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Convention on Long-range Transboundary Air Pollution

International Cooperative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes

Proceedings of the 12th Task Force Meeting in Silkeborg, Denmark, October 23-25, 1996

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1999

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Data sheet

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Abstract: The proceedings of this report are the result of the twelfth meeting of the Programme Task Force held on October 23-25 1996 at the National Environmental Research Institute in Silkeborg, Denmark. The report contains five papers submitted at the meeting covering a wide range of biological and chemical studies undertaken in various countries as part of the task group activities.

Keywords: Acidification, air pollution, freshwater, monitoring

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Preface

At the twelfth meeting of the Programme Task Force held on 23-25 October 1996, in Silkeborg, Denmark, several national experts presented information on relevant ongoing national research and monitoring activities and recent results. In the proceedings of the meeting we have compiled five of these presentations in the manuscript form in which we have received them from the respective authors. The editors have, however, undertaken a slight linguistic revision of the manuscripts. Together the five papers give a broad picture of the various lines of studies pertinent to this international task group such as biological and chemical monitoring activities, intercalibration activities and trend analysis of chemical variables.

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Swedish lake and stream macroinvertebrate survey: design and preliminary results

by Lars Eriksson, Swedish University of Agricultural Sciences, Department of Environmental Assessment, S-750 07 Uppsala, Sweden

Introduction

Planning of the first national survey of lakes and streams using macroinvertebrates began in July 1995, when unexpected funding was made available. Implementation (i.e. sampling) was stratified across the country, until the end of August in northern Sweden and November or early December in the southern parts of Sweden. Approximately 700 streams and 700 lakes were planned to be sampled. The deadline for the preliminary report was set at autumn of 1996.

Lakes and streams were randomly selected, with lakes divided into size classes according to surface area (0.01 - 100 km^2) and streams according to catchment size (two size classes, 15 - 50 and 50 - 250 km^2). Macroinvertebrate samples were collected using standardised kick sampling (European standard, EN 28 265:1994). Five (1 min) kick-samples (pooled) were taken from within 10 m stretches of stream riffles or within the lake littoral (exposed, hardbottom). The kick-samples were supplemented with a 10 min qualitative "search" sample (not pooled with the 5 kick-samples).

The majority of sampling was done by the 24 regional monitoring boards. A one day sampling course was held at the end of August 1995 for the sampling crews. The course consisted of both lectures and a field exercise to demonstrate sampling technique and clarify any questions regarding the sampling protocol.

Due to an early winter, only 550 of the lakes were sampled, however, all 700 streams were sampled. All samples were sorted at the Department of Environmental Assessment according to standardised protocols (including both sorting and subsampling). A maximum time of 2 h was allotted for sorting each sample (composite of 5 x 1 min kicks), and sub-sampling routines were implemented when it was estimated that this limit would be exceeded. Random spot checks of sub-sampling and sorting efficiently were implemented.

Six laboratories assisted with taxonomic determinations. A standardised list of some 500 taxa, agreed upon by expert opinion (weight was given to taxa necessary for index calculations and taxa that could be relatively easily identified), was used in identification. Red listed taxa were also included, but some restrictions were made regarding identification of certain taxa (e.g. Coleoptera). Intercalibrations were run with all laboratories involved in the taxonomic phase. Calibration was done according to the ICP-Waters protocol.

Results

Preliminary results showed that macroinvertebrate densities averaged 1500 individuals per sample (range 3-30000). Some 284 taxa were recorded. Large spatial differences were noted, and appeared to be correlated with geographic position or ecoregion. For example, fewer taxa and lower abundances were noted in the alpine regions. Low (Shannon index < 1.5) and high (index > 3.5) diversity sites were, however, recorded in almost all of the 24 counties. One or more red listed species were found in 117 (17%) of the stream sites, and overall, a total of 21 red listed species were documented. Two taxa in particular, *Gammarus lacustris* (Sars) *Hydropsyche saxonica* (McLachlan) were found at 34 and 32 sites, respectively.

The ecological quality of sites was assessed using a suite of indicator metrics. These ranged from metrics indicative of general ecological quality (e.g. taxa richness and diversity), to more pollution specific (e.g. the Danish Fauna Index and Saprobien index were among those used for evaluating organic stress, whereas Raddum's Index was among those used to assess acidification effects).

