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# TOTAL ORGANIC CARBON IN STREAMWATER FROM FOUR LONG-TERM MONITORED CATCHMENTS IN NORWAY

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By linear regression analyses, flux, concentration, and net charge (NC in  $\mu\text{eq}/\text{mg C}$ ) of total organic carbon (TOC) have been related to different physico-chemical parameters present in air/precipitation and streamwater at four long-term monitored catchments in Norway, during the period 1986-1992. The catchments vary a lot with respect to annual water input, acid rain, and the streamwater concentration of TOC. Thus, relationships between concentration/NC of TOC and chemical compounds in precipitation and streamwater were often catchment-specific. However, seasonal climatic changes, like air temperature and hydrology, were found to be important for the concentration variations of TOC. The correlation between concentration of nonmarine base cations ( $\Sigma\text{BC}^*$ ) and concentration of TOC at the four sites was far more significant ( $r=0.86$ ) than the corresponding correlation between nonmarine sulphate ( $\text{SO}_4^*$ ) and  $\Sigma\text{BC}^*$  ( $r=0.57$ ). This indicates the important role of organic matter in weathering reactions in the catchment. Concerning weathering and cation leaching of aluminum, the correlation between concentration of total aluminum (RAL) and  $\text{SO}_4^*$  was far more significant ( $r=0.93$ ) compared with the corresponding correlation between RAL and TOC ( $r=0.40$ ). This should be expected, because a high concentration of  $\text{SO}_4^*$  means a low pH, which is needed to dissolve substantial amounts of Al from soils. The NC of TOC was found to be most affected by compounds in precipitation, primarily the inputs of sea salts. In the most acidified areas, the influence from strong acid inputs also affects the NC of TOC, but less significantly. The concentration of  $\text{Na}^+$  in precipitation is much higher and the variations much larger compared with the concentration of  $\text{H}^+$  in precipitation in the coastal areas, like Birkenes and especially Kaarvatn. Thus, it is reasonable that the variations in sea salt inputs (primarily NaCl) are more important for the temporary variation in NC of TOC compared with  $\text{H}^+$  ions at these sites. Only at Langtjern, the most TOC-influenced site, a significant and positive correlation was found between  $\text{H}^+$  and the concentration of TOC in streamwater. This indicates that at a certain TOC level, the weak organic acids may affect the streamwater pH. A comparison between measured and calculated concentrations of organic Al indicated that the dissociation constants (pK-values) of the organic acids present at Birkenes must be higher and/or the Al-complexing constants lower compared with the constants given by the programme. At the three other sites, it was the other way around. This may explain why a negative correlation between concentrations of TOC and labile Al was present at Birkenes, while the other sites exhibited a corresponding positive correlation with respect to labile Al or  $\Sigma\text{Al}^{*+}$ . The comparison also documented larger differences in these constants between the sites, compared with monthly variations in the constants at one single site.

## INTRODUCTION

It is well known that increased acidification of soil water causes increased mineral weathering, and that natural organic acids do catalyze these processes (Inoue and Wada 1971; Huang and Keller 1972; Boyle et al. 1974; Johnson et al. 1981; Wilson 1986;

Lundström 1990). Dissolved organic carbon not only affects the cation leaching in soils (Reuss 1980; Mollitor and Raynal 1982; Krug and Isaacson 1984), it also plays an important role in the acid/base chemistry in surface waters (Driscoll et al. 1989) and solubility control of Al in soil and surface waters

(Tipping and Hurley 1988). The increased mobilization of aluminum from edaphic to aquatic environments due to acidification (e.g., Magistad 1925; Scheider et al. 1975; Wicklander 1975; Wright et al. 1977; Dickson 1978) is of major importance, because dissolved Al is shown to be toxic to many biological species. Toxic effects of Al to soil biota were already documented at the beginning of this century, (e.g., Hartwell and Pember 1918; Magistad 1925; Hardy 1926). In 1928, Ebeling claimed that Al-ions are highly toxic to fish. Today it is well documented that the most toxic Al-forms in freshwaters are present in the inorganic low-molecular weight Al-fractions (Schofield 1977; Dickson 1978, Baker and Schofield 1982; Lydersen et al. 1990), or during the initial phase when these low-molecular weight inorganic forms start to polymerize (Rosseland et al. 1992; Pol  o et al. 1994). There are numerous factors which may influence the Al-toxicity on fish, but, in general, acute toxic effects are at inorganic dissolved Al-levels of 50 to 100  $\mu\text{g Al/L}$ . Humic organic Al-complexes, on the other hand, are shown to have no acute toxic effect on fish (Skogheim et al. 1986; Lydersen et al. 1990; Witters et al. 1990).

The direct effects of pH on the complexing properties of Al are important in understanding the Al-chemistry of humic-rich soils. At a soil pH of 4.5 to 5, humic materials complex most of the Al, as already shown in 1933 (Mattson and Hester 1933). However, organic Al-complexation decreases dramatically as pH decreases below 4.5, as both the solubility and the mobility of these complexes decrease as acidity further increases (Schnitzer and Hansen 1970; Ghosh and Schnitzer 1980; Ritchie and Posner 1982). Thus, inorganic, cationic Al accompanied with  $\text{SO}_4^{2-}$ , should normally be expected in water draining from organic-rich soils at pH 4 or lower.

For artificial, simple aqueous systems, where the metal source and the structure of the organic species are known, the coordination chemistry and the reaction kinetics are well understood (Martell and Calvin 1952). In natural systems where the metal substrates and the organic chelates are poorly defined, the chemical pathways for metal dissolution-chelation are less clear (Miller et al. 1986). In a soil system, Huang and Keller (1971; 1972) observed that organic acids increased the dissolution of metals (e.g. Al) in the presence of well-characterized silicate minerals, and a Si-rich residue was left behind (as in podzols). Correspondingly, several investigations conclude that the chelating effects of organic acids may influence the precipitation products of Al-hydroxides (Kwong and Huang 1977; Kwong and Huang 1979;

Violante and Huang 1984). Miller et al. (1986) concluded that the dissolution of synthetic and noncrystalline oxides by organic acids was regulated in part by variable surface charge and steric limitations of the chelating acids. Pohlman and McColl (1986) claimed that the solubilization of metals from primary minerals was influenced by both structure and functional group composition. It is understandable that the selection of organic acids for metal dissolution studies has generally been random, mainly because of the large number of naturally occurring organic compounds in the soil. Minor systematic attempts have so far been made to study the rate of metal dissolution within classes of organic carbon (i.e., aliphatic and aromatic acids) or to quantify any secondary reactions in which these acids may be involved. One exception is the work performed by Evans and Zelazny (1990), who studied the kinetics of aluminum and sulphate release from forest soil by naturally occurring low molecular weight mono- and diprotic aliphatic acids. They found that the rate of both Al and  $\text{SO}_4^{2-}$  release was greater for the diprotic acids than for the monoprotic acids.

Natural dissolved organic carbon basically consists of hydrophobic and hydrophilic acids (Thurman 1985; Malcolm 1985), but the relative distribution between the two types of acids may vary a lot from one soil horizon to another (Cronan and Aiken 1985; Cronan 1990), which further means that the hydrological flow pattern is decisive for the distribution of these acids in surface waters (Easthouse et al. 1992).

This manuscript uses the notation (\*) as estimates of nonmarine-base cations and sulphate by use of the chloride correction factor, according to their ionic contribution (molar) with respect to chloride in seawater. This notation is common in the relevant literature.

The paper focusses on the interactions between total organic carbon (TOC) and major physico-chemistry of precipitation and streamwater from four long-term monitored catchments in Norway.

## MATERIAL AND METHODS

### *The Norwegian Monitoring Programme*

Physico-chemical precipitation and runoff data from four Norwegian catchments (Fig. 1), Birkenes, Storgama, Langtjern, and Kaarvatn, are collected under the Norwegian Monitoring Programme for Long-Range Transported Air Pollutants, which started in 1980 and is still in progress. The aim of this programme is to describe the actual situation and trends in precipitation quality, in water and soil acidification, and in

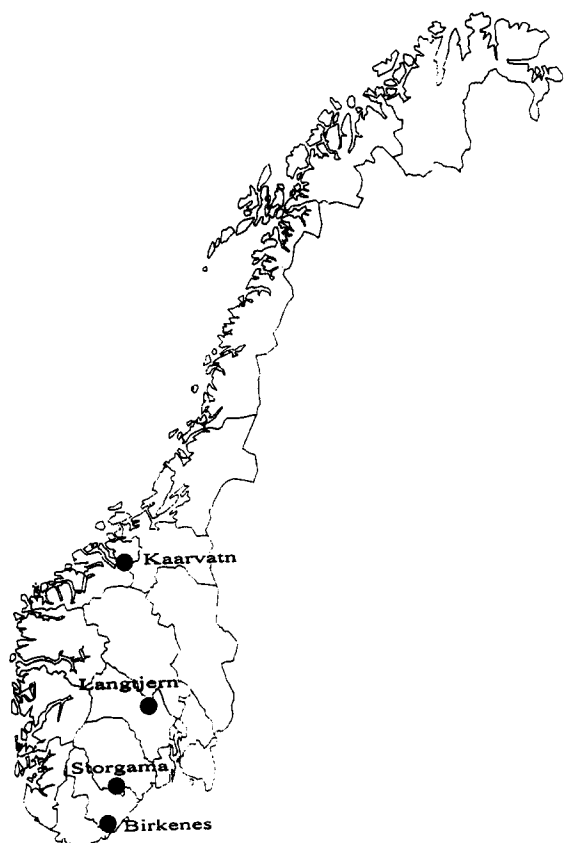


Fig. 1. The location of the four long-term monitored catchments in Norway.

damage to fish and invertebrates. The Norwegian State Pollution Control Authority (SFT) is responsible for the coordination and implementation of the programme.

