NA	NA	1
1.21	NA	NA	NA	NA	NA	NA	NA	1
1.46	NA	NA	NA	NA	NA	NA	NA	1
1.96	NA	NA	NA	NA	NA	NA	NA	1
2.46	NA	NA	NA	NA	NA	NA	NA	1
2.96	NA	NA	NA	NA	NA	NA	NA	4
4.41	NA	NA	NA	NA	NA	NA	NA	1
6.46	NA	NA	NA	NA	NA	NA	NA	1
7.20	NA	NA	NA	NA	NA	NA	NA	8
9.28	7.1	81.1	118.3	9.1	13.5	4.6	80.0	1
12.13	NA	NA	NA	NA	NA	NA	NA	8
12.32	NA	NA	NA	NA	NA	NA	NA	2
12.47	NA	NA	NA	NA	NA	NA	NA	8
12.61	NA	NA	NA	NA	NA	NA	NA	2
12.84	7.1	49.9	417.4	65.7	55.5	7.7	95.0	4
13.05	7.1	99.8	417.4	38.0	30.9	2.6	32.0	1
13.26	NA	NA	NA	NA	NA	NA	NA	2
13.51	NA	NA	NA	NA	NA	NA	NA	1
14.03	NA	NA	NA	NA	NA	NA	NA	10
14.49	NA	NA	NA	NA	NA	NA	NA	2
27.32	8.6	87.3	128.3	28.8	28.9	16.9	37.0	1

Cup lysometer 22, Peat profile Oh-Horizon, -25 cm

Time Day	Samp.In ml/day	pH	Temp. deg.C	Cond µS/cm	F-tot µM	TOC mgC/L	ALa µM	Alo µM	Ali µM	Al3+ µM
-0.55	904	4.35	11.1	44.1	3.63	3.8	28.8	6.2	22.6	17.2
-0.07	1997	4.43	10.6	42.1	3.58	3.9	28.6	6.7	21.8	16.3
0.08	2604	4.37	11.0	43.5	3.16	3.8	29.6	6.8	22.8	17.7
0.25	4824	4.37	10.5	44.3	3.26	3.9	29.6	6.9	22.7	17.6
0.33	3424	4.35	10.1	44.5	3.26	3.7	29.4	6.5	22.9	17.9
0.46	3352	4.31	9.8	46.2	3.21	3.8	29.2	6.7	22.5	17.7
0.58	896	4.43	8.6	44.2	3.42	3.8	28.9	5.4	23.6	18.3
0.96	1488	4.42	8.0	43.5	3.37	3.8	28.5	5.3	23.2	18.1
1.21	1680	4.41	5.9	44.2	3.42	3.8	27.5	5.4	22.1	17.2
1.46	510	4.47	7.3	42.2	3.40	3.8	24.4	5.8	18.6	13.8
1.96	700	4.38	7.3	45.3	3.37	3.8	30.5	5.6	24.9	19.8
2.46	350	4.44	6.8	44.3	3.42	3.7	29.9	6.1	23.7	18.5
2.96	312	4.34	8.8	46.9	3.42	4.2	29.6	5.6	24.1	19.0
4.41	76	4.19	9.5	57.5	3.58	3.9	32.2	6.2	26.1	21.0
5.46	326	4.42	8.2	44.4	3.37	4.0	29.1	6.0	23.1	17.9
6.34	562	4.39	7.7	44.8	3.47	3.9	29.7	5.8	24.0	18.7
7.20	26	(4.85)	9.0	43.6	4.05	4.1	32.7	6.5	26.2	17.4
12.61	1488	4.40	5.5	55.9	4.53	3.8	42.6	6.3	36.3	29.4
12.84	1872	4.37	7.4	61.3	4.84	3.8	47.9	6.6	41.3	33.8
13.05	2400	4.38	7.7	45.5	3.47	4.0	31.8	6.2	25.6	20.2
13.26	1680	4.41	7.5	45.4	3.47	3.9	30.7	6.0	24.7	19.4
13.51	710	4.44	7.6	44.4	3.47	3.9	31.7	5.8	25.9	20.4
14.03	949	4.41	3.6	45.0	3.53	3.9	30.3	6.0	24.3	19.4
14.49	728	4.41	2.4	44.4	3.58	3.9	30.5	6.1	24.4	19.5
27.32	419	4.32	13.9	82.7	6.32	3.4	63.2	5.7	57.4	45.6
35.32	126	4.31	24.4	69.9	6.53	3.5	52.6	3.7	48.9	34.9

