Modelling the Effects of Acid Deposition:
Estimation of Long-Term Water Quality Responses in Forested Catchments in Finland

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A modelling study has been undertaken to investigate long-term changes in surface water quality in two contrasting forested catchments; Yli-Knuutila, with high concentrations of base cations and sulphate, in southern Finland; and organically rich, acid Liuhapuro in eastern Finland. The MAGIC model is based on the assumption that certain chemical processes (anion retention, cation exchange, primary mineral weathering, aluminium dissolution and CO_2 solubility) in catchment soils are likely keys to the responses of surface water quality to acidic deposition. The model was applied for the first time to an organically rich catchment with high quantities of humic substances. The historical reconstruction of water quality at Yli-Knuutila indicates that the catchment surface waters have lost about 90 μeq l^{-1} of alkalinity in 140 years, which is about 60% of their preacidification alkalinity. The model reproduces the declining pH levels of recent decades as indicated by paleoecological analysis. Stream acidity trends are investigated assuming two scenarios for future deposition. Assuming deposition rates are maintained in the future at 1984 levels, the model indicates that stream pH is likely to continue to decline below presently measured levels. A 50% reduction in deposition rates would likely result in an increase in pH and alkalinity of the stream, although not to estimated preacidification levels. Because of the high load of organic acids to the Liuhapuro stream it has been acid before atmospheric pollution; a decline of 0.2 pH-units was estimated with increasing leaching of base cations from the soil despite the partial pH buffering of the system by organic compounds.

Introduction

There are two basic methods for relating the response of surface waters to acid deposition. The first is an empirical approach whereby extrapolations from present conditions are made using assumed relationships among pH and ionic concentrations of rainfall; and pH, alkalinity, and sulphate concentration of surface waters (*e.q.* Henriksen 1979; Church and Galloway 1984). The second method utilizes process-oriented models of hydrology and geochemistry to make the quantitative linkage between atmosheric deposition and water chemistry (*e.q.* Chen *et al.* 1979; Christophersen and Wright 1981; Booty and Kramer 1984; Schnoor *et al.* 1984; Christophersen *et al.* 1984; Cosby *et al.* 1985a, 1985b, 1986; Whitehead *et al.* 1986; Neal *et al.* 1986).

A critical question in any attempt to·predict future water quality changes is how quickly and to what extent the physical/chemical characteristics of the catchment control water quality response to changes in atmospheric deposition. This question is best addressed through the second method.

Certain chemical processes are assumed to be likely keys to the responses of surface water quality to acidic deposition. These processes include:

1) Anion retention by soils (*e.q.* soil sulphate adsorption).
2) Cation exchange by catchment soils.
3) Alkalinity generation by carbonic acid dissociation (resulting from elevated partial pressure of CO_2 in soils).
4) Dissolution of aluminium minerals and mobilization of aluminium.
5) Weathering of minerals as a source of base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+).

The MAGIC model (Model Acidification of Groundwater In Catchments) is based on mathematical representations of those processes (Cosby *et al.* 1985a). The model is conceptually simple with regard to spatial heterogeneity in the catchment. The model contains three compartments (Fig. 1) which are assumed to be internally homogeneous. This assumption implies that vertical stratification in the soils in the catchment is unimportant or, equivalently, that all water reaching the stream contacts and has its chemical quality determined by a single layer within the soil column. While this assumption is probably overly restrictive in a model intended to reproduce short-term (daily to weekly) water quality responses, the purpose of this study is to estimate long-term (*i.e.* decades) changes in annual average water quality.

In this paper a modelling exercise is undertaken for two contrasting conifer forest catchments in Finland. Yli-Knuutila in southern Finland is characterized by well buffered soils; annual average pH values in the streamwater being over 6 with high concentrations of base cations and sulphate. Liuhapuro is characterized by peatlands and dilute, acid surface waters (annual average pH 4.2-4.4) with high quantities of humic substances. Average bulk deposition of sulphur at Liuhapuro
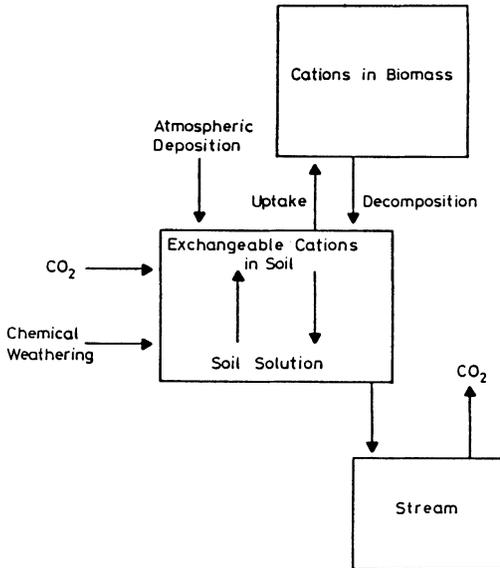
Fig. 1. Schematic view of the MAGIC model (Cosby *et al.* 1986).

during the years 1971-1982 was 0.56 g S $m^{-2}a^{-1}$, about 60% that of the deposition at Yli-Knuutila, 0.90 g S $m^{-2}a^{-1}$ (Järvinen 1986). Results are presented to compare the response of different surface waters to acid deposition and to test the relative importance of organic compounds.