#### *Description of the catchments*

The Birkenes catchment is situated at southernmost Norway, about 25 km north of Kristiansand in the county of Aust-Agder (Fig. 1). The catchment area is 0.41 km<sup>2</sup>. Altitude in the catchment ranges from 200 to 300 m and the average catchment gradient is 1:6. The granitic geology (biotite-granite) is overlain by a thin layer of soil (mean depth <20 cm). Approximately 80% of the soil is characterized as podzol and peaty podzol, low in pH and base-saturation. The forest is basically Norwegian spruce and pine with some birch. The field vegetation basically consists of various species of heather (SFT 1981).

The Storgama catchment is situated 35 km north of the Birkenes catchment, approximately 50 km inland, in the county of Telemark (Fig. 1). The catchment area is 0.6 km<sup>2</sup>. Altitude in the catchment ranges

from 580 to 690 m. About 22% of the catchment is exposed granitic bedrock, a further 49% has rankers and shallow podzols, while 19% of the area has a peat cover >30 cm in depth (Christophersen et al. 1984). In the middle of the catchment is a small shallow lake. The vegetation of the peaty rankers consists basically of pine, birch, and heather species (SFT 1981).

The Langtjern catchment is situated about 100 km northwest of Oslo, in the inland of the county of Buskerud (Fig. 1). The catchment area is 4.8 km<sup>2</sup>. Altitude in the catchment ranges from 510 to 750 m. The geology is basically biotite-gneiss and granite from precambrium. About 16% is exposed bedrock; 16% is peat; and 5% is open water (Wright and Henriksen 1980). The soil cover is relatively thin with a low organic content. About 63% is open coniferous forest with some birch with heather species as field vegetation (SFT 1981). The sampling site at Langtjern is at the outlet of Lake Langtjern, with a theoretical residence time of 58 d (SFT 1981).

The Kaarvatn catchment is situated in the north-western part of southern Norway in the county of Moere and Romsdal (Fig. 1). The catchment area is 25 km<sup>2</sup>. Altitude in the catchment ranges from 200 to 1375 m. The geology consists of heterogeneous and homogeneous gneisses and quartzites. The podzolic and peaty soil cover is thin. The vegetation is alpine, i.e. heather vegetation. Some birch is present south in the catchment. This catchment is relatively unaffected by polluted rain, i.e., the compounds of rain are basically of marine origin (SFT 1981).

#### *Physico-chemical analysis*

The pH was measured potentiometrically using a pH-meter, Orion Research 901 Ion Analyzer, with separate glass-electrode and reference-electrode (Norwegian Standard, NS 4720). Calcium, magnesium, and sodium were analysed by Induced Coupled Plasma atomic-emission spectrometry (ICP). Sulfate and chloride were measured by ion-chromatography (IC), while nitrate was measured colourimetrically (Norwegian Standard, NS 4745). Total alkalinity was measured by potentiometric titration with hydrochloric acid to pH 4.5 (Norwegian Standard, NS 4754). The total organic carbon was measured after oxidizing of organic material by peroxydisulfate and UV-radiation in a strongly acidic environment. The CO<sub>2</sub> formed is then measured spectrometrically using an infrared (IR) gas analyser (Norwegian Standard NS-ISO 8245). Aluminum was analysed by the colourimetric PCV-method (Norwegian Standard, NS 4747), on total and cation-exchanged samples.

The cation exchange procedure is described by Driscoll (1984). The Al measured on a total acidified sample is defined as total reactive Al (RAL), while the Al present in the eluate is defined as nonlabile Al (ILAL). The difference between RAL and ILAL is the labile Al-fraction (LAL), primarily representing the low molecular weight inorganic Al-species. To estimate the average charge of Al ( $\Sigma \text{Al}^{n+}$ ), the ALCHEMI-Version 4.0 was used (Schecher and Driscoll 1987; Schecher and Driscoll 1988). Both the inorganic and organic constants applied are the same as originally present in the ALCHEMI-Version 4.0. The organic Al-fractions are estimated on the basis of a triprotic acid with the given dissociation constants:  $\text{pK}_1=6.86$ ;  $\text{pK}_2=12.8$ ;  $\text{pK}_3=14.9$ , and complex constants:  $\text{Al}+\text{org}=\text{Al-org}$  ( $\text{pK}=8.38$ ) and  $\text{Al}+\text{Horg}=\text{AlH-org}$  ( $\text{pK}=13.1$ ). In the present work, total organic carbon (TOC) is measured, while the programme is based on dissolved organic carbon (DOC). In streamwater at the four sites, the differences between TOC and DOC are generally small, so TOC should be acceptable as a substitute for DOC in the programme.

#### Definition of terms

Of the strong acid anions,  $\text{Cl}^-$  is the most mobile, usually following water through the ecosystem from precipitation to runoff, i.e., input of chloride is equal to chloride output within a relatively short-time period. Because the major source of  $\text{Cl}^-$  is from sea salts, the equivalent relationship between  $\text{Cl}^-$  and other major ions of seawater is used in order to estimate the nonmarine contributions of ions present in rain and surface water. The nonmarine contribution of ions (corrected for sea salt contribution) are always marked with asterisks, and the equivalent correction equations are

$$\begin{aligned} [\text{Ca}^{2+}]^* &= [\text{Ca}^{2+}] - 0.037[\text{Cl}^-] \\ [\text{Mg}^{2+}]^* &= [\text{Mg}^{2+}] - 0.195[\text{Cl}^-] \\ [\text{Na}^+]^* &= [\text{Na}^+] - 80.56[\text{Cl}^-] \\ [\text{K}^+]^* &= [\text{K}^+] - 0.018[\text{Cl}^-] \\ [\text{SO}_4^{2-}]^* &= [\text{SO}_4^{2-}] - 0.103[\text{Cl}^-]. \end{aligned}$$

In the charge balance (CB) of surface water ( $\mu\text{eq/L}$ ):

$$\text{CB} = ([\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+] + [\text{H}^+] + [\Sigma \text{Al}^{n+}]) - ([\text{SO}_4^{2-}] + [\text{Cl}^-] + [\text{NO}_3^-] + [\text{HCO}_3^-] + [\text{A}^-]).$$

$[\text{A}^-]$  is an expression for the amount of dissolved organic ions. Assuming all ions incorporated in the charge balance are being measured, the amount of  $[\text{A}^-]$  ( $\mu\text{eq/L}$ ) can be estimated, so that charge balance is obtained. The concentration of  $\Sigma \text{Al}^{n+}$  is in the

expression the sum of positively charged Al-ions, which can be estimated by the ALCHEMI-speciation programme (Schecher and Driscoll 1987; Schecher and Driscoll 1988). By dividing the concentration of organic charges  $[\text{A}^-]$  by the concentration of total organic carbon (TOC) measured in streamwater, a net charge (NC) per mg C is calculated. NC of organics is often called the charge density (CD) of organics, but because the  $[\text{A}^-]$  is estimated on the basis of charge balance, it gives no information about the number of reactive sites present per mg of carbon. Thus, NC per mg of carbon is a more distinct term.

Because the  $\text{A}^-$  and NC are deduced from the charge balance equation present above, positive NC-values mean that the dissolved organic carbon contains an average net of negative charges per mg C. However, negative NC-values may well be present, which means an average net of positive charges per mg C. Despite negative NC, free negatively charged sites (i.e.  $\text{COO}^-$ ,  $\text{NC}=-1$ ) may well be present, but the majority of organic sites may then have a relatively higher positive net charge, i.e.  $\text{Al}^{3+} + [\text{COO}]^- = [\text{COOAl}]^{2+}$  ( $\text{NC}=+2$ ). Thus in this example, the NC of organics will be positive ( $\text{NC}=-1+2=1$ ).

#### RESULTS AND DISCUSSION

The three southern-most catchments receive relatively high concentrations of strong acids, primarily sulfuric acid, while the Kaarvatn catchment, at the northwestern coast of Norway, only receives minor concentrations (Table 1). Besides the differences in strong acid inputs, the largest differences in the physicochemistry of precipitation are closely related to the location of the catchments with respect to distance from the sea and altitude. This means that the most coastal catchments receive the highest sea salt concentrations (as wet or dry deposition), the highest annual amount of precipitation, and have the highest annual mean air temperatures. Beside catchment specific geology, these factors are highly important for the quality and quantity of both soil and vegetation, which again affect hydrological parameters as evapotranspiration and residence time of water. The interactions of all these abiotic and biotic factors are decisive for the physico-chemical quality of streamwater, total organic carbon (TOC) included.

#### Atmospheric influence on TOC

Organic matter in soil is a mixture of plant residues in various stages of decomposition and resynthesis. In general, this matter, often called humic substances (HS), has cation-exchange properties, often with ex-

Table 1. Annual means of major physico-chemical data in air/precipitation and streamwater from the four long-term monitored catchments during the period 1986-1992. TOC(Rm/1000): TOC normalized to an annual runoff of 1000 mm/m<sup>2</sup>y.  $\Sigma\text{Al}^{**}$ : Total charge of organic and inorganic Al.  $\Sigma\text{A}^+$ : Total charge of organics, when  $\Sigma\text{Al}^{**}$  is incorporated instead of  $\text{Al}^{3+}$ . NC: Net charge ( $\mu\text{eq}$ ) per mg C.