Cup lysometer 22, Peat profile Oh-Horizon, -25 cm

Time Day	NO- µeq/L	SO-- µeq/L	Na+ µeq/L	Mg++ µeq/L	Ca++ µeq/L	K+ µeq/L	Br- mg/L	Dilution Factor
-0.55	NA	NA	NA	NA	NA	NA	NA	1
-0.07	NA	NA	NA	NA	NA	NA	NA	1
0.08	NA	NA	NA	NA	NA	NA	NA	2
0.25	NA	NA	NA	NA	NA	NA	NA	1
0.33	NA	NA	NA	NA	NA	NA	NA	1
0.46	NA	NA	NA	NA	NA	NA	NA	1
0.58	NA	NA	NA	NA	NA	NA	NA	1
0.96	NA	NA	NA	NA	NA	NA	NA	1
1.21	NA	NA	NA	NA	NA	NA	NA	1
1.46	NA	NA	NA	NA	NA	NA	NA	2
1.96	NA	NA	NA	NA	NA	NA	NA	1
2.46	NA	NA	NA	NA	NA	NA	NA	2
2.96	NA	NA	NA	NA	NA	NA	NA	1
4.41	NA	NA	NA	NA	NA	NA	NA	8
5.46	NA	NA	NA	NA	NA	NA	NA	1
6.34	7.1	93.6	102.2	30.5	30.4	6.1	NA	1
7.20	7.1	106.0	107.4	28.0	21.0	0.5	2.2	4
12.61	NA	NA	NA	NA	NA	NA	NA	1
12.84	7.1	49.9	146.0	35.5	25.3	3.4	9.6	1
13.05	7.1	99.8	87.4	23.9	16.0	1.0	NA	1
13.26	NA	NA	NA	NA	NA	NA	NA	1
13.51	NA	NA	NA	NA	NA	NA	NA	1
14.03	NA	NA	NA	NA	NA	NA	NA	1
14.49	NA	NA	NA	NA	NA	NA	NA	1
27.32	NA	NA	NA	NA	NA	NA	NA	1
35.32	7.1	25.0	238.1	36.9	33.0	3.9	15.0	8

Cup lysometer 23, Peat profile C-Horizon, 1 cm

Time Day	Samp.In ml/day	pH	Temp. deg.C	Cond µS/cm	F-tot µM	TOC mgC/L	ALa µM	Alo µM	Ali µM	Al3+ µM
-0.55	641	4.51	10.8	39.7	3.90	3.0	33.0	5.6	27.4	20.7
-0.07	4114	4.52	11.1	38.9	3.86	3.2	32.4	5.6	26.7	20.0
0.00	2940	4.46	10.9	42.6	3.93	3.0	33.6	5.7	27.9	21.4
0.08	2328	4.51	11.1	40.4	3.58	3.1	28.8	7.0	21.8	16.0
0.25	3888	4.36	10.6	46.0	3.95	3.0	34.2	5.9	28.3	22.2
0.33	1488	4.51	10.3	40.1	3.90	2.9	33.5	6.2	27.3	20.7
0.46	3136	4.52	9.6	40.0	3.94	2.9	34.0	5.9	28.1	21.4
0.58	875	4.67	8.3	38.8	3.96	2.9	33.1	4.6	28.5	21.1
0.96	1640	4.59	8.0	38.8	3.97	2.8	33.2	4.6	28.7	21.8
1.21	1704	4.57	6.0	39.8	3.95	2.9	33.0	4.7	28.3	22.0
1.46	532	4.63	7.3	38.3	3.69	2.9	28.6	4.9	23.8	17.7
1.96	284	4.62	8.0	38.3	4.23	2.8	38.0	4.9	33.1	25.3
2.46	474	4.66	6.8	38.6	3.99	2.9	34.0	4.9	29.0	21.9
2.96	257	4.61	8.9	38.8	4.03	2.8	34.3	4.7	29.6	22.3
4.41	481	4.66	8.9	39.1	4.05	2.9	34.9	5.0	29.9	22.2
5.46	584	4.62	8.1	39.1	4.01	2.8	34.1	4.7	29.4	22.2
6.34	585	4.59	7.8	39.3	4.08	2.8	35.1	4.7	30.4	23.3
7.20	139	4.72	4.0	37.7	4.01	2.9	34.5	5.2	29.2	22.3
9.28	89	4.69	6.5	37.4	4.05	2.8	34.9	4.9	30.0	22.6
12.32	1035	4.88	6.8	36.1	4.08	2.9	35.5	5.1	30.4	21.2
12.47	1783	4.74	7.1	38.3	4.05	2.9	34.8	4.9	30.0	22.1
12.61	1580	4.68	5.9	38.6	4.03	2.7	34.8	5.1	29.6	22.5
12.84	1632	4.71	7.9	38.1	3.95	2.8	33.8	5.0	28.8	21.2
13.05	2126	4.62	7.7	39.3	4.00	3.3	34.7	5.6	29.1	22.1
13.26	1520	4.61	7.3	39.9	3.98	3.2	34.2	5.5	28.7	21.9
13.51	768	4.61	8.0	39.6	3.99	3.0	34.3	5.3	29.0	22.0
14.03	622	4.67	4.8	38.2	4.00	2.8	34.3	5.3	29.1	22.3
14.49	712	4.61	2.2	39.6	4.03	2.9	35.0	5.4	29.6	23.5
27.32	419	4.66	14.6	38.7	4.00	2.7	33.4	4.3	29.1	19.9
35.32	266	4.67	24.4	37.1	3.96	2.8	32.4	4.0	28.4	15.5