Conceptual Basis of the Model

The most serious effects of acidic deposition on catchment surface water quality are thought to be decreased pH and alkalinity and increased base cation and aluminium concentrations. In keeping with an aggregated approach to modelling whole catchments, a relatively small number of important soil processes – processes that could be treated by reference to average soil properties – could produce these responses.

Atmospheric deposition, mineral weathering and exchange processes in the soil and soil water are assumed to be responsible for the observed surface water chemistry in a catchment. Alkalinity is generated in the soil water by the formation of bicarbonate from dissolved CO_2 and water

$$CO_2 + H_2O = H^+ + HCO_3^- \tag{1}$$

Bicarbonate ion concentrations in soil water are calculated using the familiar relationships between the partial pressure of CO_2 and hydrogen ion activity in the soil water

$$[\text{HCO}_3^-] = K_c \frac{P_{\text{CO}_2}}{[\text{H}^+]} \qquad (2)$$

where the combined constant K_c is known for a given temperature (Stumm and Morgan 1970). The free hydrogen ion produced (Eq. 1) reacts with an aluminium mineral (*e.g.* gibbsite) in the soil. The model assumes a cubic equilibrium relationship between Al and H^+.

Generally, the cation exchange sites on the soil matrix have higher affinity for the trivalent aluminium cation than for di- or monovalent base cations. An exchange of cations between the dissolved and adsorbed phase can be represented by reactions of the type

$$\text{Al}^{3+} + 3BCX(s) = \text{Al}X_3(s) + 3BC^+ \qquad (3)$$

$$2\text{Al}^{3+} + 3BCX_2(s) = 2\text{Al}X_3(s) + 3BC^{2+} \qquad (4)$$
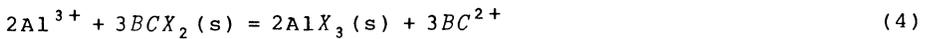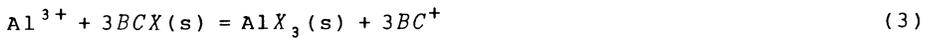
where X is used to denote an adsorbed phase and BC^+ and BC^{2+} represent base cations. The net result of these reactions is the production of alkalinity (*e.g.* $Ca(HCO_3)_2$). As CO_2 partial pressure or the availability of base cations on the soil exchange sites increases, the equilibrium reactions proceed further to the right hand side in each case resulting in higher alkalinity. When the solution is removed from the contact with the soil matrix and is exposed to the atmosphere (*i.e.* soil water enters the stream channel), the CO_2 partial pressure of the solution declines. The pH of the solution increases as CO_2 is lost to the atmosphere. Because the solution is no longer in contact with the soil matrix, cation exhange reactions no longer occur. The alkalinity and base cation concentrations are thus unchanged.

The process of acidification is controlled in part by the rate at which the exchangeable base cations in the soil are depleted. This in turn is affected by the rate of re-supply through weathering of base cations from primary minerals and the rate of loss through leaching of base cations from the soil. Leaching of base cations is affected mainly by the concentration of strong acid anions (*i.e.* SO_4^{2-}, Cl^-, NO_3^-) and base cations in the solution moving through the soil. As anions increase in concentration, there must be an equivalent increase in cation concentration to maintain a charge balance.

The model calculates the concentrations of three strong acid anions in both soil and streamwater (SO_4^{2-}, Cl^-, NO_3^-). Sulphate has an adsorbed phase in soil and the relationship between adsorbed sulphate (E_s, meq kg^{-1}) and the concentration of dissolved sulphate in soil water is assumed to follow a Langmuir isotherm (Singh 1984). If anions derived from atmospheric deposition are accompanied by H^+, as is the case for acid deposition, the excess H^+ will initially displace base cations from the soil exchange sites. As the base saturation declines, aluminium and hydrogen ions become increasingly important in maintaining the ionic charge balance in solution. The water delivered to the stream becomes more acidic as the acidic

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deposition persists. The model assumes that Al^{3+} and four base cations are involved in cation exchange between soil and soil solution. The parameters describing the cation exchange process in the model are the selectivity coefficients, S_{AlBC} (one coefficient for each base cation, Ca^{2+}, Mg^{2+}, Na^+, K^+) and the cation exchange capacity, CEC. Details of the equations and the model structure have been given by Cosby *et al.* (1985a).

Material and Methods

The precipitation stations Vihti for the catchment Yli-Knuutila and Valtimo for the catchment Liuhapuro from the network of Water and Environment Research Institute were used in this study. Precipitation chemistry was analyzed after a collection time of one month (Järvinen 1986).

Streamwater samples were collected from the measuring weirs concentrating sampling to spring and autumn periods of high flow. The number of water samples varied from 16 (Yli-Knuutila 1984) to 32 (Liuhapuro 1983) annually. All the analysis were made using the standard methods of water administration. The base cations were measured with flame-AAS; and anions Cl^- and SO_4^{2-} by automatic spectrophotometric methods. Alkalinity was titrated potentiometrically to the pH values of 4.5 and 4.2 with HCl (National Board of Waters 1981). Volume weighted averages for streamwater were calculated by weighting the observed concentration with the mean runoff of the observation day.