Parameter	Unit	Birkenes N = 6	Storgama N = 6	Langtjern N = 6	Kaarvatn N = 6
<b>Air</b>					
Air-temp.	°C	6.8 ± 0.8	6.1 ± 1.2	4.1 ± 1.1	7.4 ± 0.7
Precipitation	mm/y	1604 ± 303	1185 ± 346	910 ± 216	2397 ± 264
H <sup>+</sup>	$\mu\text{eq/L}$	49.5 ± 5.1	46.0 ± 6.5	35.8 ± 6.5	10.2 ± 3.0
Na <sup>+</sup>	$\mu\text{eq/L}$	89.9 ± 20.0	19.4 ± 5.9	6.8 ± 0.9	109 ± 45.9
NH <sub>4</sub> <sup>+</sup>	$\mu\text{eq/L}$	43.8 ± 9.1	30.9 ± 5.5	41.3 ± 12.6	9.0 ± 3.4
<b>Runoff</b>					
Runoff	mm/yr	1182 ± 338	900 ± 338	679 ± 254	2099 ± 256
Rm/Pe	%	72.5 ± 6.6	74.9 ± 7.9	72.7 ± 12.8	87.7 ± 6.9
$\Sigma\text{BC}^*$	$\mu\text{eq/L}$	65.1 ± 9.1	40.9 ± 3.7	79.0 ± 7.8	35.2 ± 7.4
SO <sub>4</sub> <sup>*</sup>	$\mu\text{eq/L}$	102 ± 8.1	63.9 ± 4.9	59.6 ± 2.7	12.8 ± 2.8
H <sup>+</sup>	$\mu\text{eq/L}$	33.5 ± 4.4	27.9 ± 5.8	12.8 ± 5.4	1.8 ± 0.4
$\Sigma\text{Al}^{n+}$	$\mu\text{eq/L}$	29.3 ± 2.5	10.4 ± 0.4	8.7 ± 0.5	0.64 ± 0.08
Al-valence	charge/atom	1.76 ± 0.08	1.74 ± 0.05	1.36 ± 0.07	0.92 ± 0.06
TOC	mg C/L	5.15 ± 0.44	4.21 ± 0.50	8.96 ± 0.57	1.02 ± 0.15
TOC	g C/m <sup>2</sup> yr	5.88 ± 1.85	3.80 ± 1.59	5.75 ± 2.12	2.02 ± 0.15
TOC(Rm/10 <sup>3</sup> )	mg C/L	5.92 ± 1.54	3.71 ± 1.45	5.95 ± 2.21	2.02 ± 0.17
$\Sigma\text{A}^+$	$\mu\text{eq/L}$	2.81 ± 7.63	6.85 ± 2.09	41.9 ± 3.2	1.69 ± 3.62
NC of TOC	$\mu\text{eq/mg C}$	0.53 ± 1.58	1.65 ± 0.73	4.77 ± 0.21	1.42 ± 3.78

changeable H<sup>+</sup>. Because the organic humic material to a large extent, acts as a complex acid cation exchange resin, cation-exchange reactions will predominate in the upper organic soil horizon (Mulder et al. 1990). This means that base-cations and other cationic metals are able to compete with H<sup>+</sup>-ions for a fixed number of exchange sites, depending on factors such as charge/size ratio and concentration. However, ion-exchange reactions are reversible reactions, and the exchanger exhibits low to moderate preference for one cation species compared with another (Bolt 1979), a preference which is further reduced when the temperature is low (Boyd 1970). This means that the concentration of a cation often is more important than the type of cation relative to ion exchange reactions in soil and surface waters.

Even though soil water periodically can enter the upper organic soil horizon, water from precipitation always has to pass this horizon, if present, on its way through the catchment. Thus, the amount of precipitation, the concentration of major cations in precipitation, and air temperature, have been related to fluxes, concentration, and net charge (NC) of total organic carbon (TOC) (Tables 2 and 3).

Based on linear regression analyses (Tables 2 and 3), high positive correlations were found between

annual amount of precipitation and annual fluxes of TOC at Birkenes ( $r=0.96$ ), Storgama ( $r=0.98$ ) and Langtjern ( $r=0.90$ ), while no such correlation was found at Kaarvatn. The same relationships were also found by use of monthly weighted averages. Why Kaarvatn exhibits no correlation between amount of precipitation and TOC-fluxes is difficult to explain, but the amount of TOC in streamwater at Kaarvatn is extremely low ( $\approx 1$  mg C/L). At Storgama (Table 3), there was also a positive significant correlation between average annual concentration of Na<sup>+</sup> in precipitation and annual TOC-fluxes ( $r=0.91$ ), but this is primarily due to the high positive correlation between annual precipitation and annual average concentration of Na<sup>+</sup> ( $r=0.97$ ). Based on monthly weighted averages, a corresponding positive, but weak ( $p<0.05$ ) correlation ( $r=0.23$ ,  $N=81$ ) between precipitation and concentration of Na<sup>+</sup> in precipitation was also found at Birkenes, while at Kaarvatn, the corresponding correlation was negative ( $r=-0.41$ ,  $N=84$ ).

At Birkenes and Storgama, only the annual-weighted mean concentrations of NH<sub>4</sub><sup>+</sup> in precipitation exhibit significant correlation with the annual-weighted mean concentration of TOC in streamwater ( $r=-0.87$ ). At Langtjern, no significant correlations were found between annual weighted TOC con-

Table 2. The linear regression coefficients (dx/dy) between annual weighted physico-chemical means in air/precipitation and flux, concentration and average net charge (NC) of total organic carbon (TOC) in streamwater at Birkenes and Storgama from 1986-1992. N=6. <sup>1</sup>: p<0.05. <sup>2</sup>: p<0.01. TOC-flux: g C/m<sup>2</sup>y. TOC: mg C/L. NC: µeq/mg C. Temp.: °C. Precip.: mm<sup>3</sup>y. H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>: µeq/L.

Birkenes		dy						
dx	TOC-flux	TOC	NC of TOC	Temp.	Precip.	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>
TOC-flux	-	-0.13	0.02	-0.21	158 <sup>2</sup>	1.47	1.46	3.89
TOC	-1.25	-	0.38	0.75	-276	-6.73	-13.5 <sup>1</sup>	-4.29
NC of TOC	0.03	0.05	-	0.37	5.01	1.50	0.84	-1.24
Temp.	-1.08	0.38	1.38	-	-161	-0.99	-1.32	3.34
Precip.	0.01 <sup>2</sup>	-0.001	0.000	-0.001	-	0.01	0.02	0.03
H <sup>+</sup>	0.19	-0.09	0.14	-0.03	37.4	-	1.42 <sup>1</sup>	0.17
NH <sub>4</sub> <sup>+</sup>	0.06	-0.06 <sup>1</sup>	0.03	-0.01	17.1	0.45 <sup>1</sup>	-	0.93
Na <sup>+</sup>	0.03	-0.004	-0.01	0.01	7.71	0.01	0.19	-
Storgama		dy						
dx	TOC-flux	TOC	NC of TOC	Temp.	Precip.	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>
TOC-flux	-	0.04	-0.26	-0.11	214 <sup>2</sup>	1.15	0.99	3.38 <sup>2</sup>
TOC	0.40	-	0.02	0.06	35.8	-9.32	-8.57 <sup>1</sup>	-0.96
NC of TOC	-1.22	0.01	-	-0.46	-283	-3.82	-1.59	-4.48
Temp.	-0.20	0.01	-0.18	-	-38.6	2.50	-2.16	-0.004
Precip.	0.004 <sup>2</sup>	0.0001	-0.001	-0.0004	-	0.01	0.01	0.02 <sup>2</sup>
H <sup>+</sup>	0.07	-0.06	-0.05	0.08	19.1	-	0.47	0.47
NH <sub>4</sub> <sup>+</sup>	0.08	-0.08 <sup>1</sup>	-0.03	-0.10	23.1	0.65	-	0.44
Na <sup>+</sup>	0.25 <sup>2</sup>	-0.01	-0.07	-0.0002	56.9 <sup>2</sup>	0.57	0.38	-

Table 3. The linear regression coefficients (dx/dy) between annual weighted physico-chemical means in air/precipitation and flux, concentration and average net charge (NC) of total organic carbon (TOC) in streamwater at Langtjern and Kaarvatn from 1986-1992. N=6. <sup>1</sup>: p<0.05. <sup>2</sup>: p<0.01. TOC-flux: g C/m<sup>2</sup> y. TOC: mg C/L. NC: µeq/mg C. Temp.: °C. Precip.: mm<sup>3</sup>y. H<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Na<sup>+</sup>: µeq/L.