Cup lysometer 23, Peat profile C-Horizon, 1 cm

Time Day	NO- µeq/L	SO-- µeq/L	Na+ µeq/L	Mg++ µeq/L	Ca++ µeq/L	K+ µeq/L	Br- mg/L	Dilution Factor
-0.55	NA	NA	NA	NA	NA	NA	NA	1
-0.07	NA	NA	NA	NA	NA	NA	NA	1
0.00	NA	NA	NA	NA	NA	NA	NA	2
0.08	NA	NA	101.9	24.7	22.1	2.4	0.2	4
0.25	NA	NA	NA	NA	NA	NA	NA	1
0.33	NA	NA	NA	NA	NA	NA	NA	4
0.46	NA	NA	NA	NA	NA	NA	NA	1
0.58	NA	NA	NA	NA	NA	NA	NA	1
0.96	NA	NA	NA	NA	NA	NA	NA	1
1.21	NA	NA	NA	NA	NA	NA	NA	1
1.46	NA	NA	NA	NA	NA	NA	NA	2
1.96	NA	NA	NA	NA	NA	NA	NA	4
2.46	NA	NA	NA	NA	NA	NA	NA	2
2.96	NA	NA	NA	NA	NA	NA	NA	1
4.41	NA	NA	NA	NA	NA	NA	NA	1
5.46	NA	NA	NA	NA	NA	NA	NA	1
6.34	NA	NA	NA	NA	NA	NA	NA	1
7.20	NA	NA	NA	NA	NA	NA	NA	1
9.28	NA	NA	NA	NA	NA	NA	NA	2
12.32	NA	NA	NA	NA	NA	NA	NA	4
12.47	NA	NA	NA	NA	NA	NA	NA	2
12.61	NA	NA	NA	NA	NA	NA	NA	1
12.84	7.1	43.7	103.5	24.6	32.8	1.7	0.2	1
13.05	NA	NA	NA	NA	NA	NA	NA	1
13.26	NA	NA	NA	NA	NA	NA	NA	1
13.51	NA	NA	NA	NA	NA	NA	NA	1
14.03	NA	NA	NA	NA	NA	NA	NA	1
14.49	NA	NA	NA	NA	NA	NA	NA	1
27.32	NA	NA	NA	NA	NA	NA	NA	1
35.32	NA	NA	113.8	23.6	31.2	1.1	0.2	2

APPENDIX C

Stream water chemical data from the streambed acidification experiments. Autumn 1987 and summer 1988 acidification.

Autumn 1987

Date	Hour	pH	pH	Temp.	Cond	F-tot	ALa	Alo	Ali	Al3+	Alr
dd.mmm.	hh.mm	Vier	Stopp	deg.C	µS/cm	µM	µM	µM	µM	µM	µM
25-Oct	10.45	4.91	4.91	6.1	37.8	NA	NA	NA	NA	NA	NA
25-Oct	13.30	4.91	4.91	6.1	37.8	10.74	18.2	4.0	14.1	37.7	NA
25-Oct	13.33	4.60	4.90	6.1	38.3	NA	NA	NA	NA	NA	NA
25-Oct	13.35	4.82	4.78	6.1	40.7	NA	19.2	4.1	15.1	NA	NA
25-Oct	13.40	4.79	4.76	6.1	40.8	NA	17.6	4.0	13.7	NA	NA
25-Oct	13.45	4.38	4.50	6.1	47.6	NA	18.9	3.7	15.2	NA	NA
25-Oct	13.47	4.03	4.28	6.1	57.3	10.79	20.0	3.7	16.3	59.1	NA
25-Oct	13.50	4.00	4.19	6.1	62.7	NA	20.8	3.6	17.2	NA	NA
25-Oct	13.51	4.00	4.17	6.1	65.1	NA	NA	NA	NA	NA	NA
25-Oct	13.52	4.00	4.12	6.1	66.6	NA	21.2	3.6	17.6	NA	NA
25-Oct	13.53	4.00	4.11	6.1	67.5	NA	NA	NA	NA	NA	NA
25-Oct	13.54	4.00	4.11	6.1	67.6	10.53	21.7	3.5	18.1	77.4	NA
25-Oct	13.55	4.01	4.10	6.1	68.3	NA	NA	NA	NA	NA	NA
25-Oct	13.56	4.01	4.11	6.1	68.3	NA	NA	NA	NA	NA	NA
25-Oct	13.57	4.01	4.10	6.1	68.6	NA	20.5	3.5	17.0	NA	NA
25-Oct	13.58	4.01	4.10	6.1	68.9	NA	NA	NA	NA	NA	NA
25-Oct	14.05	4.02	4.09	6.1	69.8	NA	NA	NA	NA	NA	NA
25-Oct	14.30	4.03	4.08	6.1	69.4	NA	20.4	3.5	16.9	NA	NA
25-Oct	15.20	4.09	4.11	6.1	67.4	NA	NA	NA	NA	NA	NA
25-Oct	16.00	4.12	4.12	6.1	64.5	10.47	19.2	3.5	15.7	57.5	NA