In the final report emphasis will be placed on evaluating large-scale patterns in the ecological quality of the sites sampled as well as extrapolated population estimates. In addition, this data will be used to establish ecological criteria for using macroinvertebrates.

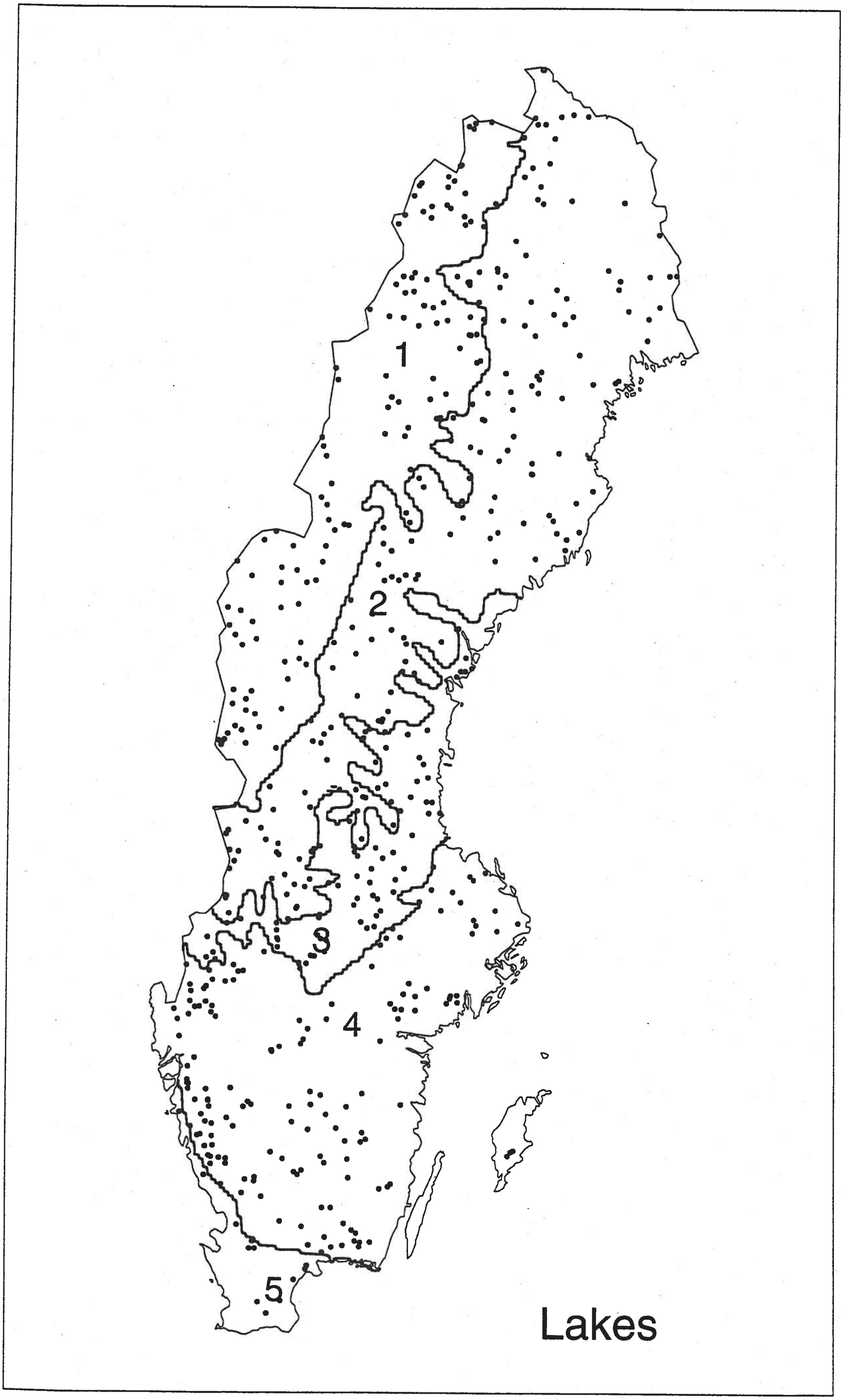


Fig. 1. Sampled lakes in the different ecoregions.