Langtjern		dy						
dx	TOC-flux	TOC	NC of TOC	Temp.	Precip.	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>
TOC-flux	-	0.03	-0.05	-0.37	91.9 <sup>1</sup>	1.53	-0.95	0.34
TOC	0.77	-	0.28	-1.09	-32.1	1.64	-17.1	-0.56
NC of TOC	-5.15	0.95	-	0.60	-515	-5.79	-7.04	-2.67
Temp.	-1.35	-0.13	0.02	-	-79.9	-1.29	-2.28	-0.48
Precip.	0.009 <sup>1</sup>	-0.0001	-0.001	-0.002	-	0.02	-0.01	0.003 <sup>1</sup>
H <sup>+</sup>	0.16	0.006	-0.01	-0.04	23.7	-	0.28	0.10
NH <sub>4</sub> <sup>+</sup>	-0.03	-0.02	-0.002	-0.02	-2.33	0.07	-	0.03
Na <sup>+</sup>	1.85	-0.10	-0.14	-0.72	195 <sup>1</sup>	5.12	5.62	-
Kaarvatn		dy						
dx	TOC-flux	TOC	NC	Temp.	Precip.	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Na <sup>+</sup>
TOC-flux	-	0.12	-0.10	-2.70	44.3	8.52	0.57	8.37
TOC	0.33	-	36.4 <sup>1</sup>	-3.46	-2569 <sup>1</sup>	21.1	-8.94	-456 <sup>2</sup>
NC of TOC	-0.0002	0.021 <sup>1</sup>	-	-0.10	-53.0	0.55	-0.29	-10.4 <sup>1</sup>
Temp.	-0.12	-0.053	-2.73	-	106.1	-2.72	-1.13	28.5
Precip.	0.00002	-0.0003 <sup>1</sup>	-0.011	0.0008	-	-0.007	-0.0011	0.17 <sup>2</sup>
H <sup>+</sup>	0.023	0.020	0.87	-0.16	-55.2	-	-0.023	-11.21
NH <sub>4</sub> <sup>+</sup>	0.0012	-0.007	-0.37	-0.055	-6.70	-0.018	-	-0.86
Na <sup>+</sup>	0.0001	-0.002 <sup>2</sup>	-0.07 <sup>1</sup>	0.007	5.62 <sup>2</sup>	-0.048	-0.005	-

centration and any of the air/precipitation parameters tested. At Kaarvatn, significant negative correlations were found between the annual weighted concentration of TOC and annual amount of precipitation ( $r=-0.89$ ), and between the annual weighted concentration of TOC and annual weighted mean concentration of  $\text{Na}^+$  in precipitation ( $r=-0.91$ ). Because of the high positive intercorrelation between annual weighted mean concentration of  $\text{Na}^+$  in precipitation and annual precipitation ( $r=0.98$ ), it means that the annual mean concentration of TOC at Kaarvatn is significantly lower during precipitation-rich years.

Based on monthly weighted averages, the only significant correlation between concentration of TOC in streamwater and air/precipitation parameters was the correlation with air temperature at Birkenes and Langtjern. At Birkenes, a positive correlation was found ( $r=0.58$ ), which means that higher monthly TOC concentrations are present during the warmest period of the year, i.e., during summer. At Langtjern however, the opposite relationship was found ( $r=-0.42$ ), which means that the highest monthly TOC concentrations normally occur during the coldest period of the year, i.e., during the winter. Winter and summer are normally low-flow periods at both sites, but there were no significant correlations between monthly precipitation or runoff and concentration of TOC in streamwater at the two sites. Thus, the reason for the differences may rely on catchment-specific factors. For example at Langtjern, more of the organic material originates from bogs, while at Birkenes much more originates from humic material derived from heather, grass, and trees. In addition, the sampling site at Langtjern is at the outlet of a lake, while no lake is present in the Birkenes catchment.

At Birkenes, Storgama, and Langtjern, no significant correlations were found between average net charge (NC in  $\mu\text{eq}/\text{mg C}$ ) of TOC in streamwater and any of the air/precipitation factors tested, both with respect to annual and monthly weighted averages. At Kaarvatn, a negative correlation existed between NC of TOC and averages weighted concentrations of  $\text{Na}^+$  in precipitation both on annual ( $r=-0.85$ ) and monthly bases ( $r=-0.23$ ). This indicates that the NC of TOC is getting less negative (or more positive) during periods of high sea salt influence. This make sense because higher sea salt influence increases the ability of base cation to complex to negative organic sites.

By analysing the annual data from all catchments together ( $N=24$ ), there were no significant correlations between annual TOC-fluxes and annual precip-

itation, or between annual TOC-fluxes and annual concentration of  $\text{Na}^+$  in precipitation. Positive and significant correlations were found between annual TOC-fluxes and annual weighted mean concentrations of TOC ( $r=0.59$ ,  $\text{H}^+$  ( $r=0.61$ ) and  $\text{NH}_4^+$  ( $r=0.61$ ). A negative significant correlation was found between annual TOC-fluxes and air temperature ( $r=-0.52$ ), which means that during cold years, there is a tendency for higher annual TOC-fluxes. A significant negative correlation was found between annual weighted concentrations of TOC in streamwater and annual amount precipitation ( $r=-0.80$ ), which indicates a general trend of decreasing annual concentration of TOC during precipitation-rich years. The only significant correlation between air/precipitation parameters and NC of TOC was the correlation with respect to amount of precipitation ( $r=-0.47$ ). The negative correlation means that the NC of TOC is getting less negative (or more positive) during the most precipitation-rich years. One explanation may be the fact that during precipitation-rich years, more less-disintegrated organic material is able to be transported out of the catchment when more water leaves the catchment as surface and subsurface runoff. This organic material is most likely less oxidized, and will therefore contain lower negative charges. But it may also be an effect of dilution, which means that when the concentration of TOC decreases as a consequence of higher water input, the NC of TOC tends to be reduced.

By analysing the monthly weighted averages of air/precipitation parameters at all sites together ( $N=325$ ), weak negative, but significant ( $p<0.05$ ), correlations were found between NC of TOC and amount of precipitation ( $r=-0.14$ ) and between NC of TOC and the concentration of  $\text{Na}$  in precipitation ( $r=-0.23$ ) (Fig. 2). Thus, the only air/precipitation factors which directly seem to affect the monthly variations in NC of TOC in streamwater at all four catchments are the amount of precipitation and the accompanying change in concentration of  $\text{Na}^+$  in precipitation, the latter directly related to precipitation changes.

#### *TOC and weathering*

It is well known that natural organic acids increase mineral weathering (Inoue and Wada 1971; Huang and Keller 1972; Boyle et al. 1974; Johnson et al. 1981; Wilson 1986; Lundström 1990), and thus cation leaching in soils (Reuss 1980; Mollitor and Raynal 1982; Krug and Isaacson 1984). This is well confirmed by annual streamwater data from the four Norwegian catchments (Fig. 3). By linear regression

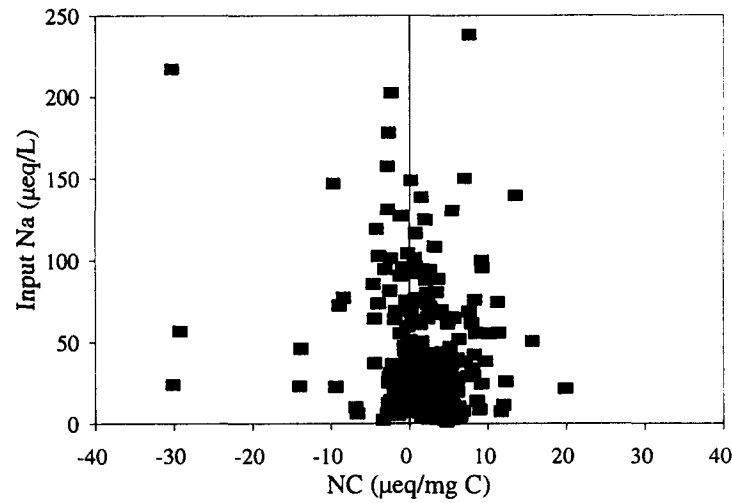


Fig. 2. The relationship between monthly NC of TOC in streamwater and monthly weighted concentration of Na in precipitation at the four catchments.

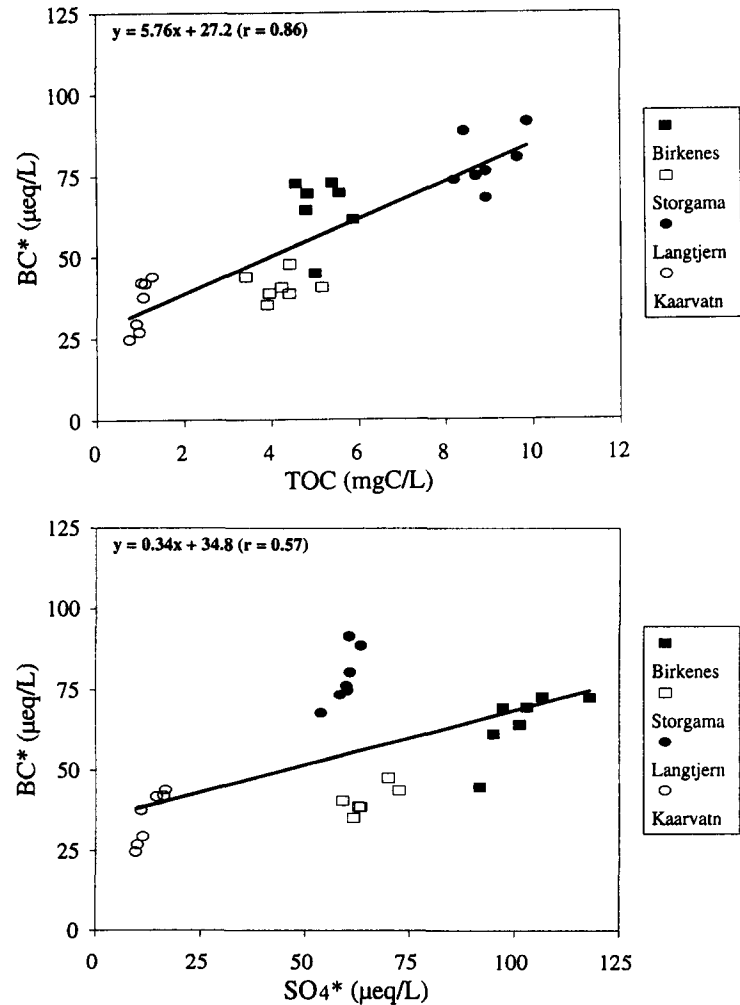


Fig. 3. The relationships between annual streamwater concentrations of TOC and nonmarine base cations (EBC\*), and between annual streamwater concentrations of nonmarine sulphate (SO<sub>4</sub>\*) and EBC\* at the four catchments from 1986-1992.



analyses on annual weighted concentration averages in streamwaters at the four sites, a much higher correlation coefficient ( $r=0.86$ ) was found between the concentration of TOC and nonmarine base cations ( $\Sigma BC^*$ ) compared with the corresponding regression between nonmarine sulphate ( $SO_4^*$ ) and  $\Sigma BC^*$  ( $r=0.57$ ). However, concerning weathering and cation leaching of aluminum (Fig. 4), the correlation between annual average concentration of total aluminum (RAL) and  $SO_4^*$  was far more significant ( $r=0.93$ ), compared with the corresponding correlation between RAL and TOC ( $r=0.40$ ). This should also be expected, because a relative high concentration of  $SO_4^*$  means a relative low pH, which is needed to dissolve substantial amounts of Al from soils.

