

Water Chemistry in the Confluence Zone Downstream a Limestone Treated Lake and an Acid Tributary: Principal Component Analyses Including Warm and Cold Winters and an Episode High in Sea-Salts

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Abstract: Extensive limestone treatment of lakes and watercourses has been carried out especially in Norway and Sweden to counteract effects of acidification. Lakes have been the most commonly treated part of the water systems. However, treatment of lakes upstream acid tributaries may introduce downstream toxic mixing zones for fish. To sort this out the outlet of a treated lake, a downstream acid tributary and two sites in the confluence zone were intensely monitored during a period of 28 months. The data accumulated come from a period (from February 1992) where significant climatic variations took place that provide a basis for studying intercorrelations between water chemistry and climatic change. The first two winters were warmer than normal and the catchments were hardly covered with snow and the lake was ice-covered only for a few days. The last winter was colder than normal, nival and the lake was ice-covered from December to April. During the second winter a low pressure over the north Atlantic gave strong south-westerly winds and large amounts of precipitation loaded with sea-salts. The principal component analysis (PCA) separates both the outlet and the tributary data into two groups while the data from the confluence zone are separated into three. Significant different water chemistry was observed in the outlet during the ice-covered period while effects of the sea-salt event splits the data from the tributary into two groups. The water chemistry in the confluence zone reflects both the ice-covered period, the sea-salt event and besides the more general situation. The PCA analysis indicates that the changing weather conditions mainly influenced on the water quality in the tributary. The water quality in the confluence zone was generally a conservative mixture of the outlet and the tributary waters except for alkalinity, H^+ and inorganic aluminium (Al_i). Generally, hydrolysing Al_i in the confluence rendered the water quality highly toxic to fish. The potential toxicity increased during the sea-salt event and during the ice-covered period of the lake due to increased concentrations of Al_i both in the outlet and the tributary waters. The results indicate that this may be a general problem in confluence zones downstream limestone treated lakes and acid tributaries.

Keywords: Acidification, limestone treatment, inorganic aluminium, confluence zone, principal component analysis, sea-salts, warm and cold winters

Introduction

Acidification of surface waters is a significant environmental problem in many areas of the world with soil underlain by siliceous bedrock. The ecological consequences have been described during the last three decades (Wright, 1983; Schindler, 1988; Bresser and Salomons, 1990). To counteract this acidification extensive liming of lakes and watercourses is taking place, especially in Sweden (Nyberg and Thørneløf, 1988) and Norway (Hindar and

Rosseland, 1988). Besides, the technique is also reported used in UK (Howells and Dalziel, 1990), Canada and US (Olem, 1991). Lakes have so far been the most commonly treated water systems (Olem, 1991).

Direct addition of bases such as CaCO_3 to the acidified lake water body improve biological habitat particularly for fish. However, the treatment may create downstream conditions potential toxic to fish. Short term experiments indicate an increased mortality of fish in artificially made zones where treated and aluminium rich acidic water mix, most probably due to imposed changes in the aluminium chemistry (Weatherley et al., 1991; Poléo et al., 1994).

In this work the brook water chemistry downstream a limestone treated lake and an acid tributary has been intensely studied during a period of about 28 months. When data of this magnitude is to be analysed, the use of multivariate techniques is a good choice. As some of the variables are interconnected, change in one property may influence the behaviour of another. Correlation obtained between any two variables measured may not reflect their true relationship. In contrast multivariate techniques consider all the variables at the same time and extract relationships between the variables and objects.

Here, we are interested in understanding the similarities and differences between the water samples collected during a period of significant climatic variations. The influence on the acid-base and the aluminium chemistry are of special interest due to the potential ecological importance of these variables especially in the confluence zone between limestone treated and acid tributary waters.

Study site

Site description and climate

The site is situated about 2.5 km from the coastline 8 km west of Kristiansand in the southernmost part of Norway (Fig. 1). The soil depth in this area is generally 20-70 cm and podzol profiles lacking or almost lacking the eluvial horizon dominate (Låg, 1957). Outcrops of bedrock, mainly felsic augen-gneiss, frequently interrupt the soil cover. Besides, there are some boggy areas (Fig. 1). The area contains naturally mixed forests dominated by conifers (mainly Scots pine), but also some deciduous trees (mainly oak and birch).