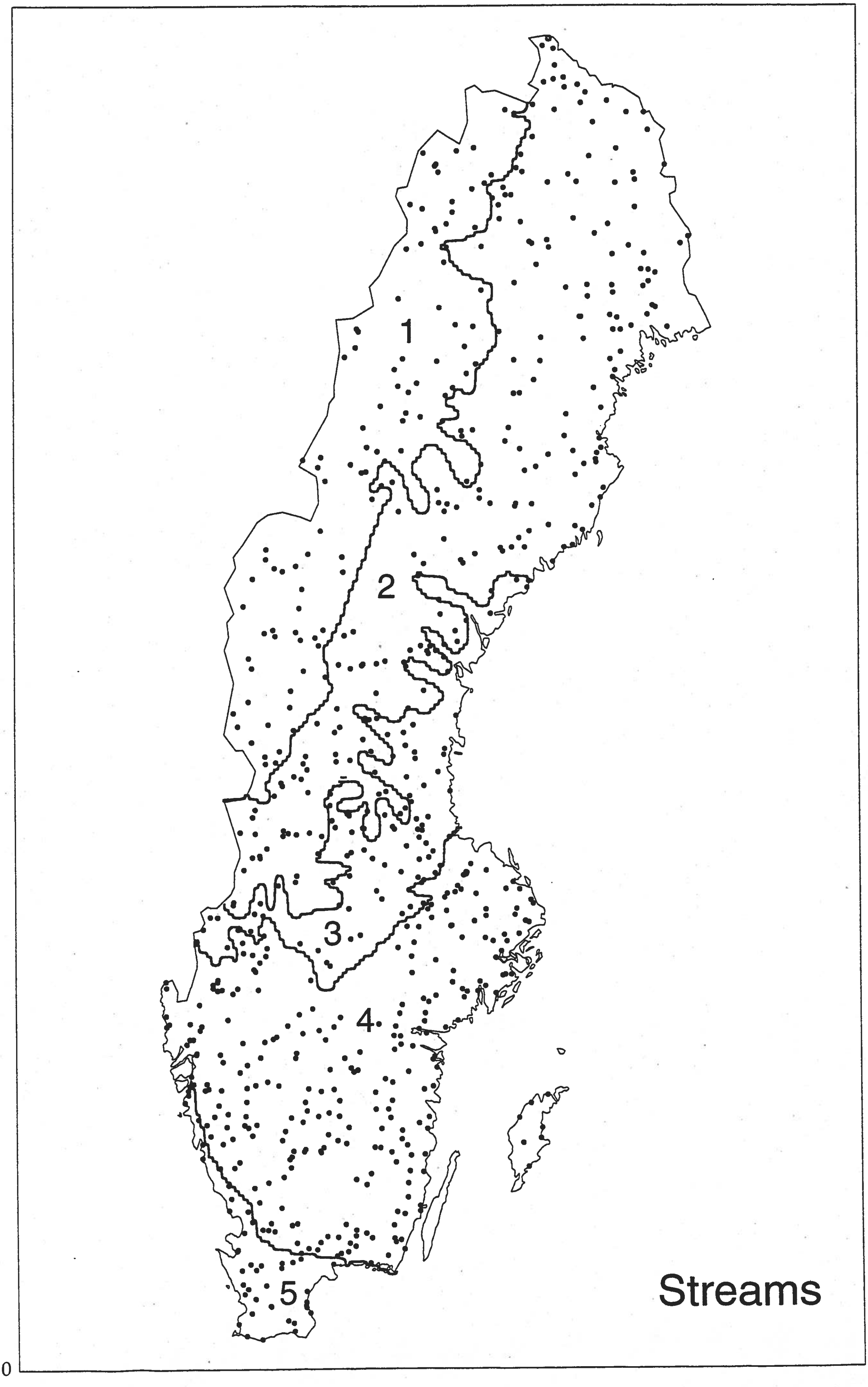


Fig. 2. Sampled streams in the different ecoregions.

ICP-water activities in Latvia, 1995-1996

by Iraida Lyulko and Polina Berg, Environmental Pollution Observation Centre, Latvian Hydrometeorological Agency, 165 Maskavas Str., LV-1019-Riga, Latvia

In 1995, observations were carried out at 64 posts and 105 profiles in 35 water bodies, including 11 lakes and water reservoirs; the number of analyses totalled more than 21 thousand. (Fig.1).