Exchangeable base cations in soil were analyzed by leaching them with a solution of ammonium acetate and acetic acid and measuring on an AAS. Exchangeable aluminium and hydrogen ions were leached to KCl solution and titrated (Nuotio *et al.* 1985).

Case 1 – Yli-Knuutila

The Yli-Knuutila conifer forest catchment (0.07 km^2) of southern Finland (Fig. 2) consists mainly of Norway spruce (*Picea abies*); the volume of growing stock is high, $162 \text{ m}^3/\text{ha}$. The catchment is rather steep, max and min altitudes are 92 and 42 m respectively, mean slope being 16.0 % (Seuna 1983). The soil at the Yli-Knuutila is sand and fine sand moraines for a notable part (67 %); one third of the catchment being silt and clay moraines (Mustonen 1963). There is no arable land or lakes in the catchment. The only anthropogenic factor affecting the stream water chemistry is atmospheric deposition. Chemical characteristics of precipitation and streamwater in 1984 are shown in Table 1.

Bulk precipitation was acid (pH 4.17) and had high concentrations of sulphate, $122 \text{ } \mu\text{eq } l^{-1}$, and nitrate, $60 \text{ } \mu\text{eq } l^{-1}$. Average bulk deposition of sulphate in that
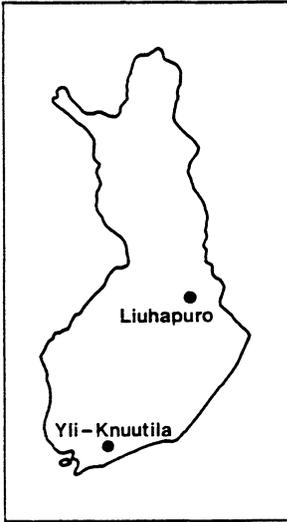
Fig. 2. Location of the study catchments Yli-Knuutila and Liuhapuro.

station was 2.8 g m^{-2}a^{-1} (0.9 g S m^{-2}a^{-1} during the years 1971-82 (Järvinen 1986).

Base cation concentrations in precipitation are fairly high. They were compared to the long-term averages at Vihti and the average concentrations measured from

Table 1 – Chemical characteristics of precipitation and streamwater at Yli-Knuutila. Values of bulk precipitation are annual averages for 1984, values of streamwater are volume weighted annual averages for 1984.

	Bulk precipitation μeq l^{-1}	Streamwater μeq l^{-1}
Ca^{2+}	49.4	400.3
Mg^{2+}	13.7	300.8
Na$^+$	28.8	166.7
K$^+$	5.4	28.2
NH$_4^+$	75.9	6.6
H$^+$	68.4	0.8
Cations	241.6	903.4
SO$_4^{2-}$	122.1	585.0
Cl$^-$	26.3	101.2[1]
NO$_3^-$	60.0	80.4
HCO$_3^-$	–	74.0
Anions	208.4	840.6
pH	4.17	6.10

1. 1985

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Table 2 − Annual averages of base cation concentrations in precipitation at Vihti in 1984 and 1972-85; and average values in 1976-84 in snowpack at Karkkila.

μeq l^{-1}	Vihti precipit. 1984	Vihti precipit. 1972-85	Karkkila snowpack 1976-84 (Soveri 1985)
Ca^{2+}	49.4	50.4	30.6
Mg^{2+}	13.7	17.5	12.3
Na^+	28.8	22.6	19.0
K^+	5.4	13.2	7.4

snowpack in 1976-84 at the Karkkila groundwater station 20 km from Vihti (Table 2) (Soveri 1985). The concentrations of magnesium and potassium in snowpack at Karkkila and in bulk precipitation at Vihti are of approximately the same order, but sodium and mainly calcium seem to be higher at Vihti, probably because of dust from the arable areas during the snow-free period.

High concentrations of calcium, magnesium and sulphate dominate the stream water chemistry. Sodium, chloride and nitrate also are relatively important on an equivalent basis. The sum of cations of stream water in 1984 (0.90 meq l^{-1}) was 3.7 times that of the incoming water (0.24 meq l^{-1}). Based upon an annual evapotranspiration loss of 73.6% in the same year, the concentration factor would be 3.8, which almost equals the difference of ionic strength between stream and precipitation water. Not only do concentrations in stream water change but the proportions of ionic or dissolved species change as well, indicating internal biological and chemical reactions in the catchment soils.

There is alkalinity left in the stream water volume weighted average being 0.074 meq l^{-1} in 1984. During the high flow alkalinity drops down to zero. pH values of down to 5.5 were observed during the snowmelt peak in spring 1985 volume weighted annual average being 5.9 in 1985 and 6.1 in 1984.

Ammonium nitrogen deposited into the catchment was used very effectively by the vegetation; the concentration in the stream water was less than one tenth of that of precipitation. Nitrate nitrogen behaved in a different way, however. Concentrations in the streamwater were higher than in precipitation; the main reasons being probably effective nitrification of ammonium to nitrate and also fairly high deposition of nitrate.