The Lake Terjevann catchment covers 1.1 km² and the altitude ranges from 19 to 119 m above sea level. About 23 % of the catchment was forested with Norway spruce about 40 years ago. There are no activities in the catchment other than the treatment of the lake water body with limestone. The lake (Table 1) was treated for the first time in 1980 and then annually during the period 1984-91. Apart from the very first treatment in 1980 when coarse seashells were used, finely grounded (≤ 0.2 mm) limestone with a CaCO_3 content of about 77 % (limestone SR from NORCEM, Norway) has been used. The dose was 2.7 mg calcium carbonate per litre lakewater in 1980, 20.5 mgL⁻¹ in the autumn of 1984 and then 7.6, 7.6, 7.3, 7.1, 11.5, 7.2 and 12.9 mgL⁻¹ in the period 1985 to 1991. In January 1993 a gauge (Crump overflow) was installed at the outlet of the lake.

Table 1. Morphometric data of Lake Terjevann.

Maximum length (l): 618 m
Maximum depth (z_m): 35 m
Mean depth (z): 12 m
Surface area (A): 0.09 km²

Volume (V): 10^6 m^3
Theoretical retention time: 0.72 year

The tributary catchment covers about 1.5 km^2 and the altitude ranges from 18 to 128 m above sea level. There are two lakes in the catchment (Fig. 1). The tributary and the outlet brook confluence about 30 meters downstream Lake Terjevann. The sampling points E and F are situated about 50 and 200 meters downstream the confluence point, respectively. There are no other well-defined tributaries between the sampling points C and F (Fig. 1).

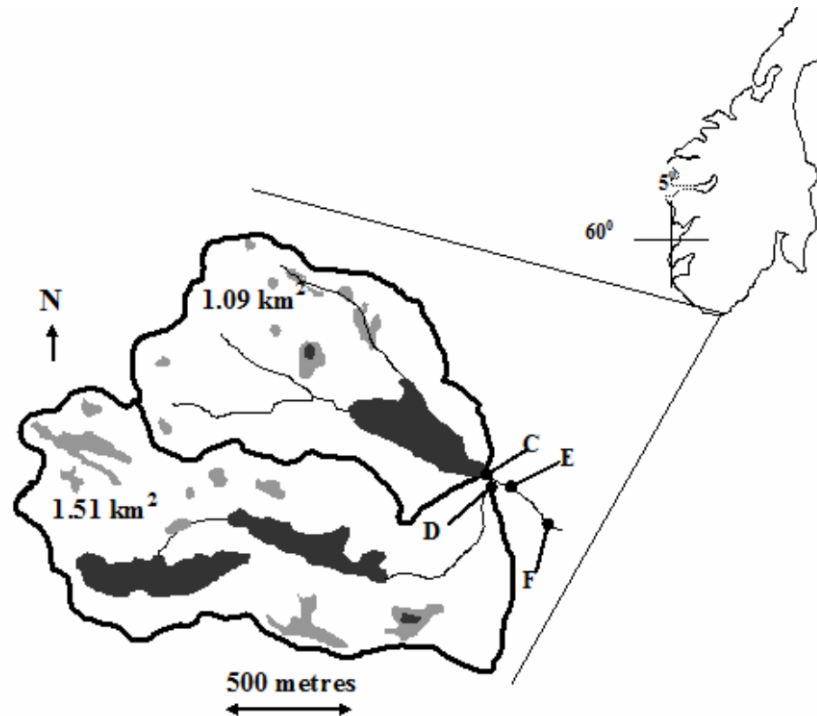


Figure 1. The Lake Terjevann area with the sampling points C (outlet of the lake), D (the tributary), E and F (the confluence zone). Light grey areas denote bogs, dark grey areas the pond and lakes.

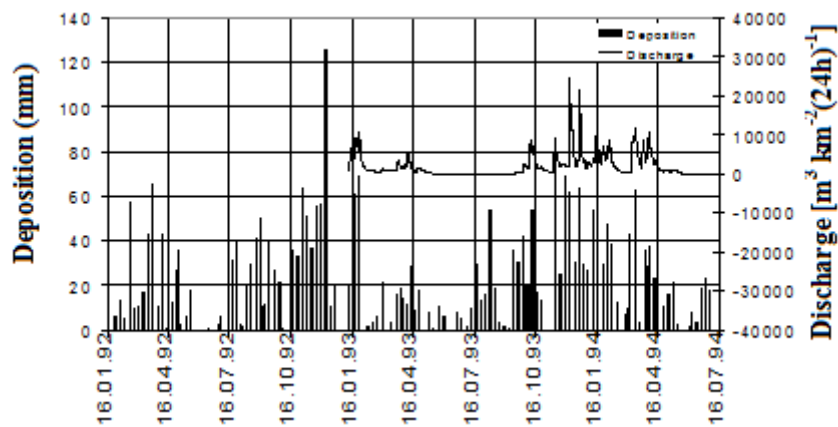


Figure 2. Deposition and discharge at Lake Terjevann. (The bar represents the total weekly deposition).