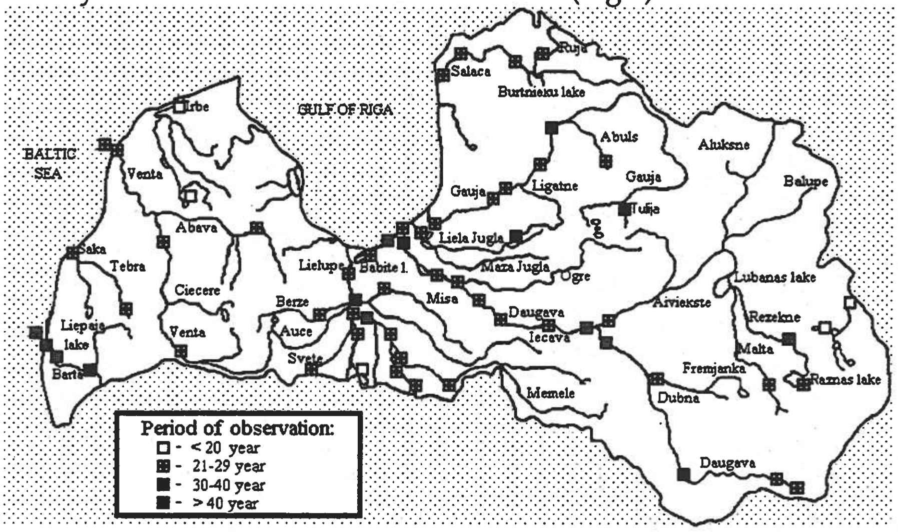


Fig. 1. Water pollution observation network

In the first stage, the following posts were proposed for the ICP-Water programme (Table 1):

Basin	River, lake	Site	Watershed area (km^2)	Mean annual flow (km^3)	Period of observa-tion
Salaca river	Burtnieku lake	Burtnieku	33.4		1956-1959; from 1973
Gauja river	Tulija	Zoseni	33.4	0.01	from 1946
	Gauja	Valmiera	6150	1.43	from 1947
Daugava river	Daugava	Daugavpils	64,600	13.62	from 1947
	Liela Jugla	Zaki	663	0.20	from 1954
Lielupe river	Lielupe	Jelgava	12,000	2.08	from 1947
Small rivers, Baltic Sea	Barta	Dukupji	1750	0.59	from 1954

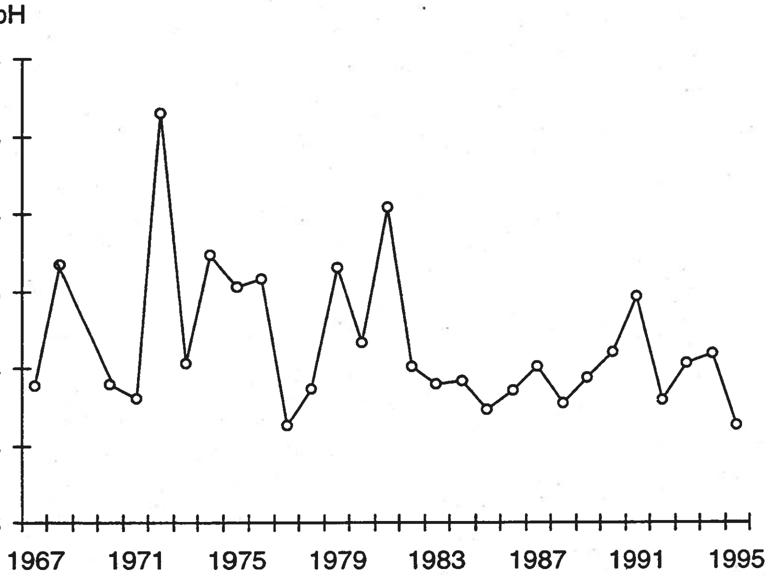
We were guided by the fact that the posts i) have long data series; ii) provide information on the main water basins and physico-geographical areas; iii) have measured water flow data. Investigations and generalizations made at the posts have shown that they are representative for water quality trend assessments.

According to the Minutes of the 11th Meeting of the Programme Task Force, the observation data had been reported to NIVA: hydrochemical data for 1992-1995 from the posts; benthos data that covered the years 1994-1995; characteristics of monitoring sites and analytical methods (following the requirements set forth in the ICP-WATERS PROGRAMME MANUAL).

Along with the data given in Table 1, hydrochemical data and site information were submitted for the bog stream Zvirbuli. A 30-year long data series available for the stream might be useful in acidification studies, both background and transboundary pollutant transport; the latter greatly effects bog water.