*Relationships between TOC and other physico-chemical parameters in streamwater*

The highest streamwater concentration of TOC is normally present at Langtjern (Table 1), with an annual weighted mean concentration of  $8.96\pm0.57$  mg C/L. This is more than 40% higher compared with the second most organic-rich streamwater at Birkenes ( $5.15\pm0.44$  mg C/L). However, the annual mean fluxes of TOC are about equal at the two sites. By assuming the difference in TOC-concentration only being an effect of different annual runoff at the two sites, i.e., a dilution effect only, a normalized runoff value (e.g. 1000 mm/y) should give identical TOC-concentrations in the streamwater at both sites. This was also found (Table 1). The Birkenes catchment contains relatively dense populations of Norwegian spruce and pine, while the Langtjern catchment primarily

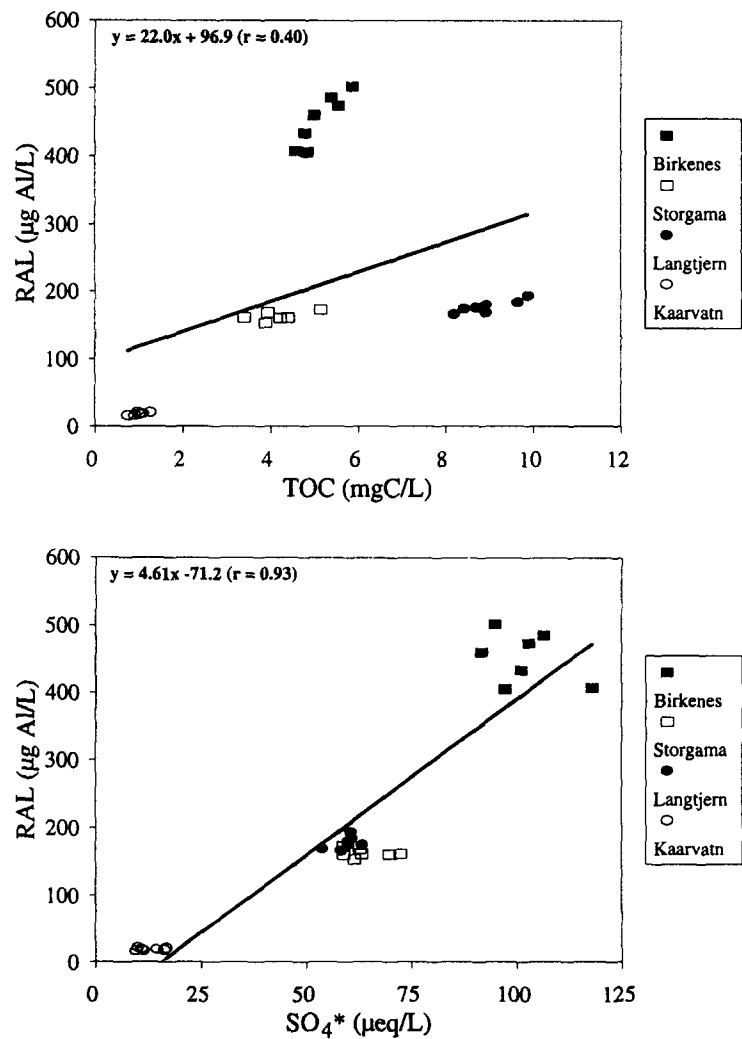


Fig. 4. The relationships between annual streamwater concentrations of TOC and total reactive aluminium (RAL), and between annual streamwater concentrations of nonmarine sulphate ( $SO_4^*$ ) and RAL at the four catchments from 1986-1992.

contains an open coniferous forest. Both catchments are well covered by heather species as field vegetation and contain areas with bogs, but the Langtjern catchment contains a relatively large lake and several smaller lakes. Thus, even though the annual fluxes of TOC in streamwater are almost similar at the two sites, the quality of TOC may differ. The other two catchments, Kaarvatn and Storgama, contain more exposed bedrock areas, have a generally thinner soil cover, and are far less forested. This may explain the lower annual concentrations and fluxes of TOC in the streamwater at these sites.

By linear regression analyses, there was a strong tendency of decreasing TOC concentration by increasing amount of runoff at Birkenes ( $r=-0.45$ ) and Kaarvatn ( $r=-0.79$ ). Further, there was a strong tendency of decreasing NC of TOC by increasing runoff at Storgama ( $r=-0.56$ ), Langtjern ( $r=-0.55$ ), and Kaarvatn ( $r=-0.80$ ), which means that fewer free negative organic sites are present during the most runoff-rich years. At Birkenes no such significant correlation was found, but tendencies of decreasing NC of TOC and concentration of TOC by increasing runoff and precipitation were present at all sites. This indicates a decrease in NC of TOC by decreasing concentration of TOC.

By linear regression analysis, the most significant and positive correlation was found between the monthly weighted concentration of TOC in streamwater and the air temperature at Birkenes (Table 4), a relationship which is documented earlier. Concerning the TOC concentrations, the most significant cor-

relation at all sites was the relationship with respect to aluminum (Tables 4-7), i.e. either inorganic dissolved Al (LAL:  $\mu\text{g Al/L}$ ) or total average charge of Al ( $\Sigma\text{Al}^{n+}$ ). At Birkenes, there was a negative correlation between TOC and LAL, which means that inorganic dissolved Al increases when the concentration of TOC decreases (Table 4). At Storgama, it was the other way around (Table 5). At Langtjern and Kaarvatn (Tables 6 and 7), the most significant correlations were found between TOC and  $\Sigma\text{Al}^{n+}$ , and the correlations were positive at both sites. The fact that no corresponding significant correlations were found between TOC and  $\Sigma\text{Al}^{n+}$  or between TOC and LAL when runoff-data from all four sites were analysed together (Table 8), indicates that the relationship between TOC and aluminum is catchment-specific.

In the streamwater at all sites (Tables 4-7), non-marine Na ( $\text{Na}^*$ ) exhibited the most significant correlation with respect to NC of TOC ( $\mu\text{eq/mg C}$ ). The positive correlations mean that when Na is temporarily retained in the soil, the concentration of  $\text{Na}^*$  is decreasing, and thus the NC of TOC. Decreasing NC of TOC means that more cations are retained on negative organic sites, so that NC of TOC is getting less negative or more positive (Fig. 5). The second most important factor concerning NC of TOC varies from catchment to catchment, i.e.  $\text{SO}_4^*$  at Birkenes, LAL at Storgama, TOC-flux at Langtjern, and  $\Sigma\text{Ions}$  at Kaarvatn. The streamwater concentration of  $\text{SO}_4^*$  exhibited a significant and negative correlation with NC of TOC only at Birkenes and Storgama, while a negative correlation between  $\Sigma\text{Ions}$  and NC of

Table 4. The most significant correlation coefficients ( $r$ ) between monthly air temperature means, physico-chemical concentration means in runoff and flux, concentration and average net charge (NC) of total organic carbon (TOC) in streamwater at Birkenes from 1986-1992 ( $N=82$ ). The  $r$ -values are presented in parentheses, and negative values indicate negative correlations and vice versa.

Birkenes		Degree of significance
TOC-flux	$\text{g C/m}^2\text{mth}$	Runoff (0.95) > $\text{H}^+$ (0.51) > $\Sigma\text{Ca}^*,\text{Mg}^*$ (-0.41) > $\Sigma\text{Al}^{n+}$ (0.23)
TOC	$\text{mg C/L}$	Air-temp (0.58) > LAL (-0.33) > CD (0.25) > $\text{SO}_4^*$ (-0.24)
NC of TOC	$\mu\text{eq/mg C}$	$\text{Na}^*$ (0.44) > $\text{SO}_4^*$ (-0.32) > $\Sigma\text{Ions}$ (-0.29) > TOC (0.25) > Air-temp (0.21)
Air-temp.	$^{\circ}\text{C}$	TOC (0.58) > LAL (-0.37) > $\Sigma\text{Al}^{n+}$ (-0.34) > $\Sigma\text{Ions}$ (-0.32) > CD (0.21)
Runoff	$\text{mm/m}^2\text{mth}$	TOC-flux (0.95) > $\text{H}^+$ (0.47) > $\Sigma\text{Ca}^*,\text{Mg}^*$ (-0.44) > $\Sigma\text{Al}^{n+}$ (0.32) > LAL (0.22)
$\text{H}^+$	$\mu\text{eq/L}$	$\Sigma\text{Al}^{n+}$ (0.63) > $\Sigma\text{Ca}^*,\text{Mg}^*$ (-0.51) = TOC-flux (0.51) > LAL (0.49) > Runoff (0.47)
$\text{Na}^*$	$\mu\text{eq/L}$	$\Sigma\text{Ions}$ (-0.48) > LAL (-0.47) > CD (0.44) > $\Sigma\text{Al}^{n+}$ (-0.43) > $\text{SO}_4^*$ (0.32)
$\Sigma\text{Ca}^*,\text{Mg}^*$	$\mu\text{eq/L}$	$\text{H}^+$ (-0.51) > $\text{SO}_4^*$ (0.48) > Runoff (-0.44) > TOC-flux (-0.41) > $\Sigma\text{Al}^{n+}$ (-0.36)
LAL	$\mu\text{g/L}$	$\Sigma\text{Al}^{n+}$ (0.95) > $\Sigma\text{Ions}$ (0.58) > $\text{H}^+$ (0.49) > $\text{Na}^*$ (-0.47) > Air-temp (-0.37)
$\Sigma\text{Al}^{n+}$	$\mu\text{eq/L}$	LAL (0.95) > $\text{H}^+$ (0.63) > $\Sigma\text{Ions}$ (0.54) > $\text{Na}^*$ (-0.43) > $\Sigma\text{Ca}^*,\text{Mg}^*$ (-0.36)
$\text{SO}_4^*$	$\mu\text{eq/L}$	$\Sigma\text{Ca}^*,\text{Mg}^*$ (0.48) > $\text{Na}^*$ (0.32) = CD (-0.32) > $\Sigma\text{Ions}$ (0.27) > TOC (-0.24)
$\Sigma\text{Ions}$	$\mu\text{eq/L}$	LAL (0.58) > $\Sigma\text{Al}^{n+}$ (0.54) > $\text{Na}^*$ (-0.48) > $\text{H}^+$ (0.41) > Air-temp (-0.32)