A maritime climate prevails on the southernmost coast of Norway. The monthly mean temperature is commonly below 0 °C in December, January and February and highest in July (Table 2). The annual mean deposition is about 1300 mm and the distribution is characterised by deposition maxima during late autumn and winter (Table 2). Deposition is generally higher than evapotranspiration except for a period from about the middle of June to the middle of August as indicated by lack of discharge from the catchments and the lake (Fig. 2) during this period.

Table 2. Monthly deposition (mm) in Søgne about 1 km west of Lake Terjevann and mean monthly air temperature (°C) in 1992-94 and mean values 1961-90 at Kjevik airport about 16 km east of the catchment.

	<u>Deposition</u>				<u>Temperature</u>			
	1992 ^a	1993 ^a	1994 ^a	1961-90 ^a	1992 ^b	1993 ^b	1994 ^b	1961-90 ^a
January	2.6	2.7	0.2	-1.7	62.8	149.1	176.0	121
February	2.8	2.2	-4.2	-1.8	85.6	31.7	67.0	80
March	3.9	2.8	1.7	1.0	145.9	52.1	173.1	87
April	4.6	6.5	5.8	4.6	118.8	66.1	87.1	59
May	12.3	12.6	10.4	9.9	26.3	24.7	25.7	86
June	16.9	13.7	13.1	14.0	9.4	17.7	70.7	75
July	15.4	14.2	18.6	15.5	93.0	70.0	16.7	88
August	14.0	13.3	16.3	14.8	151.1	77.7	141.9	118
September	11.7	9.7	10.9	11.5	100.0	129.1	184.4	141
October	4.7	6.0	7.3	7.9	131.6	104.6	145.0	164
November	3.6	1.3	5.2	3.1	199.2	176.5	144.8	164
December	1.9	-0.6	3.4	-0.1	156.5	212.4	208.5	116
Total	-	-	-	-	1280.2	1111.7	1440.9	1299

^aNorwegian Meteorological Institute, DNMI.

^bNorwegian Institute for Air Research, NILU.

The area receives a high atmospheric deposition of sea salts in addition to the long range transported acidic sulphur and nitrogen compounds (Table 3).

Table 3. Volume-weighted mean concentrations of main ions (μeqL^{-1}) in deposition 1992-94 in Søgne about 1 km west of Lake Terjevann (monitored by the Norwegian Institute for Air Research; SFT 1993, 1994, 1995).

	H ⁺	Na ⁺	Mg ²⁺	Ca ²⁺	K ⁺	NH ₄ ⁺	Cl ⁻	SO ₄ ²⁻	^a SO ₄ ²⁻	NO ₃ ⁻
1992	47	128	28	9	4	35	140	65	49	42
1993	47	192	43	13	7	45	232	83	60	51
1994	40	111	25	10	4	39	123	61	47	44

^anon marine

In 1992 and 1993 the area experienced unusually mild winters (Table 2). The catchments were covered with snow only for a few days and the lake was hardly ice-covered. The winter of 1994, except for January, was colder than normal (Table 2) and the lake was ice-covered from December 16 1993 to April 4. Total amounts of deposition were about normal in 1992, lower than normal in 1993 and higher than normal in 1994 with a somewhat different distribution the three years (Table 2, Fig. 2). The vital importance of wind direction on deposition quality is indicated by the strong fluctuations in chloride concentration in the deposition during 1992-94 (Fig. 2). An extremely low pressure over the North Atlantic in 1993 from January 4 to 24 gave strong south-westerly winds and large amounts of deposition (149 mm, Fig. 2) loaded with sea-salts. The anomaly of this event is illustrated by the volume-weighted mean concentration of 1.02 meqL^{-1} Cl⁻ in deposition these three weeks compared to the average of the volume-weighted annual means from 1992 and 1994 of about 0.13 meqL^{-1} (Table 3). Almost 60 % of the annual wet deposition of Cl⁻ in 1993 occurred during these three weeks.

Methods

Sampling and Chemical analysis

Samples of drainage water were collected almost weekly in clean polyethylene bottles from the sampling points C (the outlet of Lake Terjevann), D (the acid tributary) and E and F (Fig. 1). Temperature was measured immediately. The samples were transported to the laboratory for further processing that started within one hour after sampling.