According to data for the most recent years, pH values of 3.5-4.5 (with some values near 6.0) were the most common in the beginning of the 1970's (Fig.2).

Fig. 2. Long-term changes of pH (annual mean) in Zvirbuli stream



A calculated complex hydrochemical index shows that the Latvian surface waters in 1995 were classified as conditionally clean(96%) and moderately polluted(4%); the ICP waters fall under the former.

Judging from the Saprobia Index data, Latvian rivers included in the ICP-Waters are classified as:
Liela Jugla - Zaki - β-mesosaprobility
Berta-Dukupji - β-mesosaprobility
Lielupe-Jelgava - β-α-mesosaprobility

Long-term observations showed that the water objects under ICP-Waters had been exposed to nutrient loading, and nutrient contents did not decrease.

Comparisons of data from ICP-Waters and small forest catchments under ICP-IM, situated in the same geographical regions, showed higher or similar (for Ptot) nutrient loading to the former. This is due to anthropogenic influence on the water bodies independent of direct impact from the sources (Fig.3).

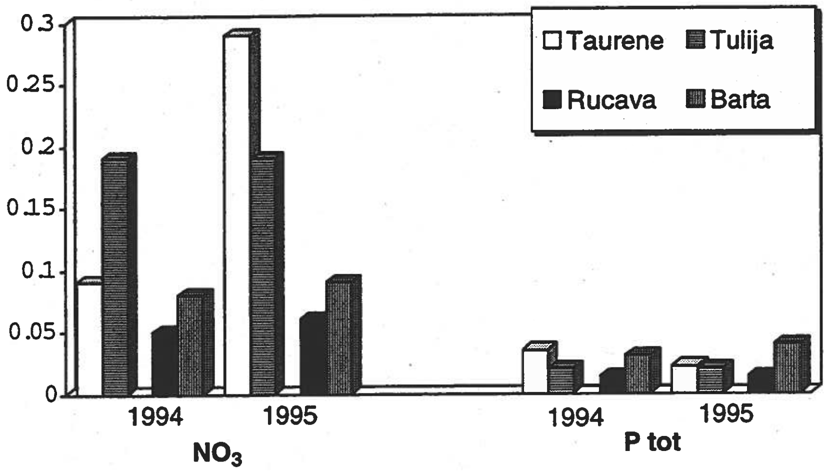


Fig. 3. Nutrient contents (mean annual concentrations, mg/l)

Some problems and suggestions:
We participated in two intercomparisons under the ICP-IM and ICP-Waters programmes. This year, we only have preliminary results. Preparatory work is going on for a hydrobiological intercalibration.

Table 2. Intercalibration under ICP-IM and ICP-Water, 1995

Indeks	Sample: expected value/reported value				Note
	1	2	3	4	
pH	5.09	5.10	6.07	6.05	
Conductivity	1.79	1.79	2.33	2.42	Ms/m
NO_3-N	57	55	156	181	µg/l
Cl	0.84	1.8	0.67	1.0	mg/l
SO_4-S	2.30	6.30	5.32	6.60	mg/l
Ca	0.87	0.81	1.59	1.61	mg/l
Mg	0.19	0.37	0.83	0.73	mg/l
Na	1.20	1.31	0.90	0.97	mg/l
K	0.52	0.59	0.20	0.24	mg/l

Significant differences were found for sulphate, Mg and in some cases, Cl (Table 2). This is likely due to values that were 5-10 times lower than values normally measured in Latvia waters. Such low concentrations require different measurement methods. Preliminary intercalibration results for 1996 show low similarity for pH, since we have no special electrode for pH measurements, and for alkalinity measurements (lack of special electrodes and digital burettes).

A financial contribution and technical support are desirable for laboratory studies, and intercalibrations should be implemented in the future.

The two IM stations in Latvia, Rucava and Zoseni provided the sampling and their analysis from brooks and a lake.

It's obvious that the analytical methods run under the two ICPs should be co-ordinated during the preparation of the Manual.

It would be desirable for our hydrochemistry and hydrobiology specialists to take short-term training sessions at relevant institutes, and have operational manuals (methods) and references.

Long-term data is stored as hand-written (typed) records, and trend assessments and other calculations are performed manually (lack of reliable programmes).