Model Inputs and Soil Parameters

Atmospheric deposition of base cations and strong acid anions was calculated using concentrations of each ion in precipitation and the precipitation volume. Annual precipitation at Yli-Knuutila in 1984 was 750 mm, of which 198 mm, 26.4%, appeared as runoff in stream.
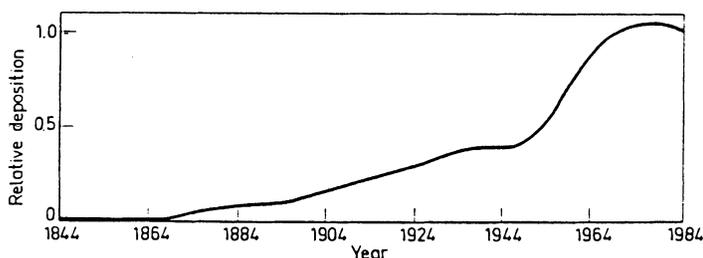
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Fig. 3. Shape used to scale the historical deposition sequence of the catchments. The curve is scaled to present day excess deposition above background deposition.

Sulphate deposition in excess of sea salt inputs was increased by a constant factor, 1.3, to account for dry deposition of anthropogenically derived sulphur. The factor was estimated smaller than the one estimated very near the coal fired power plant in the Marsjön catchment in southern Finland by Uotila (1987). The annual sulphur deposition in open area there was some 1.0 g m^{-2}, but including the dry deposition as the canopy throughfall the average deposition in the area totalled some 1.7 g S m^{-2}, *i.e.* 1.7 times the wet deposition (Uotila 1987).

A basic assumption of the modelling exercise was that the catchment was in steady state with constant background levels of deposition prior to 1844. A 140 yr deposition history was estimated for southern Finland based on estimate of changes in sulphur dioxide emissions in the whole of Europe and Finland (Kulmala 1985; Ministry of the Environment 1984). The deposition curve for Yli-Knuutila was assumed to have an identical shape to the emission data. The magnitude of the curve for each ion that increased in concentration in precipitation between 1844 and 1984 was scaled to this shape such that present day measured deposition rates of each ion at Yli-Knuutila were matched. The deposition of those ions that did not increase in concentration, *i.e.* chloride, were assumed to have flat trajectories. The shape of the deposition curve is given in Fig. 3. The background (1844) and present day (1984) concentrations of each ion in precipitation used in the model are given in Table 3.

Observed soil data in the Yli-Knuutila are given in Table 4. The observations were assumed to be representative in a catchment scale. Cation exchange capacity for Yli-Knuutila soils was set to 46 meq/100 g (Table 4). The initial base saturation of the soil was estimated from the measured data: $E_{Ca} = 20.0\%$, $E_{Mg} = 4.0\%$, $E_{Na} = 1.0\%$ and $E_K = 3.0\%$. Values for the selectivity coefficients were predetermined in the model from base cation weathering inputs and the initial base saturation of the soil. The values of the selectivity coefficients used for Yli-Knuutila in this study are:

$$S_{AlCa} = 10^{2.40} \qquad S_{AlK} = 10^{-3.63}$$
$$S_{AlMg} = 10^{4.21} \qquad S_{AlNa} = 10^{0.60}$$

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Table 3 – Present day (1984) and background (1844) concentrations of cations and anions in the deposition sequence used to drive the model for Yli-Knuutila.

	1984 μeq l^{-1} measured	1844 μeq l^{-1} calculated background
Ca^{2+}	49.4	1.0
Mg^{2+}	13.7	5.0
Na^+	28.8	22.6
K^+	5.4	0.5
NH_4^+	50.0[1]	0.1
H^+	61.1[2]	1.8
SO_4^{2-}	122.1	2.7
Cl^-	26.3	26.3
NO_3^-	60.0	2.0
pH	4.21	5.74

1. estimated
2. calculated by the model

Table 4 – The amount of exchangeable base cations, base saturation and CEC in the Yli-Knuutila catchment (Geological Survey of Finland, unpublished data).

	meq/100 g	%
Ca^{2+}	9.22	20.1
Mg^{2+}	1.73	3.8
Na^+	0.30	0.6
K^+	1.28	2.6
Al^{3+}	12.10	26.4
H^+	21.25	46.3
Base saturation		27.3
CEC	45.88	

The model assumes that there is a long-term net input of base cations from mineral weathering. Weathering rates are difficult to determine and they are treated as lumped, constant inputs to the model. The model is very sensitive to weathering rates, and we succeeded in calibrating the model for Yli-Knuutila only by using weathering rates chosen from a narrow range of values. Estimated weathering rates for Yli-Knuutila are:

Ca   17.0 meq/m^2/yr
Mg   10.5 meq/m^2/yr
Na   1.8 meq/m^2/yr
K   1.8 meq/m^2/yr

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Two scenarios are used for projecting future water quality in Yli-Knuutila. The first scenario assumes continued deposition at current (1984) rates for the next 140 years. The second scenario assumes a 50 % reduction of the deposition in excess of sea salts during the next 20 years.

Results and Discussion – Case 1

Volume weighted annual concentrations of variables estimated by the model for 1984 can be compared with those measured at Yli-Knuutila in 1984 (Table 5). The historical reconstruction of water quality at Yli-Knuutila indicates that the catchment surface waters have lost 90 µeq l^{-1} of alkalinity, which is about 60 % of their preacidification alkalinity, in 140 yrs (Table 5, Fig. 4). That estimate is about the same as average estimate of acidification in the small clearwater forest lakes of the southern coastal area in Finland (Kämäri 1985). During the same period the sum of base cations, SBC, has increased up to three times from the preacidification background value (Fig. 5). The increase in SBC is due to increased leaching of base cations from the soil exchange sites mainly due to increased quantities of sulphate passing through the soil layers and also due to increased inputs of base cations in precipitation. The importance of sulphate anions for transport of cations through the soil was pointed out more than 30 years ago by Gorham (1958) and has later been discussed by many authors, *e.g.* Seip (1980). In the small forested catchment next to Yli-Knuutila, named Teeressuonoja, a relationship was detected by Lepistö (1984) between deposition of sulphate and leaching of base cations, calcium and magnesium, on an annual basis.