Absorbance at 254 (od₁) and 410 (od₂) nm (1 cm quartz cuvettes; Hitachi Model V-2000 UV/VIS Spectrophotometer) were measured on unfiltered samples. pH was measured with standard equipment (Radiometer Ion-85, G202C pH- and K201 reference electrodes). Aluminium species in unfiltered samples were fractionated using the procedure of Driscoll (1984). The samples were passed through a strongly acidic cation-exchange column (DOWEX-50Wx8, 20-50 mesh, Na⁺-form). The operationally defined fractions, total acid reactive aluminium (Al_t) and non-labile monomeric (mainly organically complexed) aluminium (Al_o) which passed the resin, were analysed by flow injection analysis (FIA) using the pyrocatechol-violet method (Tecator, 1985). The labile aluminium fraction, mainly

monomeric, inorganic aluminium (Al_i), was calculated as the difference between Al_t and Al_o . Major cations (Na^+ , Ca^{2+} , Mg^{2+} , K^+) besides iron and manganese were analysed by atomic absorption spectroscopy (Perkin Elmer AAS Model 1100). Samples for Ca^{2+} analyses had lanthanum added to a concentration of 0.5 gL^{-1} while samples for total iron and manganese were acidified to pH 1.5 with 4M H_2SO_4 just after arriving at the laboratory. Major anions (Cl^- , SO_4^{2-} , NO_3^-) were determined by flow injection analysis (FIA) using the thiocyanate method (Tecator, 1983), colorimetrically by the thorin method (Henriksen and Bergmann-Paulsen, 1974), and by a diazotization reaction (Brewer and Riley, 1965) respectively. Alkalinity (Alk) was determined by titration with 0.05M HCl with a conductometric (Radiometer CDM83 Conductivity Meter, PP1042 Conductivity Cell) end point determination (Golterman et al., 1978). Alkalinity values at pH between about 5.0 and 4.5 are calculated from the equation $Alk = 27.298pH - 124.36$ ($n = 168$, $R^2 = 0.72$) achieved from the titrated samples and including zero alkalinity at pH below 4.5. An ionic balance of $\pm 5.5\%$ between cations (H^+ , Al_i , Na^+ , Ca^{2+} , Mg^{2+} , K^+) and anions (Cl^- , SO_4^{2-} , NO_3^- , Alk) indicates that the major constituents have been analysed with fair accuracy in all samples.

Data analysis

Principal component analysis (PCA) is a technique that extracts relationships between variables and between objects. Use of PCA in this study could enlighten the relationships between the water samples and will enable us to understand the relationships between the measurements with respect to the climatic variations that have taken place during the sampling period.

The data that includes 4 sampling sites (C, D, E, F) sampled 75 times and analysed for 17 parameters, can be put in a matrix of size 300×17 where the water samples are represented by rows while columns represent the variables (measurements). In order to give equal priority to the variables, each variable is divided by its maximum value. It means that all the variables are given values in between 0 and 1. This type of normalisation removes unwanted leverages caused by variations in the concentrations between the metals as well as values of the other variables. The samples are numbered from 1 to 75 to represent individual sampling. The suffix number x in c_x , d_x , e_x , f_x represent identical sampling time.

The PCA analysis of the data was carried out by using SERIUS multivariate data analysis program (Kvalheim and Karstang, 1987). The data from sampling sites C, D, E and F were analysed individually to identify relationships between the variables that could explain the influence of climatic variations and imposed episodes that have taken place in and around the sampling sites.

Results

Outlet

The large range of the 17 variables measured in the outlet of the lake (Table 4, sample site C) is mainly induced by the ice-covered period when the outlet was very much influenced by the inlets. The inlet water passed almost unchanged through the lake in the upper 2 meters and this period was characterised by cold acidic and aluminium rich outlet water (Fig. 3b,c). Effects of the sea-salt event on the outlet water were not significant as the highly acidic and aluminium rich inlet water (Andersen and Seip, 1999) mixed with the wind exposed treated lake water.

In the PCA plot the samples from sampling site C clearly separates into two groups (Fig. 4a). The smaller group contains the water samples sampled during the period when the lake was ice covered (c59-c68). The larger group contains water samples sampled during other periods. A look at the corresponding loading plot (Fig. 5a) shows that the variables such as alkalinity, Ca^{2+} and pH lie along the positive direction of the PCA component 1 and the variables such as aluminium and manganese lie along the negative direction of the PCA component 1. It means that an increase in alkalinity goes along with an increase in Ca^{2+} and pH. At the same time an increase in alkalinity means less aluminium in the sample. It is clear from this plot that alkalinity is one of the main factors that explain the variance in the data. The picture is something expected for the outlet water from a limestone treated lake. The high loading of the variable temperature (in situ) along component 1 (Fig. 5a) indicates that an increase in temperature goes along with an increase in alkalinity and a decrease in aluminium. Besides, the variable temperature has a high loading along component 2 (Fig. 5a).

Table 4. Mean values and range of the variables temperature, UV/VIS absorbance at 254 and 410 nm, pH, aluminium species, calcium, magnesium, sodium, potassium, iron, manganese, chloride, sulphate, nitrate and alkalinity measured at the outlet of Lake Terjevann (site C), in the tributary (site D) and in the confluence zone downstream (site E and F) during the period February 1992 to June 1994. Besides, area-weighted mean values of the C and D samples are included (G).