We trust that, under the ICP-Waters, our observational network will meet international standards. This is very important for Latvia and Europe, since Latvian waters greatly effect the water quality in the Baltic Sea.

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Performances of analytical methods for freshwater analysis assessed through inter-comparison exercises. I. Total alkalinity

by A. Marchetto[1], M. Bianchi[2], F. Geiss[2], H. Muntau[2], G. Serrini[2], G. Serrini-Lanza[2], G.A. Tartari[1] and R. Mosello[1]

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Abstract

In 1991-95, five intercomparison excercises were held, in the framework of an activity connecting laboratories participating in different projects (Environmental studies in the Mediterranean Basin, Italian Network for the study of wet deposition, Acidification of mountain lakes: palaeolimnology and ecology, Limnological studies of Lake Leman). The number of participants increased from 72 in 1991 to 115 in 1995. The chemical variables considered were pH, conductivity, alkalinity and major ions (Ca, Mg, Na, K, ammonium, sulphate, chloride and nitrate).

Alkalinity resulted in the most critical measurements, and some analytical techniques were inadequate for the values considered (around 0.04 to 0.13 meq l^{-1}). This paper discusses the errors associated with alkalinity measurements, comparing the performance of different techniques and showing the improvement in the results obtained by the laboratories participating in the entire set of exercises.

Introduction

Five intercomparison exercises on rainwater samples have been performed from 1991 to 1995 in the framework of the project "Analytical Quality Control and Assessment Studies in the Mediterranean Basin (AQUACON)", as part of the "Protection of the Environment" program, executed by the Environment Institute of the Joint Research Centre (JRC-EI) in collaboration with the Istituto Italiano di Idrobiologia of the Italian National Research Council (CNR-III). The program, developed by the EU-member countries belonging to the Mediterranean area in close partnership with the Environment Institute, is aimed at the identification, quantification and reduction of random and systematic errors associated with the most important branches of environmental analysis. At their request, other research teams working in the environmental field joined the exercises, involving eventually the laboratories participating in the following projects: Analytical Quality Control and Assessment Studies in the Mediterranean Basin (AQUACON), Acidification of Mountain Lakes: Paleolimnology and Ecology (AL:PE), International Commission for the Protection of Lake Leman, Italian network for the study of wet deposition chemistry (RIDEP). Furthermore, a group of South American laboratories involved in freshwater research asked to participate in the exercises.

The aim of this report is to present the methods used for sample preparation and data elaboration, and to discuss the results of the five intercomparison exercises, with respect to the alkalinity values. The list of participating laboratories and the entire set of results are reported elsewhere (Mosello *et al.*, 1993a, 1993b, 1994, 1995, 1996).

Methods

Sample preparation

For each exercise, two samples prepared specifically for alkalinity measurements, were obtained at the JRC-EI in 1991 by diluting lake water, and in 1992-95 by dissolving sodium hydrogen carbonate in water of the highest quality (nanopure U.W.S. Barnstead). Potassium chloride was also added to increase the ionic strength, up to a conductivity of about 30 $\mu S\ cm^{-1}$ at 20 °C. The prepared solutions were stabilized with the addition of about 0.2% volume of chloroform.

Bottling was performed by hand, rinsing the previously conditioned 500 ml polypropylene bottles (two weeks with nanopure water) with the samples and then completely filling them up. Alkalinity values were chosen in the range of those present in some episodes of atmospheric deposition in southern Europe, i.e. same range measured in many remote European lakes, and in areas characterized by poorly buffered water.

Samples were sent to the participating laboratories by mail, and the stability of the samples was checked by analysing samples kept in a dark at room temperature by the two organizing laboratories over the period allowed for the exercise. The results (not shown) demonstrate the stability of the solutions, for the duration of the exercise.

Sample homogeneity and stability

An estimation of the variance of alkalinity samples was obtained by measuring alkalinity for each solution in ten randomly selected bottles. All measurements were performed in one laboratory by the same analyst using the same analytical method for each variable. The variance due to the analytical method for each variable was then estimated by repeating the measurement ten times on the same bottle of each sample. Alkalinity hetereogeneity in the solutions was then estimated as the square root of the difference of the variances of samples and methods. Results were below 1.5% for most samples, and in some cases even below 1% (Table 1).

Table 1. Number of laboratories participating in the five intercomparison exercises and expected values (meq l^{-1}). Asterisks denote samples with heterogeneity lower than 1%.