Table 5. The most significant correlation coefficients ( $r$ ) between monthly air temperature means, physico-chemical concentration means in runoff and flux, concentration and average net charge (NC) of total organic carbon (TOC) in streamwater at Storgama from 1986-1992 (N=79). The  $r$ -values are presented in parentheses, and negative values indicate negative correlations and vice versa.

Storgama		Degree of significance
TOC-flux	g C/m <sup>2</sup> mth	Runoff (0.97) > $\Sigma$ Ca*,Mg* (-0.30) > Na* (-0.25) > TOC (0.22) > H <sup>+</sup> (0.21)
TOC	mg C/L	LAL (0.54) > $\Sigma$ Al <sup>n+</sup> (0.26) > $\Sigma$ Ca*,Mg* (0.22) > TOC-flux (0.22)
NC of TOC	$\mu$ eq/mg C	Na* (0.49) > LAL (0.32) > SO <sub>4</sub> * (-0.26) > $\Sigma$ Ions (-0.25)
Air-temp.	°C	$\Sigma$ Ca*,Mg* (-0.68) = $\Sigma$ Ions (-0.68) > $\Sigma$ Al <sup>n+</sup> (-0.65) > SO <sub>4</sub> * (-0.53) > LAL (-0.50)
Runoff	mm/m <sup>2</sup> mth	TOC-flux (0.97) > Ca*,Mg* (-0.34) > Na* (-0.27) > $\Sigma$ Al <sup>n+</sup> (-0.23) > SO <sub>4</sub> * (-0.22)
H <sup>+</sup>	$\mu$ eq/L	$\Sigma$ Ions (0.71) > $\Sigma$ Al <sup>n+</sup> (0.70) > SO <sub>4</sub> * (0.65) > $\Sigma$ Ca*,Mg* (0.43) > Air-temp (-0.30)
Na*	$\mu$ eq/L	CD (0.49) > Runoff (-0.27) > TOC-flux (-0.25) > LAL (0.24) > $\Sigma$ Ca*,Mg* (0.21)
$\Sigma$ Ca*,Mg*	$\mu$ eq/L	SO <sub>4</sub> * (0.90) > $\Sigma$ Al <sup>n+</sup> (0.83) > $\Sigma$ Ions (0.82) > Air-temp (-0.68) > H <sup>+</sup> (0.43)
LAL	$\mu$ g/L	TOC (0.54) > Air-temp (-0.51) > $\Sigma$ Al <sup>n+</sup> (0.40) > $\Sigma$ Ca*,Mg* (0.36) > CD (0.32)
$\Sigma$ Al <sup>n+</sup>	$\mu$ eq/L	$\Sigma$ Ions (0.92) > SO <sub>4</sub> * (0.86) > $\Sigma$ Ca*,Mg* (0.83) > H <sup>+</sup> (0.70) > Air-temp (-0.65)
SO <sub>4</sub> *	$\mu$ eq/L	$\Sigma$ Ca*,Mg* (0.90) > $\Sigma$ Ions (0.87) > $\Sigma$ Al <sup>n+</sup> (0.86) > H <sup>+</sup> (0.65) > Air-temp (-0.54)
$\Sigma$ Ions	$\mu$ eq/L	$\Sigma$ Al <sup>n+</sup> (0.92) > SO <sub>4</sub> * (0.87) > $\Sigma$ Ca*,Mg* (0.82) > H <sup>+</sup> (0.71) > Air-temp (-0.68)

TOC was found at Birkenes, Storgama, and Kaarvatn. Only at Langtjern was a significant (positive) correlation found between  $\Sigma$ Ca\*, Mg\*, and NC of TOC in stream water.

A significant negative correlation between air temperature and concentration of Na<sup>+</sup> in precipitation was present at all stations, i.e., Birkenes ( $r=-0.42$ ), Storgama, ( $r=-0.31$ ), Langtjern ( $r=-0.32$ ), and Kaarvatn ( $r=-0.50$ ). This means that the influence from sea salts is

highest during the coldest periods of the year, i.e. during the winter. If the winter temperature is low, the precipitation will be accumulated as snow, and the effects of high sea salt inputs during the winter will not be revealed in the streamwater until the initial springmelt. This is almost always the normal situation at Kaarvatn (Figs. 6 and 7). At Birkenes, the winter temperature during the last years has often been >0°C, which means that high inputs of sea salts are

Table 6. The most significant correlation coefficients ( $r$ ) between monthly air temperature means, physico-chemical concentration means in runoff and flux, concentration and average net charge (NC) of total organic carbon (TOC) in streamwater at Langtjern from 1986-1992 (N=84). The  $r$ -values are presented in parentheses, and negative values indicate negative correlations and vice versa.

Langtjern		Degree of significance
TOC-flux	g C/m <sup>2</sup> mth	Runoff (0.98) > $\Sigma$ Ca*,Mg* (0.38) > H <sup>+</sup> (0.33) > NC (-0.32) > LAL (0.27)
TOC	mg C/L	$\Sigma$ Al <sup>n+</sup> (0.70) > $\Sigma$ Ca*,Mg* (0.59) > $\Sigma$ Ions (0.53) > Air-temp (-0.46) > H <sup>+</sup> (0.35)
NC of TOC	$\mu$ eq/mg C	Na* (0.62) > TOC-flux (-0.32) > $\Sigma$ Ca*,Mg* (0.31) > Runoff (-0.29) > H <sup>+</sup> (-0.25)
Air-temp.	°C	$\Sigma$ Ions (-0.71) > $\Sigma$ Al <sup>n+</sup> (-0.68) > SO <sub>4</sub> * (-0.61) > $\Sigma$ Ca*,Mg* (-0.60) > H <sup>+</sup> (-0.50)
Runoff	mm/m <sup>2</sup> mth	TOC-flux (0.98) > $\Sigma$ Ca*,Mg* (-0.44) > NC (-0.29) = H <sup>+</sup> (0.29) > LAL (-0.27)
H <sup>+</sup>	$\mu$ eq/L	$\Sigma$ Al <sup>n+</sup> (0.74) > Air-temp (-0.50) > SO <sub>4</sub> * (0.47) > $\Sigma$ Ions (0.42) > TOC (0.35)
Na*	$\mu$ eq/L	NC (0.62) > $\Sigma$ Ca*,Mg* (0.54) > $\Sigma$ Ions (0.34) > SO <sub>4</sub> * (0.28) > TOC-flux (-0.24)
$\Sigma$ Ca*,Mg*	$\mu$ eq/L	$\Sigma$ Ions (0.85) > SO <sub>4</sub> * (0.69) > Air-temp (-0.60) > TOC (0.59) > Na* (0.54)
LAL	$\mu$ g/L	$\Sigma$ Al <sup>n+</sup> (0.56) > Air-temp (-0.27) = TOC-flux (-0.27) = Runoff (-0.27) = H <sup>+</sup> (0.27)
$\Sigma$ Al <sup>n+</sup>	$\mu$ eq/L	H <sup>+</sup> (0.74) > TOC (0.70) > Air-temp (-0.68) > $\Sigma$ Ions (0.64) > LAL (0.56)
SO <sub>4</sub> *	$\mu$ eq/L	$\Sigma$ Ions (0.91) > $\Sigma$ Ca*,Mg* (0.69) > Air-temp (-0.61) > $\Sigma$ Al <sup>n+</sup> (0.56) > H <sup>+</sup> (0.47)
$\Sigma$ Ions	$\mu$ eq/L	SO <sub>4</sub> * (0.91) > $\Sigma$ Ca*,Mg* (0.85) > Air-temp (-0.71) > $\Sigma$ Al <sup>n+</sup> (0.64) > TOC (0.53)

Table 7. The most significant correlation coefficients (*r*) between monthly air temperature means, physico-chemical concentration means in runoff and flux, concentration and average net charge (NC) of total organic carbon (TOC) in streamwater at Kaarvatn from 1986-1992 (N=84). The *r*-values are presented in parentheses, and negative values indicate negative correlations and vice versa.