	C		D		E		F		G
	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
Temp. ($^{\circ}\text{C}$)	7.0	0.4-22.9	6.0	0.1-16.9	6.5	0.1-21.5	6.5	0.1-21.4	6.4
Abs ₂₅₄	0.142	0.08-0.25	0.296	0.02-0.61	0.229	0.12-0.33	0.225	0.12-0.33	0.231
Abs ₄₁₀	0.013	0.01-0.02	0.031	0.02-0.08	0.023	0.01-0.03	0.022	0.01-0.03	0.023
pH	6.10	4.64-7.09	4.63	4.32-6.36	5.17	4.46-6.77	5.15	4.46-6.66	5.25
Al_t (μgL^{-1})	267	140-435	471	253-658	382	187-506	377	182-520	385
Al_o (μgL^{-1})	219	129-274	244	125-370	242	153-317	239	126-309	234
Al_i (μgL^{-1})	48	4-188	227	26-501	140	7-326	138	8-325	152
Ca^{2+} (mgL^{-1})	2.78	0.82-5.22	1.42	0.61-5.61	2.04	0.83-5.38	2.01	0.83-4.44	1.99
Mg^{2+} (mgL^{-1})	1.05	0.76-1.28	1.24	0.71-2.11	1.17	0.76-1.90	1.17	0.78-1.89	1.16
Na^+ (mgL^{-1})	8.61	6.6-10.8	10.31	6.7-16.4	9.64	7.0-14.3	9.64	7.0-14.5	9.60
K^+ (mgL^{-1})	0.43	0.31-0.52	0.58	0.41-1.12	0.52	0.41-0.68	0.51	0.41-0.65	0.52
Fe_t (μgL^{-1})	62	21-134	254	142-1296	172	92-439	155	83-274	174
Mn_t (μgL^{-1})	28	13-55	74	31-102	54	16-84	53	19-75	55
Cl^- (mgL^{-1})	15.4	11.1-19.8	18.9	11.1-35.0	17.4	11.8-27.1	17.4	11.8-27.3	17.4
SO_4^{2-} (mgSL^{-1})	2.51	1.94-3.00	2.57	1.88-4.31	2.61	2.04-4.22	2.60	2.05-4.31	2.54
NO_3^- (μgNL^{-1})	212	138-525	173	16-539	194	36-541	194	60-541	189
Alk (μeqL^{-1})	41	2-167	4	0-76	17	0-68	15	0-57	20

Tributary

The water samples from the tributary, site D, are generally more acidic and rich in aluminium compared to the C samples (Table 4) except for in periods with very low flow and during the ice-covered period of the lake (Fig. 3b,c). The extraordinary high salinity (e.g. Cl^-), aluminium concentrations and acidity indicated by the range (Table 4) are an effect of the sea-salt event. Due to the sea-salt loading, the concentration of Cl^- almost doubled from about 16 to 30 mgL^{-1} in the tributary (Fig. 3a) and it took almost a year before the salt concentration returned to pre-event levels. The salt influenced on the aluminium concentrations most probably by ion exchange with Na^+ (Andersen and Seip, 1999). The Al_i concentration more than doubled from about 200 to 420 and further to about 500 μgL^{-1} (Fig. 3c) and the concentration was generally higher than pre-event levels for almost a year.