The main problem in the long-term water quality models like MAGIC is the lack of long times series of data from natural systems for verifying the results. Such extended records exist for very few, if any, catchments. Paleoecological studies, however, offer a possibility to compare the simulation results to the changes in natural systems (*e.g.*, Wright *et al.* 1986). According to the model the decline in pH of streamwater at Yli-Knuutila has been 0.4 pH units, from 6.6 to 6.2 during the 140 yr period (Fig. 4). The majority of the decline has occurred in the last 30 years. Tolonen and Jaakkola (1983) have made diatom and chemical analyses of the sediments of four small oligohumous forest lakes in southern Finland near the catchment studied. They measured the pH of fresh sediment cores from the study lakes and distinguished two types; a great but gradual fall in pH from about 6.1 to about 5.0 (Orajärvi and Hauklampi); and a very abrupt fall from about 6.2 (or 6.4) to about 5.1 (5.2) (Sorvalampi and Häkläjärvi), *i.e.* 1.1-1.2 units. The main reason for a smaller decline in this study is probably the higher preacidification pH value and well buffered soils of Yli-Knuutila.

Pätilä (1982) studied water chemistry from 23 small oligotrophic lakes in Espoo and Vihti, in the same district as the catchment studied here. He found that pH-values in the lakes have decreased approximately 0.5 pH-units from the years 1965-

Table 5 – Model output of streamwater quality variables at different points in the simulation and a comparison with measured values in 1984 in Yli-Knuutila.

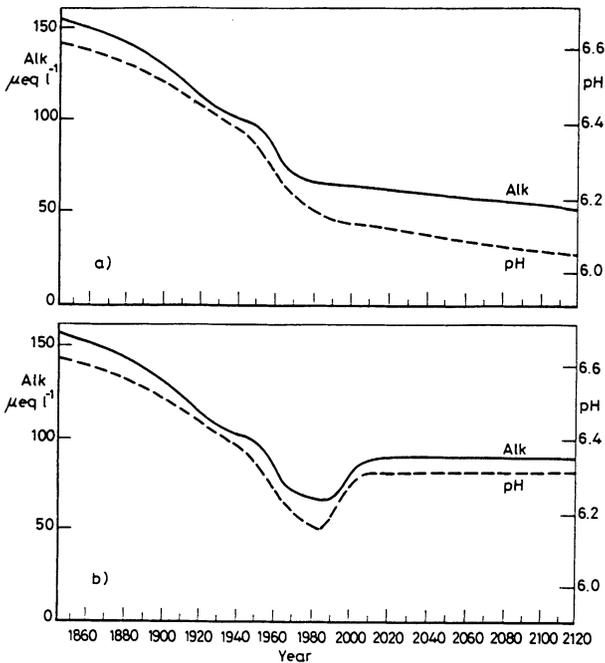| $\mu eq\ l^{-1}$	Model output 1844 background	Model output 1984	Yli-Knuutila measured 1984
H^+	0.3	0.6	0.8
Ca^{2+}	90	377	400
Mg^{2+}	72	281	301
Na^+	95	171	167
K^+	11	23	28
NH_4^+	0	6	7
SO_4^{2-}	13	603	585
NO_3^-	3	89	80
Cl^-	100	100	103[1]
HCO_3^-	152	65	74
Cations	268	858	904
Anions	268	857	841
pH	6.6	6.2	6.1

1. mean value of 1983 and 1985

Fig. 4.
Simulation of alkalinity and pH at Yli-Knuutila in response to two scenarios of future atmospheric deposition:
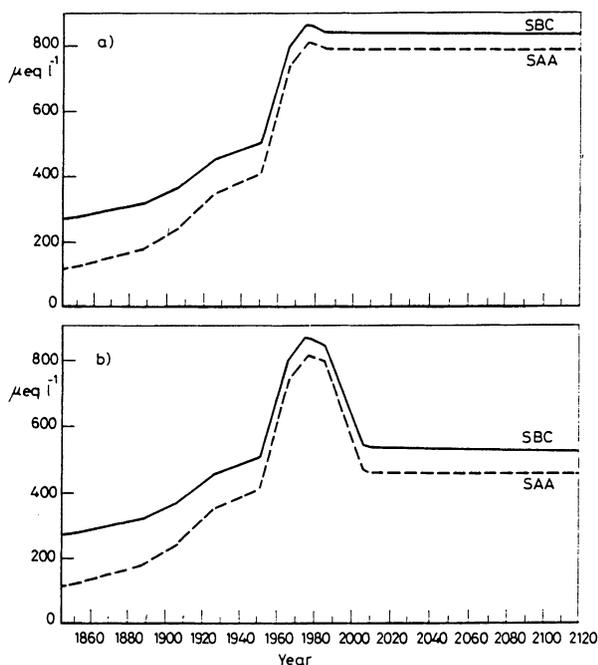a) no reduction;
b) 50% reduction in 1985-2005.