Date	Hour	Cl-	NO-	SO--	Na+	Mg++	Ca++	K+
dd.mmm.	hh.mm	µeq/L	µeq/L	µeq/L	µeq/L	µeq/L	µeq/L	µeq/L
25-Oct	10.45	NA	NA	NA	NA	NA	NA	NA
25-Oct	13.30	357.2	2.8	124.8	189.3	21.7	124.8	3.3
25-Oct	13.33	NA	NA	NA	NA	NA	NA	NA
25-Oct	13.35	NA	NA	NA	NA	NA	NA	NA
25-Oct	13.40	NA	NA	NA	NA	NA	NA	NA
25-Oct	13.45	NA	NA	NA	NA	NA	NA	NA
25-Oct	13.47	357.2	2.8	180.9	189.3	22.6	94.8	3.3
25-Oct	13.50	NA	NA	NA	NA	NA	NA	NA
25-Oct	13.51	NA	NA	NA	NA	NA	NA	NA
25-Oct	13.52	NA	NA	NA	NA	NA	NA	NA
25-Oct	13.53	NA	NA	NA	NA	NA	NA	NA
25-Oct	13.54	357.2	2.8	199.6	197.5	31.3	384.2	3.8
25-Oct	13.55	NA	NA	NA	NA	NA	NA	NA
25-Oct	13.56	NA	NA	NA	NA	NA	NA	NA
25-Oct	13.57	NA	NA	NA	NA	NA	NA	NA
25-Oct	13.58	NA	NA	NA	NA	NA	NA	NA
25-Oct	14.05	NA	NA	NA	NA	NA	NA	NA
25-Oct	14.30	NA	NA	NA	NA	NA	NA	NA
25-Oct	15.20	NA	NA	NA	NA	NA	NA	NA
25-Oct	16.00	357.2	2.8	174.7	197.5	30.9	(484.0)	3.6