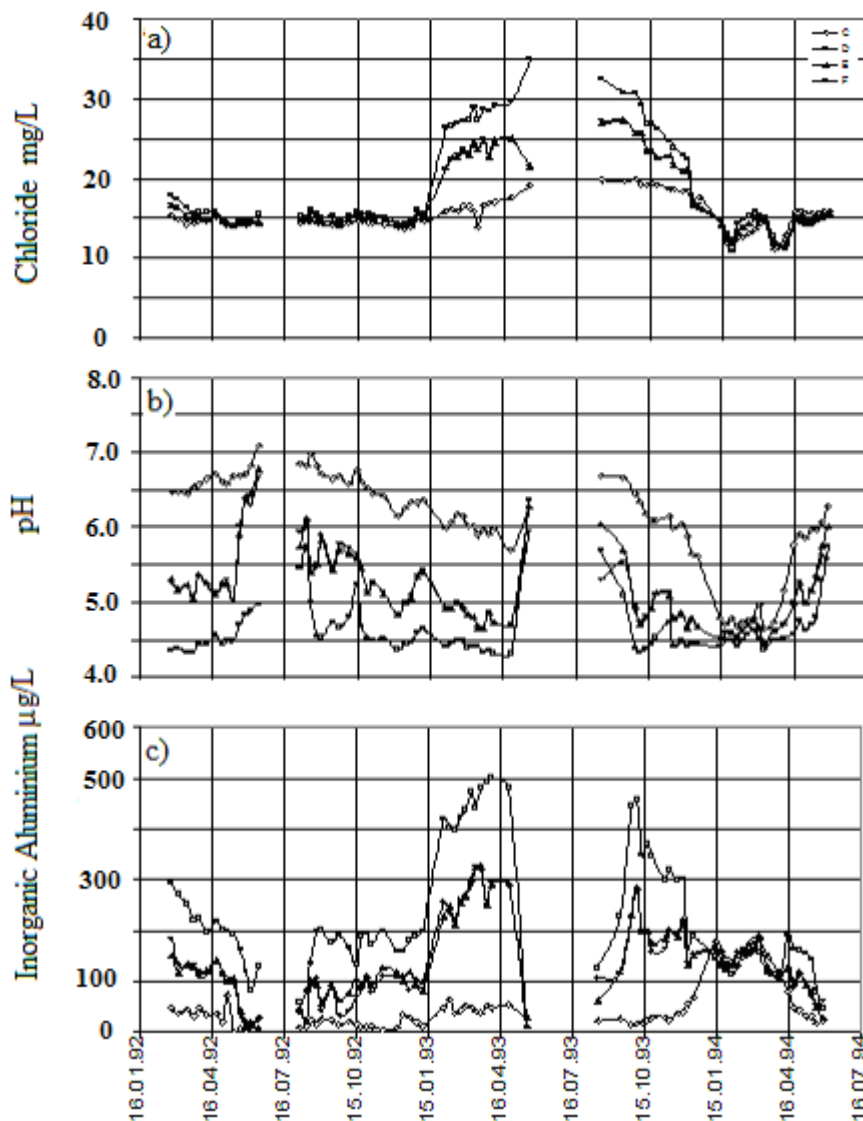


Figure 3. Concentrations of Cl^- , hydrogen (pH) and inorganic aluminium (Al_i) in brook waters from the sampling sites C (outlet of the Lake Terjevann), D (the tributary), E and F (the confluence zone) in 1992-94.

The samples from site D also separates into two groups in the PCA plot (Fig. 4b). However, the number of samples falling into these groups is more even than in the previous case. The

group containing the samples d33 to d56, falling in the positive side of the PCA component 1, represent samples from the period when the drainage from the catchments were affected by the sea-salt event. The grouping in the loading plot (Fig. 5b) is now more influenced (along PCA component 1) by the variables such as Na^+ , Mg^{2+} , Cl^- , manganese and inorganic aluminium. Variables such as temperature, alkalinity, Ca^{2+} and pH lie along component 2 but not as dominant as in the case of the C samples. An axis passing through the origin and the points representing the salt concentrations (Na^+ , K^+ , Mg^{2+} and Cl^-) lie nearly normal to an axis passing through the origin and the points representing the variables temperature, alkalinity and pH (Fig. 5b). In other words this indicates that the concentrations of Na^+ , K^+ , Mg^{2+} and Cl^- are independent of temperature or alkalinity or pH. The concentrations of Ca^{2+} and SO_4^{2-} are however influenced by these variables.

The relationship between the temperature and total and inorganic aluminium is the same as for the C samples.