Kaarvatn		Degree of significance
TOC-flux	g C/m <sup>2</sup> month	Runoff (0.87) > Air-temp (0.71) > ΣCa*,Mg* (-0.65) > SO <sub>4</sub> * (-0.42) > ΣIons (-0.41)
TOC	mg C/L	ΣAl <sup>n+</sup> (0.63) > TOC-flux (0.40) > LAL (0.26)
NC of TOC	μeq/mg C	Na* (0.37) > ΣIons (-0.26)
Air-temp.	°C	ΣCa*,Mg* (-0.83) > Runoff (0.75) > TOC-flux (0.71) > ΣIons (-0.53) > SO <sub>4</sub> * (-0.52)
Runoff	mm/m <sup>2</sup> month	TOC-flux (0.87) > Air-temp (0.75) > ΣCa*,Mg* (-0.74) > SO <sub>4</sub> * (-0.47) > ΣIons (-0.42)
H <sup>+</sup>	μeq/L	Na* (-0.73) > ΣAl <sup>n+</sup> (0.57) > SO <sub>4</sub> * (-0.44) > Runoff (0.42) > ΣIons (0.40)
Na*	μeq/L	H <sup>+</sup> (-0.73) = ΣIons (-0.73) > SO <sub>4</sub> * (0.42) > ΣAl <sup>n+</sup> (-0.38) > NC (0.37)
ΣCa*,Mg*	μeq/L	Air-temp (-0.83) > Runoff (-0.74) > TOC-flux (-0.65) = ΣIons (0.65) > SO <sub>4</sub> * (0.56)
LAL	μg/L	ΣAl <sup>n+</sup> (0.49) > TOC (0.26) > Na* (-0.23)
ΣAl <sup>n+</sup>	μeq/L	TOC (0.63) > H <sup>+</sup> (0.57) > LAL (0.49) > Na* (-0.38) > ΣIons (0.31)
SO <sub>4</sub> *	μeq/L	ΣCa*,Mg* (0.56) > Air-temp (-0.52) > Runoff (-0.47) > H <sup>+</sup> (-0.44) > Na* (0.42)
ΣIons	μeq/L	Na* (-0.73) > ΣCa*,Mg* (0.65) > Air-temp (-0.53) > Runoff (-0.42) > TOC-flux (-0.41)

manifested much faster in the streamwater chemistry (Figs. 8 and 9). At both sites, the lowest NC of TOC is closely related in time to these sea salt events.

When the streamwater data from all catchments were analysed together, the most significant correlation was found between monthly concentration of TOC and nonmarine base cations (ΣCa\*, Mg\*) (Table 8). This may confirm the strong influence of TOC on weathering and base-cation leaching. The negative correlation between runoff and concentra-

tion of TOC (-0.32) and between runoff and concentration of ΣCa\*, Mg\* (-0.51), indicates that longer residence time of water will strengthen the positive TOC/ΣCa\*, Mg\* relationship. This should be expected because the influence from weathering on surface water chemistry will increase by increasing residence time of water within the weathering zone, or in the soil. Evaluating all sites together, Na\* exhibited the most significant and positive correlation with respect to NC of TOC. The second most important factor

Table 8. The most significant correlation coefficients (*r*) between monthly air temperature means, physico-chemical concentration means in runoff and flux, concentration and average net charge (NC) of total organic carbon (TOC) in streamwater from the four catchments from 1986-1992 (N=329). The *r*-values are presented in parentheses, and negative values indicate negative correlations and vice versa.

All catchments		Degree of significance
TOC-flux	g C/m <sup>2</sup> month	Runoff (0.55) > H <sup>+</sup> (0.36) > TOC (0.26) > ΣAl <sup>n+</sup> (0.25) > SO <sub>4</sub> * (0.22)
TOC	mg C/L	ΣCa*,Mg* (0.69) > SO <sub>4</sub> * (0.44) > H <sup>+</sup> (0.40) > Runoff (-0.32) > Na* (0.26)
NC of TOC	μeq/mg C	Na* (0.35) > ΣIons (-0.28) > TOC (0.22) > LAL (-0.15) > ΣCa*,Mg* (0.14)
Air-temp.	°C	ΣCa*,Mg* (-0.37) > Runoff (0.32) > H <sup>+</sup> (-0.20) > SO <sub>4</sub> * (-0.17) > TOC-flux (0.15)
Runoff	mm/m <sup>2</sup> month	TOC-flux (0.55) > ΣCa*,Mg* (-0.51) > Air-temp (0.32) = TOC (-0.32) > SO <sub>4</sub> * (-0.25)
H <sup>+</sup>	μeq/L	SO <sub>4</sub> * (0.72) > ΣAl <sup>n+</sup> (0.64) > LAL (0.46) > ΣIons (0.44) > TOC (0.40)
Na*	μeq/L	NC (0.35) > TOC (0.26) > ΣCa*,Mg* (0.24) > SO <sub>4</sub> * (0.21) > ΣIons (-0.17)
ΣCa*,Mg*	μeq/L	TOC (0.69) > SO <sub>4</sub> * (0.56) > Runoff (-0.51) > Air-temp (-0.37) > ΣIons (0.34)
LAL	μg/L	ΣAl <sup>n+</sup> (0.96) > ΣIons (0.88) > SO <sub>4</sub> * (0.75) > H <sup>+</sup> (0.46) > ΣCa*,Mg* (0.28)
ΣAl <sup>n+</sup>	μeq/L	LAL (0.96) > ΣIons (0.85) > SO <sub>4</sub> * (0.65) > H <sup>+</sup> (0.64) > ΣCa*,Mg* (0.28)
SO <sub>4</sub> *	μeq/L	ΣAl <sup>n+</sup> (0.81) > LAL (0.75) > ΣIons (0.74) > H <sup>+</sup> (0.72) > ΣCa*,Mg* (0.56)
ΣIons	μeq/L	LAL (0.88) > ΣAl <sup>n+</sup> (0.85) > SO <sub>4</sub> * (0.74) > H <sup>+</sup> (0.44) > ΣCa*,Mg* (0.34)

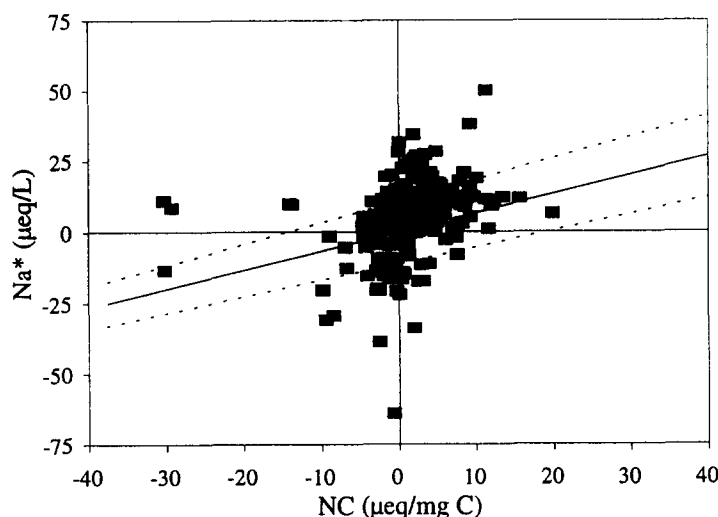


Fig. 5. The relationship between nonmarine Na ( $\text{Na}^*$ ) and NC of TOC in streamwater at the four catchments, based on monthly weighted averages from 1986-1992. The dotted lines indicate  $\pm 1$  S.D.

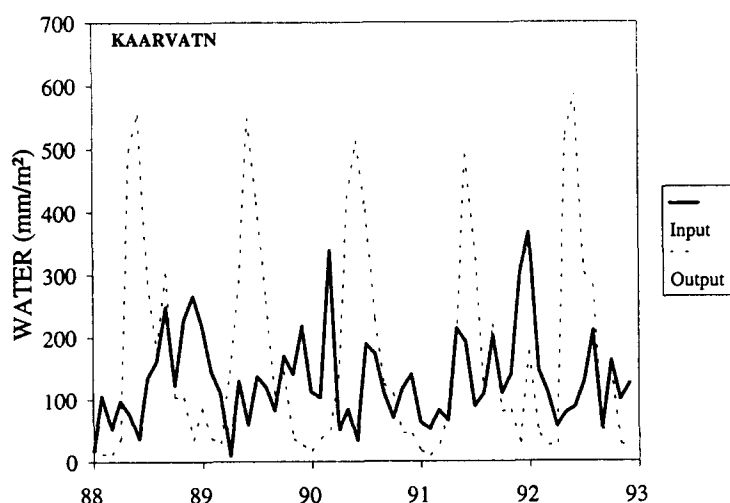


Fig. 6. The monthly input and output of water ( $\text{mm/m}^2$ ) at Kaarvatn from 1988-1992.

concerning NC of TOC was the negative correlation with respect to  $\Sigma\text{ions}$  in streamwater. The negative relationship means that at high ionic strength, more cations are complexed to organic sites, and the NC of TOC in streamwater is getting less negative (or more positive). The third most significant factor for NC of organic was the positive correlation between NC of TOC and concentration of TOC, which means that if TOC increases, the NC of organics also increases which further means that NC of TOC is getting more negative (or less positive).