Summer 1988

Date	Hour	pH	pH	Temp.	Cond	F-tot	ALa	Alo	Ali	Al3+	Alr
dd.mmm.hh.mm		Vier	Stopp	deg.C	µS/cm	µM	µM	µM	µM	µM	µM
Start	before	4.75	4.78	15.5	36.7	NA	11.9	4.1	7.8	NA	13.9
Start	in mix	4.30	NA	15.8	54.8	NA	11.6	3.0	8.6	NA	16.3
21-Jun	19.49	4.15	4.80	15.9	37.4	6.05	11.5	4.0	7.4	16.6	17.0
21-Jun	19.52	4.01	4.78	15.9	37.3	NA	11.0	4.8	6.1	NA	NA
21-Jun	19.55	4.17	4.78	15.8	36.9	NA	11.1	4.8	6.3	NA	NA
21-Jun	19.58	4.22	4.80	15.7	36.7	NA	11.2	4.7	6.5	NA	NA
21-Jun	20.01	4.24	4.80	15.8	36.5	NA	NA	3.9	NA	NA	NA
21-Jun	20.04	4.24	4.81	15.7	36.4	NA	11.1	4.6	6.5	NA	NA
21-Jun	20.07	4.23	4.81	15.5	36.4	NA	11.5	4.3	7.1	NA	NA
21-Jun	20.10	4.22	4.81	15.5	36.5	NA	11.3	4.0	7.3	NA	NA
21-Jun	20.13	4.21	4.81	15.5	36.5	NA	NA	NA	NA	NA	NA
21-Jun	20.16	4.20	4.82	15.5	36.3	NA	11.5	4.0	7.5	NA	NA
21-Jun	20.19	4.22	4.82	15.0	36.3	NA	NA	NA	NA	NA	NA
21-Jun	20.22	4.22	4.82	15.1	36.3	NA	10.9	4.2	6.7	NA	NA
21-Jun	20.25	4.22	4.83	14.9	36.2	NA	NA	NA	NA	NA	NA
21-Jun	20.28	4.21	4.82	14.9	36.4	NA	NA	NA	NA	NA	NA
21-Jun	20.31	4.21	4.81	15.1	36.4	NA	11.7	4.0	7.6	NA	NA
21-Jun	20.34	4.22	4.81	15.0	36.3	NA	NA	NA	NA	NA	NA
21-Jun	20.37	4.21	4.81	14.8	36.4	NA	NA	NA	NA	NA	NA
21-Jun	20.40	4.21	4.82	15.0	36.4	NA	10.8	5.0	5.8	NA	NA
21-Jun	20.43	4.23	4.82	14.8	36.6	NA	NA	NA	NA	NA	NA
21-Jun	20.46	4.20	4.83	14.9	36.4	NA	11.7	4.2	7.5	NA	NA
21-Jun	20.51	4.20	4.82	14.7	36.3	NA	12.0	4.1	7.9	NA	NA
21-Jun	21.00	4.21	4.81	14.6	36.7	NA	11.6	4.1	7.5	NA	NA
21-Jun	21.05	4.22	4.80	14.5	37.1	6.53	11.6	4.0	7.6	15.8	NA
21-Jun	21.10	4.21	4.78	14.7	37.6	NA	11.9	4.1	7.8	NA	NA
21-Jun	21.15	4.20	4.74	14.6	38.5	NA	12.4	4.0	8.4	NA	NA
21-Jun	21.20	4.21	4.70	14.7	39.7	NA	12.8	4.0	8.8	NA	NA
21-Jun	21.25	4.21	4.67	14.7	40.1	NA	12.2	4.3	7.9	NA	NA
21-Jun	21.30	4.20	4.64	14.6	40.8	NA	12.5	3.7	8.8	NA	NA
21-Jun	21.35	4.20	4.63	14.4	41.3	NA	12.5	3.8	8.7	NA	NA
21-Jun	21.40	4.20	4.61	14.8	42.0	6.47	12.7	3.9	8.8	25.5	NA
21-Jun	21.45	4.21	4.59	14.9	42.5	NA	13.1	4.0	9.1	NA	NA
21-Jun	21.50	4.21	4.57	15.1	43.1	NA	13.3	3.3	10.0	NA	NA
21-Jun	21.56	4.21	4.54	14.8	43.8	NA	13.4	3.4	9.9	NA	NA
21-Jun	22.00	4.21	4.53	14.6	44.2	NA	12.9	3.4	9.6	NA	NA
21-Jun	22.05	4.21	4.52	14.7	44.6	NA	12.9	3.4	9.5	NA	NA
21-Jun	22.10	4.21	4.52	14.6	45.1	NA	13.4	3.4	10.0	NA	NA
21-Jun	22.15	4.21	4.50	15.0	45.5	NA	13.3	3.4	9.9	NA	NA
21-Jun	22.20	4.21	4.49	14.6	45.9	NA	12.6	3.5	9.1	NA	NA
21-Jun	22.25	4.21	4.49	14.7	46.2	NA	12.9	3.3	9.6	NA	NA
21-Jun	22.30	4.21	4.48	14.7	46.5	NA	13.4	3.4	10.0	NA	NA
21-Jun	22.35	4.21	4.47	14.7	46.7	6.58	13.7	3.3	10.4	37.5	20.5
21-Jun	22.40	4.21	4.45	14.6	47.0	NA	13.5	3.2	10.3	NA	NA
21-Jun	22.45	4.20	4.45	14.7	47.2	NA	13.0	3.6	9.4	NA	NA
21-Jun	22.50	4.20	4.45	14.6	47.3	NA	13.6	3.3	10.3	NA	NA
21-Jun	22.55	4.20	4.45	14.9	47.4	NA	NA	NA	NA	NA	NA
21-Jun	23.00	4.20	4.45	14.9	47.5	NA	13.8	3.4	10.4	NA	NA
21-Jun	23.05	4.20	4.44	14.8	47.7	NA	NA	NA	NA	NA	NA
21-Jun	23.10	4.20	4.44	14.2	48.1	NA	13.3	3.4	9.9	NA	NA
21-Jun	23.15	4.20	4.43	14.2	48.0	NA	NA	NA	NA	NA	NA
21-Jun	23.20	4.20	4.43	14.2	48.3	NA	13.4	3.3	10.0	NA	NA
21-Jun	23.25	4.20	4.43	14.6	48.7	NA	NA	NA	NA	NA	NA
21-Jun	23.30	4.20	4.42	14.5	48.4	NA	13.5	3.3	10.2	NA	NA
21-Jun	23.35	4.20	4.42	14.4	48.6	NA	NA	NA	NA	NA	NA
21-Jun	23.40	4.20	4.42	14.3	48.8	NA	NA	NA	NA	NA	NA
21-Jun	23.45	4.20	4.41	14.4	49.0	NA	13.9	3.3	10.6	NA	NA
21-Jun	23.50	4.20	4.41	14.3	49.0	NA	NA	NA	NA	NA	NA
21-Jun	23.55	4.20	4.40	14.2	49.1	NA	NA	NA	NA	NA	NA
22-Jun	24.00	4.20	4.41	14.6	49.2	NA	13.7	3.2	10.5	NA	NA
22-Jun	0.10	4.20	4.40	14.5	49.8	NA	13.9	3.2	10.6	NA	NA
22-Jun	0.20	4.20	4.41	13.9	48.6	NA	NA	NA	NA	NA	NA
22-Jun	0.30	4.20	4.40	13.9	48.8	NA	NA	NA	NA	NA	NA
22-Jun	0.40	4.20	4.39	13.9	49.2	NA	NA	NA	NA	NA	NA
22-Jun	0.50	4.20	4.39	13.9	49.4	NA	NA	NA	NA	NA	NA
22-Jun	1.00	4.20	4.39	13.9	49.7	NA	14.1	4.4	9.8	NA	NA
22-Jun	1.10	4.20	4.38	13.8	48.6	NA	NA	NA	NA	NA	NA
22-Jun	1.20	4.20	4.39	14.0	49.7	NA	NA	NA	NA	NA	NA
22-Jun	1.30	4.20	4.38	13.9	50.1	NA	14.5	4.0	10.6	40.1	22.6