Exercise	Participating laboratories	Expected values Low value	High value
1991	72	0.037	0.124*
1992	80	0.038	0.118*
1993	99	0.039	0.134
1994	108	0.039	0.121
1995	115	0.041*	0.130*

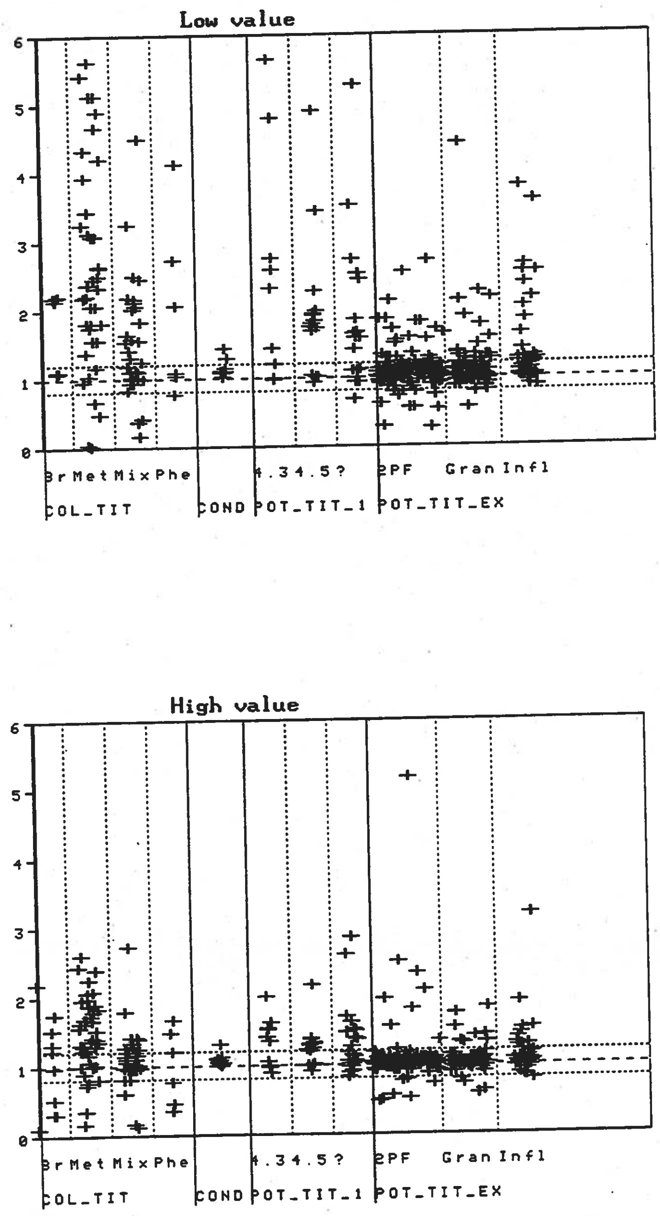


Fig. 1. Distribution plot of the alkalinity value. Lines indicate expected values ± 20%. Unit: expected value. Method legend in Table 2. Extreme outliers are not shown

Data presentation

The participating laboratories were requested to perform a single analysis for each sample. Target values (Table 1) were calculated as the mean of the values obtained by the organizing laboratories, using either the Gran's method (Midgley & Torrance, 1979) or the two-end points potentiometric titration (A.P.H.A. 1981; Rodeir, 1981).

The data for each sample and each laboratory were normalized by dividing for the expected value. As the expected values for the five exercises were relatively similar (Table 1), the results were grouped in a set of "low values" and a set of "high values". Normalized data were then plotted in distribution graphs (Fig. 1), with the expected values.

A range of ± 20% of the expected values was also plotted; these plots do not represent a goal to be reached, but only aid in seeing the data distribution. Extreme outliers were not considered in the graph, nor the Youden plot (Fig. 2). This graphical presentation uses the data from two samples, analyzed using the same analytical method, and then plotted in a scatter diagram (Youden & Steiner, 1975) to distinguish between random and systematic errors.

Hypothetically, if the analyses were only affected by random errors, the results would be spread over the whole diagram. However, the results are usually concentrated in the lower left and the upper right quadrant, forming an elliptical pattern along the 45° line passing through the expected values. This is due to systematic errors which underestimate or overestimate the concentrations in both samples.