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Fig. 5. Simulation of the sum af base cation concentrations (SBC) and strong acid anion concentrations (SAA) at Yli-Knuutila in response to two scenarios of future atmospheric deposition: a) no reduction; b) 50 % reduction in 1985-2005.

67 to 1979-80 and seasonal changes have increased significantly compared to the 1960s.

Continued deposition at current levels results in further deterioration of the water quality at Yli-Knuutila; *i.e.* decreasing pH and alkalinity (Fig. 4) with steady conditions in the sum of base cations and strong acid anions (Fig. 5). A reduction by 50 % of deposition over a 20 yr period (1985-2005) results in an improvement of water quality with considerably smaller leaching of base cations from the forest soil. This is followed by reasonably steady conditions (Figs. 4, 5). Even a reduction of 50 % does not return the buffer capacity to preacidification levels.

Case 2 – Liuhapuro

Study Area
The Liuhapuro catchment (1.65 km^2) lies in the eastern Finland near the town of Nurmes (Fig. 2). Coniferous forests dominate in the area; volume of growing stock is 105 m^3/ha. Peatlands are typical in the district, the percentage in the catchment is 45. There is no arable land or lakes in the catchment and the only anthropogenic

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Table 6 – Chemical characteristics of bulk precipitation and streamwater at Liuhapuro. Values of bulk precipitation are annual averages for 1983, values of streamwater are volume weighted annual averages for 1983 and 1978-85.

μeq l^{-1}	Bulk precipit. 1983	Streamwater 1983	Streamwater 1978-85
Ca^{2+}	18.3	67.0	70.6
Mg^{2+}	4.7	47.1	50.0
Na^+	9.5	47.5	46.1
K^+	3.4	7.1	12.1
NH_4^+	13.0^3	0.4	–
H^+	34.8	54.1	54.8
Cations	83.7	223.2	233.6
SO_4^{2-}	53.3	82.3	59.4
Cl^-	8.5	14.1^1	25.4
NO_3^-	21.5	0.4	0.5
A^-	–	103.6^2	
Anions	83.3	200.4	
pH	4.46	4.27	4.26

1. 1984
2. estimated according Oliver *et al.* (1983)
3. estimated

factor affecting streamwater chemistry is atmospheric deposition. The mineral soil consists of silty and sandy moraines. Liuhapuro is also a control basin in the Nurmes-research of National Board of Waters and Environment and National Board of Forestry on hydrological and hydrochemical effects of silvicultural treatments.

Chemical characteristics of bulk precipitation and streamwater in Liuhapuro are shown in Table 6. Bulk precipitation was moderately acid with the average pH of 4.46 in 1983. Average bulk deposition of sulphur in 1971-82 was 0.56 g S $m^{-2}a^{-1}$ (Järvinen 1986), about 60 % that of the deposition at Yli-Knuutila.

Streamwater of Liuhapuro is more acid than precipitation and charactirized by high quantities of humic substances. Organic anions [A^-], are the main factors affecting to the difference between measured sum of cations and anions in streamwater. Estimate of organic anion concentration, [A^-], that results from the dissociation of humic material, HA, can be made from the measured pH and DOC values in highly colored natural waters, where most of the organic carbon is humic material (Oliver *et al.* 1983).

Volume weighted average of COD in 1983 was 42.2 mg O_2 l^{-1}. Dissolved organic carbon concentration, 17.2 mg l^{-1}, was calculated according the relationship from Finnish forest lakes and reservoirs given by Kortelainen *et al.* (1986). The DOC is

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then multiplied by 10 µeq/mg DOC to calculate the organic acid concentration, 172 µeq l^{-1}. Dissociation of humic material is assumed to follow a simple equation

$$HA \equiv H^+ + A^-$$ (5)

The mass action quotient of the fulvic and humic acids in the sample can be estimated using the empirical equation (Oliver *et al.* 1983)

$$pK = 0.96 + 0.90pH - 0.039(pH)^2$$ (6)

In 1983 mean pH of stream water was 4.27 so pK value estimated was 4.09. These values are then substituted into Eq. (7) (Oliver et al. 1983)

$$[A^=] = \frac{K[C_T]}{K + [H^+]}$$ (7)

C_T is the organic (fulvic + humic) acid concentration yielding a value 103.6 µeq l^{-1} for [A$^-$]. When adding organic acid concentration [A$^-$] to the sum of inorganic anions a good charge balance is observed (Table 6). There are also aluminium and silica components, however, which are affecting to the total sum of weak acid anions.

Organic anions contribute about 50 % of anions at Liuhapuro. This agrees well with Kerekes *et al.* (1986), who found that organic anions may constitute up to 50 % of the anions in colored surface water from peaty catchments in Nova Scotia, Canada.

Sulphate was clearly dominant inorganic anion, 82 µeq l^{-1} in 1983. Range of pH values was 4.0-5.8 with the lowest values occurring during the high flow. pH value of down to 3.9 was observed during the flow peak caused by autumn rains in 1984. Streamwater is rather dilute; the ionic sum of cations was 0.23 meq l^{-1} in 1983. Calcium was dominant cation, 67 µeq l^{-1} and the second important was hydrogen ion, 54 µeq l^{-1}.