Date	Hour	pH	pH	Temp.	Cond	F-tot	ALa	Alo	Ali	Al3+	Alr
dd.mmm.	hh.mm	Vier	Stopp	deg.C	μS/cm	μM	μM	μM	μM	μM	μM
22-Jun	1.40	4.20	4.38	13.8	50.2	NA	NA	NA	NA	NA	NA
22-Jun	1.50	4.20	4.38	13.8	50.5	NA	14.9	4.3	10.6	NA	NA
22-Jun	4.10	4.23	4.32	13.5	52.9	6.58	14.5	3.5	11.0	43.8	22.0
22-Jun	6.50	4.26	4.31	13.8	53.8	NA	14.2	4.3	10.0	NA	NA
22-Jun	9.10	4.29	4.29	13.8	54.9	NA	15.0	4.3	10.7	NA	NA
22-Jun	16.30	4.36	4.36	13.8	51.3	5.79	14.0	4.4	9.7	38.7	19.4

Date	Hour	Cl-	NO-	SO--	Na+	Mg++	Ca++	K+
dd.mmm.	hh.mm	μeq/L	μeq/L	μeq/L	μeq/L	μeq/L	μeq/L	μeq/L
Start	before	NA	NA	NA	NA	NA	NA	NA
Start	in mix	NA	NA	NA	NA	NA	NA	NA
21-Jun	19.49	321.4	2.8	124.8	222.2	16.5	84.8	11.5
21-Jun	19.52	NA	NA	NA	NA	NA	NA	NA
21-Jun	19.55	NA	NA	NA	NA	NA	NA	NA
21-Jun	19.58	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.01	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.04	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.07	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.10	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.13	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.16	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.19	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.22	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.25	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.28	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.31	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.34	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.37	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.40	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.43	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.46	NA	NA	NA	NA	NA	NA	NA
21-Jun	20.51	NA	NA	NA	NA	NA	NA	NA
21-Jun	21.00	NA	NA	NA	NA	NA	NA	NA
21-Jun	21.05	300.0	2.8	112.3	214.0	14.3	74.9	7.9
21-Jun	21.10	NA	NA	NA	NA	NA	NA	NA
21-Jun	21.15	NA	NA	NA	NA	NA	NA	NA
21-Jun	21.20	NA	NA	NA	NA	NA	NA	NA
21-Jun	21.25	NA	NA	NA	NA	NA	NA	NA
21-Jun	21.30	NA	NA	NA	NA	NA	NA	NA
21-Jun	21.35	NA	NA	NA	NA	NA	NA	NA
21-Jun	21.40	300.0	2.8	137.2	222.2	22.2	(424.2)	9.0
21-Jun	21.45	NA	NA	NA	NA	NA	NA	NA
21-Jun	21.50	NA	NA	NA	NA	NA	NA	NA
21-Jun	21.56	NA	NA	NA	NA	NA	NA	NA
21-Jun	22.00	NA	NA	NA	NA	NA	NA	NA
21-Jun	22.05	NA	NA	NA	NA	NA	NA	NA
21-Jun	22.10	NA	NA	NA	NA	NA	NA	NA
21-Jun	22.15	NA	NA	NA	NA	NA	NA	NA
21-Jun	22.20	NA	NA	NA	NA	NA	NA	NA
21-Jun	22.25	NA	NA	NA	NA	NA	NA	NA
21-Jun	22.30	NA	NA	NA	NA	NA	NA	NA
21-Jun	22.35	300.0	2.8	143.5	214.0	16.5	179.6	7.2
21-Jun	22.40	NA	NA	NA	NA	NA	NA	NA
21-Jun	22.45	NA	NA	NA	NA	NA	NA	NA
21-Jun	22.50	NA	NA	NA	NA	NA	NA	NA
21-Jun	22.55	NA	NA	NA	NA	NA	NA	NA
21-Jun	23.00	NA	NA	NA	NA	NA	NA	NA
21-Jun	23.05	NA	NA	NA	NA	NA	NA	NA
21-Jun	23.10	NA	NA	NA	NA	NA	NA	NA
21-Jun	23.15	NA	NA	NA	NA	NA	NA	NA
21-Jun	23.20	NA	NA	NA	NA	NA	NA	NA
21-Jun	23.25	NA	NA	NA	NA	NA	NA	NA
21-Jun	23.30	NA	NA	NA	NA	NA	NA	NA
21-Jun	23.35	NA	NA	NA	NA	NA	NA	NA
21-Jun	23.40	NA	NA	NA	NA	NA	NA	NA
21-Jun	23.45	NA	NA	NA	NA	NA	NA	NA
21-Jun	23.50	NA	NA	NA	NA	NA	NA	NA
21-Jun	23.55	NA	NA	NA	NA	NA	NA	NA
22-Jun	24.00	NA	NA	NA	NA	NA	NA	NA
22-Jun	0.10	NA	NA	NA	NA	NA	NA	NA