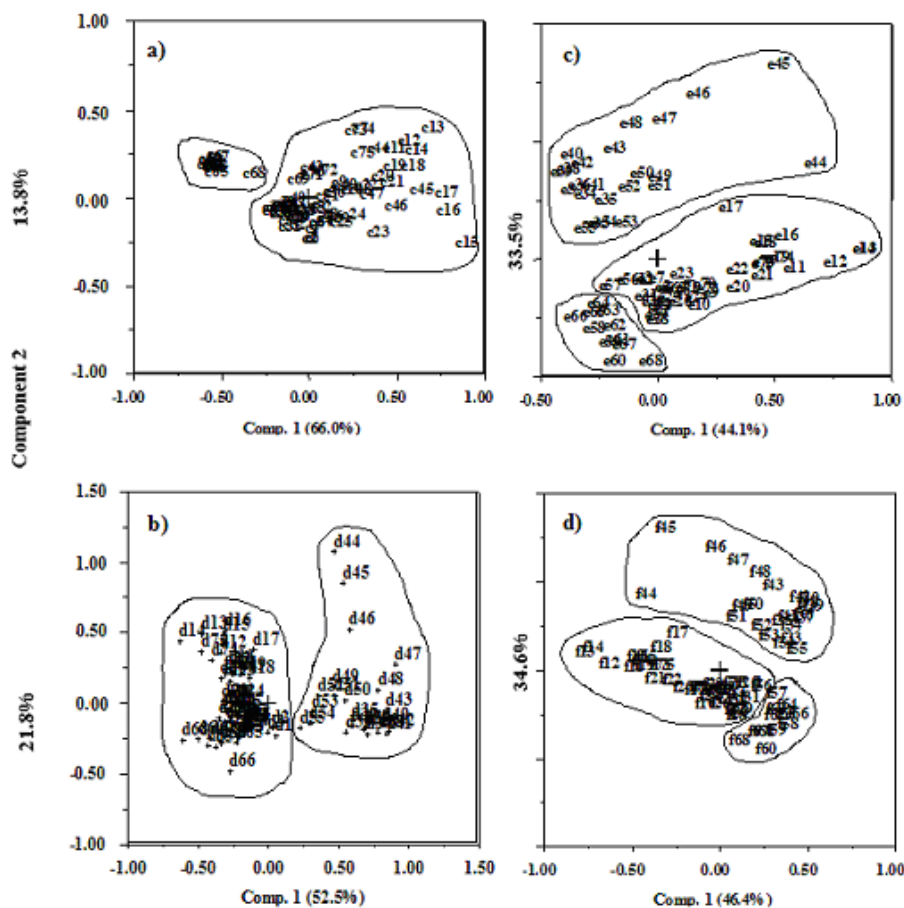


Figure 4. Principal component analysis of the samples from a) site C (outlet of Lake Terjevann), b) site D (the tributary), c) site E and d) site F (the confluence zone).

The confluence zone

The water quality that is produced in the confluence zone by the mixing of the outlet and the tributary waters is generally less acidic and less rich in aluminium than the tributary and vice versa regarding the outlet (Table 4, Fig. 3b,c). The pronounced effect of the sea-salt event on the tributary waters was transferred to the mixed waters and e.g. the inorganic aluminium (Al_i) concentration in the confluence zone increased abruptly from about 85 to 250 and further

to about $325 \mu\text{gL}^{-1}$ (Fig. 3c). During the period with ice-cover and acidic outlet water from the lake, the downstream waters were all acidic and rich in Al_i (Fig. 3b,c).

Regarding the PCA plots it may be worthwhile to look at the groupings in the PCV plots of the samples in the above two cases. The samples c59-c68 (the ice-covered period) and c1-c33 together with c69-c75 lie at the opposite sides of the PCA component 1 (Fig. 4a). In the case of samples D, all the corresponding samples d1-d33 and d59-d75 lie in the same group and on the negative side of the PCA component 1 (Fig. 4b). As the downstream samples E and F are mixtures of C and D, it should be expected that the variable influence on the samples C and D should separate E and F into three groups (33-56, 59-68 and 1-33 together with 70-75). Even though, the samples are not compactly defined into groups, three groups among the samples E and F are indicated (Fig. 4c,d). The samples from the sea-salt episode (33-56) influence the separation more than the samples from the lake ice-covered period (59-68).