Model Inputs and Soil Parameters

The year 1983 was selected for calibration of the model because of the most frequent data of sulphate in streamwater. From Table 6 can be seen that mean stream water chemistry in 1983 does not differ much from the mean values in the observation period 1978-85. Annual precipitation at Liuhapuro in 1983 was 766 mm, of which 480 mm, 63 %, was runoff.

Sulphate deposition in excess of sea salt inputs was increased by a constant factor, 1.1, (Yli-Knuutila 1.3) to account for dry deposition of anthropogenically derived sulphur. The same deposition curve (Fig. 3) was used for Liuhapuro as for Yli-Knuutila. The background (1843) and present day (1983) concentrations of each ion in precipitation are given in Table 7.

Background (1843) deposition inputs were calculated from the sea salt fraction

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Table 7 – Present day (1983) and background (1843) concentrations of cations and anions in the deposition sequence used to drive the model for Liuhapuro.

	1983 μeq l^{-1} measured	1843 μeq l^{-1} calculated background
Ca^{2+}	18.3	0.3
Mg^{2+}	4.7	1.6
Na^+	9.5	7.3
K^+	3.4	0.2
NH_4^+	13.0[1]	0.1
H^+	34.8	1.4
SO_4^{2-}	53.3	0.9
Cl^-	8.5	8.5
NO_3^-	21.5	1.5
pH	4.46	5.85

1. estimated

of current deposition at Liuhapuro. Nitrate was assumed to have a concentration of 1.5 μeq l^{-1} in background precipitation. Present day NH_4 concentration was reduced in the same way as at Yli-Knuutila to get a charge balance and the observed pH value for the model input precipitation. There is, however, some problems with contamination and accuracy of nutrient concentrations in the summer because of the long collection time, one month.

Soil parameters used in the model at Liuhapuro can be seen in Table 8. Maximum adsorption capacity of sulphate was assumed to be bigger than that at Yli-Knuutila. In many studies it has been noticed that peatlands are effective 'adsorbers' of sulphate (*e.q.* Braekke 1980). Microbial reduction of sulphate is, however, an important factor neutralizing acid deposition falling upon peatlands. CEC was assumed to be about the same as at Yli-Knuutila. This value, 50 meq/100 g soil, is typical of peaty podzols in Finland (*e.g.* Nysten and Hyyppä 1987). Equilibrium constant, K_{Al}, is lower than at Yli-Knuutila but still in the range of acceptable

Table 8 – Soil parameters used to drive the model for Liuhapuro

1.50	E_{mx}	Maximum adsorption capacity of sulphate meq kg^{-1}
100.00	C	Half saturation concentration, meq m^{-3}
50.00	CEC	Cation exchange capacity, meq/100 g
$10^{7.70}$	K_{Al}	Equilibrium constant
$10^{2.49}$	S_{AlCa}	Selectivity coefficient
$10^{2.44}$	S_{AlMg}	Selectivity coefficient
$10^{-1.53}$	S_{AlNa}	Selectivity coefficient
$10^{-3.63}$	S_{AlK}	Selectivity coefficient

values given by Cosby *et al.* (1985b). Model required lower K_{Al} value to give adequate simulation. This is reasonable since for the more acidic conditions gibbsite would not be expected in the soil. The lower value probably represents an ion exchange reaction within the soil or some other solubility control presently not identified. Carbon dioxide pressure in the soil was set to 0.02 atm, about 60 times atmospheric pressure.

In the model runs total organic acid concentration of 155 µeq l^{-1} was used instead of estimated concentration, 172 µeq l^{-1}. pK value of the fulvic and humic acids of 4.09 (Eq. 6) was used to describe the dissociation of humic material. The same values were used for soil and streamwater. Weathering rates were estimated in the same way as for Yli-Knuutila and they are for Liuhapuro:

Ca   18.0 meq/m^2/yr
Mg   12.0 meq/m^2/yr
Na   12.0 meq/m^2/yr
K   1.6 meq/m^2/yr

Estimates of weathering rates for calcium, magnesium and potassium are about the same for both catchments, for sodium the one for Liuhapuro is much higher.

Results and Discussion – Case 2

Concentrations of variables estimated by the model for 1983 can be compared with the volume weighted mean annual values of those variables measured at Liuhapuro (Table 9). The reconstructed trajectories of the pH, total stream base cation, SBC, and strong acid anion, SAA, concentrations (Fig. 6) all show accelerating rates of change in response to the increased atmospheric deposition of sulphate. The increase in SBC is due to increased leaching of base cations from the soil exchange sites in response to increased quantities of sulphate passing through the soil layers. Calcium and magnesium concentrations have increased 60-70% from the preacidification values estimated by the model. The increase in SAA is due to increased stream SO_4 concentration as deposition is increasing and the sulphate adsorption capacity of the soil begins to saturate.

Because of the high load of organic acids to the stream, it has been acid already before atmospheric pollution and the mean annual pH has not been much affected. According to the model there has, however been a decline of 0.2 pH-units. H$^+$ concentration is estimated to have increased 10 µeq l^{-1}, from 26 to 36 µeq l$^{"-1}$ by 1983. The addition of H_2SO_4 of atmospheric origin has increased the acidity of dilute, organic waters at Liuhapuro despite the effective buffering system of organic compounds.