Date dd.mmm	Hour hh.mm	Cl- µeq/L	NO- µeq/L	SO-- µeq/L	Na+ µeq/L	Mg++ µeq/L	Ca++ µeq/L	K+ µeq/L
22-Jun	0.20	NA	NA	NA	NA	NA	NA	NA
22-Jun	0.30	NA	NA	NA	NA	NA	NA	NA
22-Jun	0.40	NA	NA	NA	NA	NA	NA	NA
22-Jun	0.50	NA	NA	NA	NA	NA	NA	NA
22-Jun	1.00	NA	NA	NA	NA	NA	NA	NA
22-Jun	1.10	NA	NA	NA	NA	NA	NA	NA
22-Jun	1.20	NA	NA	NA	NA	NA	NA	NA
22-Jun	1.30	300.0	2.8	162.2	214.0	18.3	254.5	7.7
22-Jun	1.40	NA	NA	NA	NA	NA	NA	NA
22-Jun	1.50	NA	NA	NA	NA	NA	NA	NA
22-Jun	4.10	321.4	2.8	162.2	205.8	16.5	194.6	6.7
22-Jun	6.50	NA	NA	NA	NA	NA	NA	NA
22-Jun	9.10	NA	NA	NA	NA	NA	NA	NA
22-Jun	16.30	321.4	2.8	149.7	222.2	22.2	(509.0)	7.7

APPENDIX D

The pH to pAl^{3+} slope < 3.

Any discussion based on few data may seem far fetched. Though a seek to understand these data may give valuable suggestions of soil processes that need to be verified.

The wide range of pH observed in the podzol O/H-horizon causes a large variation in the degree of protonation of the functional sites and thereby in tertiary structure of the organic molecule. In addition the preferred initial exchange of Al from the weakest functional sites causes a shift to only more strongly complexed Al left on the exchange matrix. These changes may couse a decrease in the apperent pK_{sel} value of the exchanger and a typical increase in pQ is therefore observed with decreasing pH; -9.29 at pH 5.01 to -5.92 at pH 3.55. The constraint of cubic relationship in Eqn. 8 applies only to a solubility control with a constant pK_s value (J.Mulder pers. comm.) which is probably not the case for the organic complexity sites over the wide range of pH and pAl^{3+} values we observe.
Ignoring data from the day 13 and 14 event due to non equilibrium conditions, no large variation in pQ are found for "acid" samples with pH < 3.8, and during "normal" conditions with pH > 3.9. Though based on only three data points each, the relationship between H^+ and Al^{3+} were close to cubic during both the "acid" (Eqn. 13) and "normal" (Eqn. 14) condition.