The NC of TOC seems to be most affected by precipitation compounds, primarily the inputs of sea

salts. In the most acidified areas, the influence from strong acid inputs also affect the NC of TOC, but less significantly. Because the dissolved organic materials often are organic acids and therefore are carrying negatively-charged sites, the relationship between the  $\text{H}^+$ -concentration of precipitation and the average pK-values of organics is decisive to which extent the  $\text{H}^+$  in precipitation is able to change the NC of TOC. At least in more coastal areas, like at Birkenes, and especially at Kaarvatn, the concentration of  $\text{Na}^+$  in precipitation is much higher and the variations much larger compared with the concentration of  $\text{H}^+$  in precipitation. Thus, it is reasonable

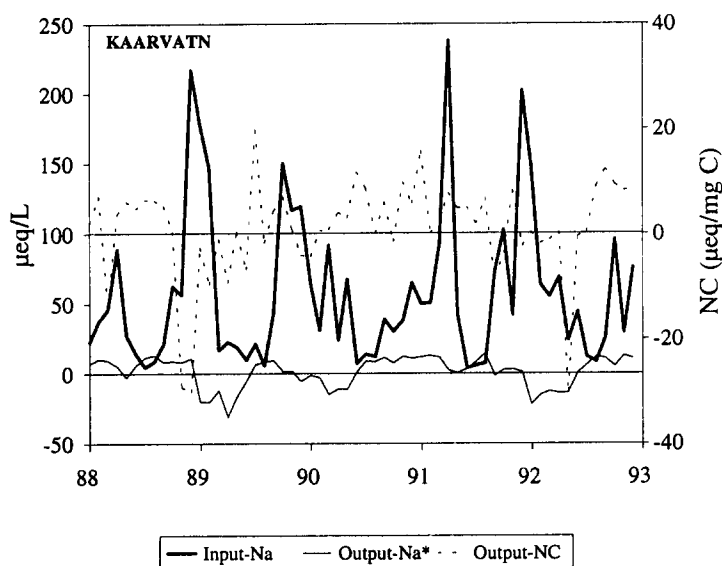


Fig. 7. The monthly weighted average concentration of Na in precipitation, and nonmarine Na (Na\*) and NC of TOC in streamwater at Kaarvatn from 1988-1992.

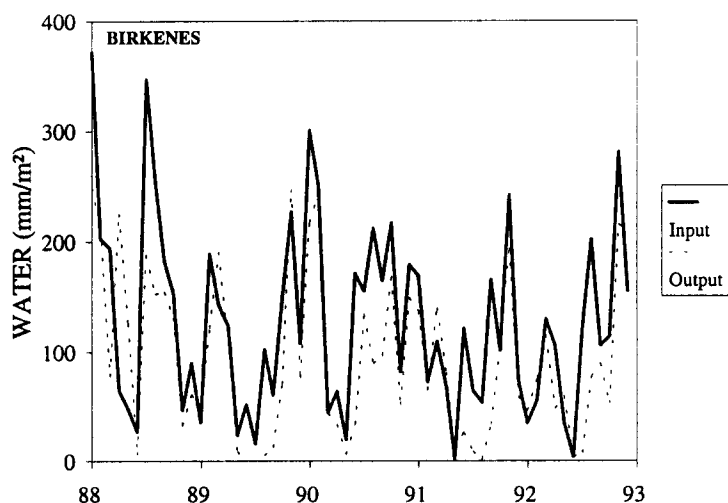


Fig. 8. The monthly input and output of water ( $\text{mm/m}^2$ ) at Birkenes from 1988-1992.

that the variations in sea salt inputs (primarily NaCl) are more important for the temporary variation in NC of TOC compared with  $\text{H}^+$  ions at these sites. It is only at Langtjern, the most TOC-influenced streamwater, where a significant and positive correlation was found between  $\text{H}^+$  and the concentration of TOC. This indicates that at certain TOC concentrations, the weak organic acids may affect the streamwater pH. Thus at high TOC concentrations, the average pK-value of the organic acids might well be the measured water pH.

#### Humic dissociation and complexing constants

Variations in the NC of TOC may give information about the quality of organic complexes, such as to what extent cations, including  $\text{H}^+$ -ions, are able to change the NC of TOC. Whether a negative organic site is a carboxyl group or phenol group etc., is however, impossible to figure out by a NC calculations. By the ALCHEMI-speciation programme, it is possible to estimate the concentration of organic aluminum (ILAL), by feeding the programme with measured concentrations for total reactive aluminum

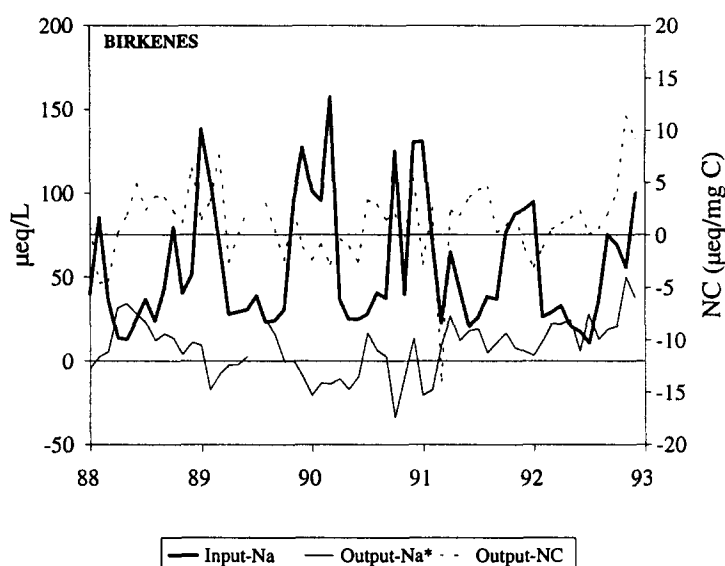


Fig. 9. The monthly weighted average concentration of Na in precipitation, and nonmarine Na (Na\*) and NC of TOC in streamwater at Birkenes from 1988-1992.

Table 9. The linear regression between measured (dx) and estimated (dy) nonlabile Al (ILAL) in streamwater at the four sites.

	N	$y = (a \pm \text{std. dev})x + b$
Birkenes	82	$y = (1.11 \pm 0.03)x$ ( $r = 0.78$ )
Storgama	79	$y = (0.48 \pm 0.02)x$ ( $r = 0.64$ )
Langtjern	84	$y = (0.56 \pm 0.01)x$ ( $r = 0.82$ )
Kaarvatn	84	$y = (0.20 \pm 0.01)x$ ( $r = 0.80$ )
All catchments	329	$y = (0.83 \pm 0.02)x$ ( $r = 0.83$ )

(RAL) and major chemical dissolved compounds, including TOC. By use of the organic constants given by the programme (see Material and Methods), the concentration of ILAL can be calculated. The pK-values and the Al-complexing constants given by the programme are empirically made. Despite the constants being wrong or only applicable to a certain degree for the Norwegian catchments, they are at least constant, which means that the relative changes between measured ILAL and calculated ILAL in runoff may give useful information about the quality of functional groups present on the organic structures in streamwater at the four sites.

Based on monthly weighted concentration averages from 1986-1992, the programme overestimated the concentrations of ILAL in streamwater at Birkenes, while the programme underestimated the amount of nonlabile Al (ILAL) at the three other sites (Table 9). Accordingly, the opposite should be the case concerning the concentration of LAL, because  $RAL = ILAL + LAL$ . At Birkenes, the programme overestimated the ILAL by about 10%, while the programme underestimated

the same Al-fraction by 52%, 44%, 80% at Storgama, Langtjern, and Kaarvatn, respectively. The regression coefficients between measured and estimated ILAL (dx/dy) were significantly different at the four sites, which means that there are large variations in the quality of organics between the sites. Since the uncertainties in the linear regression coefficients at each site were rather small (one std. dev.=2-5%), it indicates that the monthly changes in quality of TOC at one site, are much smaller than the quality differences in TOC between the sites.

At Birkenes, the dissociation constants should be higher or the Al-complexing constants lower compared with the constants given by the ALCHEMI programme. For the other three stations, the dissociation constants should be lower, or the Al-complexing constants higher compared with the constants originally present in the ALCHEMI programme. The best correlation between measured and estimated ILAL was found when data from all sites were put together. The regression coefficient was 0.83 (Fig. 10). The programme is therefore relatively applicable when data from several sites are put together, and confirm the empirical background for the given constants in the programme.

The fact that there seems to be a gradient in the organic-complexing constants of Al from Birkenes to Kaarvatn might be an important observation, especially in light of the fact that qualitative changes in the functional groups of organic substances seems to occur during acidification, i.e., a decrease in the carboxylic acidity and an increase in phenolic acidity by acidification (Malcom and Gjessing 1993). Thus,

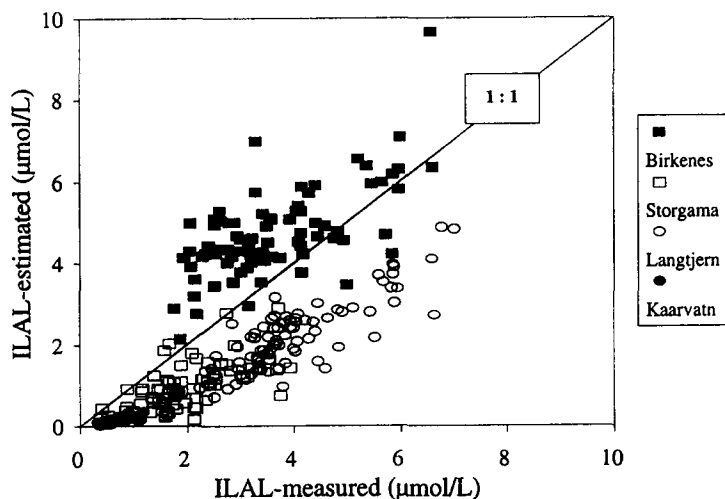


Fig. 10. The relationship between measured and calculated concentration of nonlabile aluminium (ILAL) in streamwater at the four catchments, based on monthly weighted averages from 1986-1992. The regression equation is  $y=0.83$  ( $r=0.83$ ).

lower-average complexing constants should be expected in the most acidified areas, because phenolic groups normally exhibit lower complexing strength compared with carboxylic groups. In addition, the molecular weight of dissolved organic carbon seems to increase when pH is lowered (Shaw et al. 1993). This may also cause reduced metal complexing capacity and strength of dissolved organic compounds.

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