Simola *et al.* (1985) had one highly coloured lake, Iso-Hanhijärvi (pH 4.9, colour 180 mg Pt/l) in their diatom analysis of ten small oligotrophic lakes in Finland. They found a naturally quite low pH-level with a temporarily elevated pH-regime around the turn of this century, and a recent slight decline. Without the temporari-

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Table 9 – Model output of streamwater quality variables at different points in the simulation, and a comparison with measured volume weighted mean values in 1983 at Liuhapuro.

$\mu eq\ l^{-1}$	Model output 1843 background	Model output 1983	Liuhapuro measured 1983
H^+	26	36	54
Ca^{2+}	38	65	67
Mg^{2+}	28	45	47
Na^+	37	47	48
K^+	4	5	7
NH_4^+	0	0	0
SO_4^{2-}	2	81	82
Cl^-	14	14	14[1]
NO_3^-	0	2	0
A^-	118	109	104[2]
Cations	133	198	223
Anions	134	206	200
pH	4.6	4.4	4.3

1. 1984
2. estimated according Oliver *et al.* (1983)

ly elevated pH-regime the reconstruction of pH agrees quite well with the pH history predicted for the highly organic surface waters made in this study. Wright *et al.* (1986) applied the MAGIC model to acid lake Hovvatn with original pH of 5.0 (paleolimnological reconstruction) and present day level of 4.3 to 4.5. The model indicated quite similar pH history except that the original pH was somewhat higher.
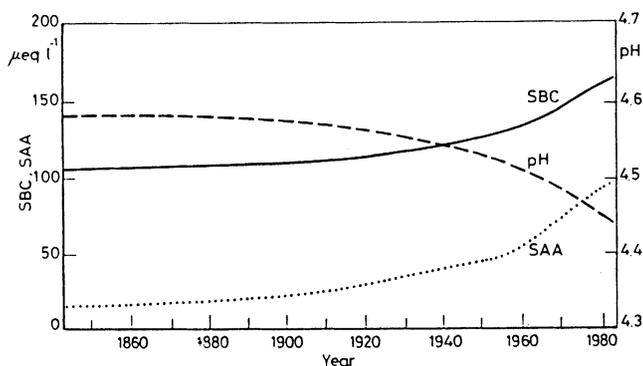

Fig. 6.
Model reconstruction of the sum of base cations (SBC), strong acid anions (SAA) and pH for the period 1843-1983 at Liuhapuro.

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Conclusions

Application of the model to a peaty catchment with high concentrations of organic acids in streamwater presents no difficulty. The model was capable of reconstructing streamwater chemistry in two very different types of catchments and surface waters. Similar success has been obtained applying the model to catchments in Scotland receiving large amounts of neutral sea salts (Cosby *et al.* 1986) and recently in Wales (Whitehead *et al.* 1987).

There has been a significant change in the quality of the surface waters of Yli-Knuutila with declining alkalinity (90 μeq l^{-1}) and increasing sulphate; together with the leaching of high quantities of base cations, mainly calcium and magnesium, from the soils. The response of the organic rich soils of Liuhapuro has been different, however. Liuhapuro was acid before the atmospheric pollution, a recent decline of 0.2 pH-units has been estimated with increasing leaching of base cations from the soils.

The accuracy of the model results, however, cannot be directly addressed except to say that values produced by the model for present day streamwater quality variables are consistent with the measurements available. This is a major problem inherent in all efforts to model acid deposition effects; lack of data needed for rigorous identification of model structures and estimation of parameter values. Our understanding of soil and surface water acidification by atmospheric deposition is improving as the results of process level field and laboratory experiments become available.

Catchment surface water is controlled by catchment soils and complex, process-oriented models of acidification thus contain soil and soil water variables that are infrequently measured in the field, or there may be point measurements, which are not spatially representative. On the other hand models of long-term responses can, strictly speaking, only be calibrated and verified using long time series data (decades) from natural systems, which exist for very few, if any, catchments. Despite the limitations, there is much that can be learned from the process of constructing and testing acidification models. We can conduct simulation experiments in which alternate model structures (or parameter values) are compared to each other. Speculative simulation exercises may also indicate new or different data that can be brought to bear on the problem (*e.g* Neal *et al.* 1986). Paleolimnological data such as diatom remains in lake sediments allow pH reconstruction, however, providing independent evidence by which the relationships between acid deposition, soil acidification and surface water acidification can be tested (*e.g* Wright *et al.* 1986).

Deposition of sulphate in Finland was clearly higher during the 1970s compared to the 1950s (Järvinen and Haapala 1980). There has been no distinct change in the air-borne sulphur load in southern Finland, however, since the beginning of the 1970s (Kulmala 1985). The paleolimnological works of Tolonen and Jaakkola (1983) and Simola *et al.* (1985) suggest that the levels of acidity have increased in

recent decades mainly in small oligotrophic, oligohumous lakes. The results here support these conclusions and give an indication of future acidity in surface waters.

Despite a 40% decrease of sulphur dioxide emission levels in Finland from 1980 to 1983, mainly due to drastic decrease in the use of heavy fuel oil (Kulmala 1985), a continuing decline in streamwater pH is predicted if further reductions in deposition are not achieved.

Acknowledgements

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