Eqn. 13 $$pAl^{3+} - 2.4pH = -6.0$$

Eqn. 14 $$pAl^{3+} - 3.4pH = -7.0$$

No clear relationship is found between pH and pAl^{3+} in the peat organic layers. The cause for this non linearity may also be due to changes in the pK_{sel} value of the Al complexing sites. Detailed studies of variations in pQ reveal interesting factors concerning the peat response to a salt charge. Initially, due to depletion of the easely exchanged Al on the exchange sites by frequent rain on the previous days, pQ_{sel} was ≈ -7.7 . The response to the added salt was an exchange by the added Na^+ with H^+ and Al^{3+}. A close to cubic relationship between the increase in H^+ and Al^{3+} caused pQ_{sel} to remain close to -7.7 . During the hydrologic stable period until day 13 the $[H^+]$ decreased to below pre-salt values while $[Al^{3+}]$ remained generally stable. This may be due to slow reorganization of exchangeable and complexed Na, H and Al on the functional sites, creating a new equilibrium at a lower pK_{sel} value ($\approx$-8.4). This new equilibrium permited for the new major cubic release of H^+ and Al^{3+} during the onset of the event on day 13.

Figure captions

Figure 1. 3 dim. view and topographic map of Birkenes catchment with stream sampling locations (BIE 01, Stream-D) and salt addition plots (D1, D3). Insert shows approximate location in Norway.

Figure 2. Cup lysimeter data from the summer of 1988 showing soil solution pAli as a function of pH in the H-, O-, P-,E-, B- and C-horizon of the hillslope soils. Letters in graph refer to soil horizon (P=Peat). Natural Gibbsite solubility line using $pK_s=-8.77$ (25°C) is indicated.

Figure 3. Discharge ($L\ s^{-1}$) and concentrations of H^+ and Al^{3+} for the autumn of 1986.

Figure 4. 3-dim. plot of soil water bromide vs. time and the sampling location at the podzol profile. The plot is based on 18 data points and smoothed slightly.

Figure 5. Total organic carbon, $[Al^{3+}]$ and $[H^+]$ vs. time at the cup lysimeter 10 in the O/H-horizon of the podzol profile. TOC is given as µM Carbon.

Figure 6. Total organic carbon, $[Al^{3+}]$ and $[H^+]$ vs. time at the cup lysimeter 11 in the E-horizon of the podzol profile. TOC is given as µM Carbon.

Figure 7. Total organic carbon, $[Al^{3+}]$ and $[H^+]$ vs. time at the cup lysimeter 12 in the E-horizon of the podzol profile. TOC is given as µM Carbon.

Figure 8. Total organic carbon, $[Al^{3+}]$ and $[H^+]$ vs. time at the cup lysimeter 13 in the Bhs-horizon of the podzol profile. TOC is given as µM Carbon.

Figure 9. Total organic carbon, $[Al^{3+}]$ and $[H^+]$ vs. time at the cup lysimeter 14 in the Bs-horizon of the podzol profile. TOC is given as µM Carbon.

Figure 10. Total organic carbon, $[Al^{3+}]$ and $[H^+]$ vs. time at the cup lysimeter 15 in the B/C-horizon of the podzol profile. TOC is given as µM Carbon.

Figure 11. Plot of soil solution pH vs. pAl^{3+} at all sampling location in the podzol profile. Natural Gibbsite solubility line using $pK_s=-9.79$ (temp. corrected to mean temp.=8.1°C) is indicated.

Figure 12. 3-dim. plot of soil solution $pQ = pAl^{3+} - 3pH$ at all sampling location in the podzol profile. The plot is based on 128 data points and smoothed slightly.

Figure 13. 3-dim. plot of soil water Br^- vs. time and the sampling location at the peat profile. The plot is based on 11 data points and smoothed slightly.

Figure 14. Total organic carbon, [Al^{3+}] and [H^+] vs. time at the cup lysimeter 21 in the Of-horizon of the peat profile. TOC is given as µM Carbon.

Figure 15. Total organic carbon, [Al^{3+}] and [H^+] vs. time at the cup lysimeter 22 in the Oh-horizon of the peat profile. TOC is given as µM Carbon.

Figure 16. Total organic carbon, [Al^{3+}] and [H^+] vs. time at the cup lysimeter 23 in the C-horizon of the peat profile. TOC is given as µM Carbon.

Figure 17. Plot of soil solution pH vs. pAl^{3+} at all sampling location in the peat profile. Natural Gibbsite solubility line using $pK_s=-9.79$ (temp. corrected to mean temp.=8.1°C) is indicated.

Figure 18. 3-dim. plot of soil solution $pQ = pAl^{3+} - 3pH$ at all sampling location in the peat profile. The plot is based on 84 data points and smoothed slightly.

Figure 19. Chemical fluctuations during a autumn streambed acidification.

Figure 20. Chemical fluctuations during a summer streambed acidification.