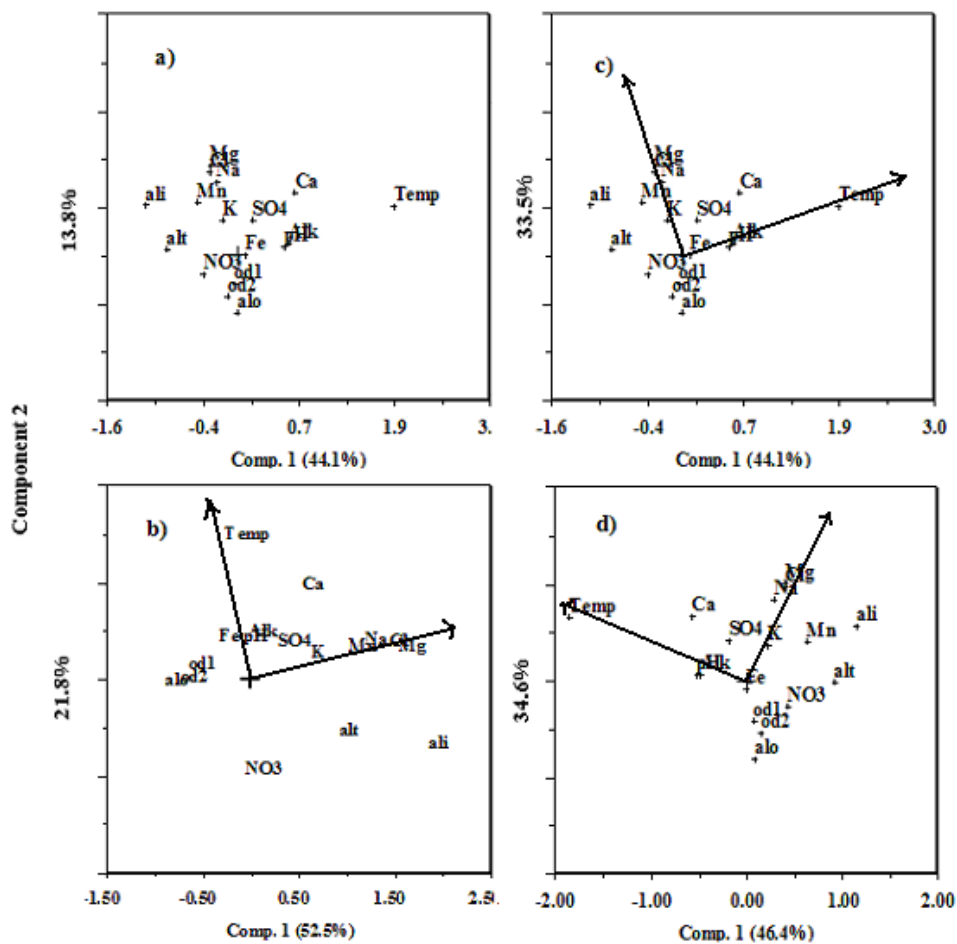


Figure 5. Principal component analysis (loading plots) of the samples from a) site C (outlet of Lake Terjevann), b) site D (the tributary), c) site E and d) site F (the confluence zone).

The loading plots from the analysis of the samples from E and F are depicted in Figures 5c and d. They show, as for the D samples, that an axis passing through the origin and the points representing the salt concentrations (Na^+ , K^+ , Mg^{2+} and Cl^-) lie nearly normal to an axis passing through the origin and the points representing the variables temperature, alkalinity and pH. In other words the concentrations of Na^+ , K^+ , Mg^{2+} and Cl^- are independent of

temperature or alkalinity or pH. The concentrations of Ca^{2+} and SO_4^{2-} are however influenced by these variables.

It is also possible to identify the same negative correlation between temperature and concentrations of total reactive aluminium or inorganic aluminium among E and F samples as among the C and D samples.

Discussion

The principal component analysis extracts the samples that are similar in chemical profiles; the sea-salt event, the ice-covered period and all the other samples. Besides, the extracted relationships indicating that an increase in temperature goes along with an increase in alkalinity and a decrease in aluminium are as expected. An increase in temperature increases the evapotranspiration and decreases the water flow and the influence of high alkalinity and low aluminium groundwater on the drainage is increased. The indicated independence of Na^+ , K^+ , Mg^{2+} , Cl^- from temperature or alkalinity or pH, is obvious. The influence of alkalinity on Ca^{2+} is most probably mainly due to the treatment with CaCO_3 . However, the indicated influence of temperature or alkalinity or pH on SO_4^{2-} is difficult to explain.

Calculation of the area weighted mean concentration of the mixing of the C and the D samples (Table 4) compared to the mean concentrations of the E and F samples indicate a conservative mixing in the confluence zone. However, the somewhat lower alkalinity than expected is probably due to reaction with H^+ from hydrolysis of inorganic aluminium as indicated by a lower Al_i concentration than expected (Table 4). Generally high labile inorganic aluminium (Al_i) concentrations and pH fluctuations around about pH 5.2 (Fig. 3b,c) render the water quality in the confluence zone highly toxic to fish (Baker and Schofield, 1982). This may explain why fish (brook trout) is observed downstream the lake only as far as the tributary. During the sea-salt event the water in the confluence zone was potentially even more toxic due to the increased Al_i concentrations. The situation was most probably the same during the period with ice-cover on the lake as aluminium is known to hydrolyse significantly at lower pH by lower temperatures (Lydersen, 1990). The only periods with a chemically reasonable water quality in the confluence zone are in the summertime with low flow. However, the water level in these periods is generally too low for fish.

Conclusion

Principal component analysis is a useful tool in extracting samples that are similar in chemical profiles. The sea-salt event, the ice-covered period of the lake and the rest were exhibited by the samples from the confluence zone.

The differences in chemistry arose mainly due to climatic variations and therein imposed episodes. It is however difficult from the PCA analysis to make any conclusions regarding the variables such as concentrations of Fe_t , SO_4^{2-} , NO_3^- and UV/VIS absorption of the water samples at 254 and 410 nm.

Generally the water quality in the confluence zone was highly toxic to fish due to hydrolysing aluminium. During the sea-salt event the potential toxicity was increased due to increased concentrations of labile inorganic aluminium. Ice-cover on the lake had the same effect as the

inlet acidic and aluminium rich water drained almost unchanged through the lake in the upper few meters under the ice.

Highly toxic water quality is most probably a common problem introduced by treating lakes upstream acid tributaries with limestone.

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