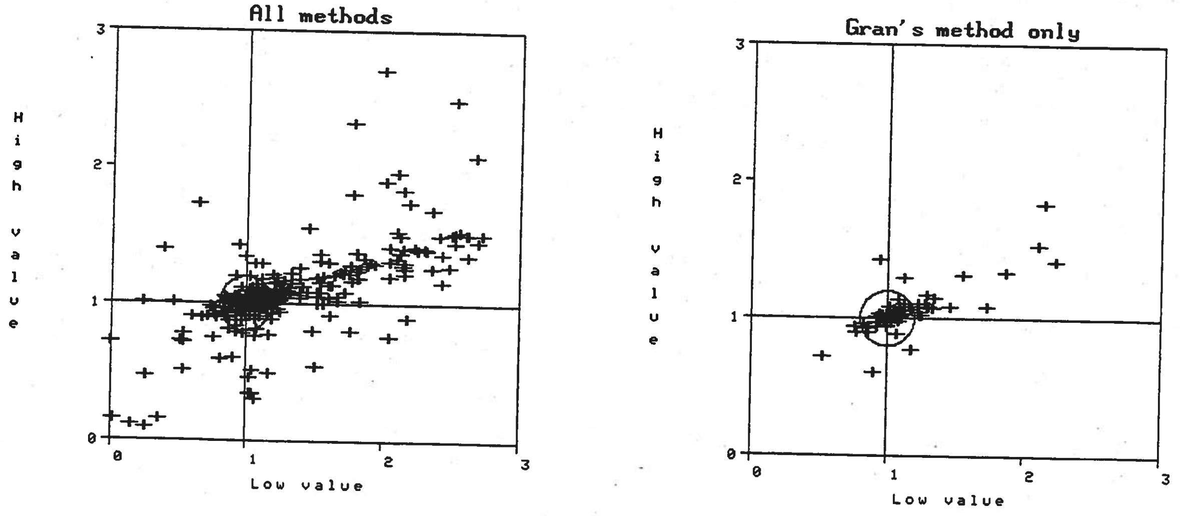


Fig. 2. Youden plot of the alkalinity value. Circle indicates expected value ± 20%. Unit: expected value. Points three times higher than the expected value are not shown.

Table 2. Analytical method used, and robust estimate of the mean normalized value and standard deviation (σ) of the results. Asterisks denote significantly different values (probability level of 0.01; either t-test or F-test) from those obtained for the Gran's method.

Method	Legend	Low values			High values		
		No.	mean	σ	No.	mean	σ
Potentiometric titration with extrapolation of the end point	POT_TIT_EX						
Gran's method	Gran	81	1.075	0.162	82	1.015	0.074
two end point	2PF	143	1.063	0.159	143	1.010	0.065
inflection point detection	Infl	42	1.255	0.341*	42	1.082	0.185*
Conductometric titration	COND	12	1.091	0.054*	42	1.040	0.048
Potentiometric titration with a fixed end point	POT_TIT_1						
to pH 4.3	4.3	10	2.852	2.189*	11	1.387	0.453*
to pH 4.5	4.5	15	1.730*	0.625*	15	1.209*	0.185*
to unspecified pH	?	20	1.914	1.140*	24	1.212	1.856*
Colorimetric titration							
Bromochresol green	Br	8	1.618*	0.582*	6	0.971	0.555*
Methyl orange	Met	41	2.805*	1.877*	42	1.480	0.563*
Mixed indicator	Mix	35	1.449	0.728*	35	1.099	0.253*
Phenolphtalein	Phe	6	1.870	1.288*	6	0.971	0.543*

Robust statistics

Outlier rejection is not correct practice when included in the evaluation and comparison of the precision of analytical methods, as it can produce a smaller standard deviation (σ) for methods producing a larger number of outliers. An alternative approach is robust statistics (e.g. Huber, 1984), which shifts from outlier rejections to outlier accommodation, i.e. extreme values are downweighted which is then compensated for. In this paper we used the iterative technique known as H15, assuming a value of 1.5 for the constant *c* (Analytical Method Committee, 1989). The procedure begins by assigning to the estimated robust mean (m_0) the median of the sample values (x_i), and to the estimated robust σ (s_0) the median of the quantities ($|x_i - m_0|$)/0.6745. Then, at each *n*-th iteration, all values higher than $m_{n-1} + c\ s_{n-1}$ or lower than $m_{n-1} - c\ s_{n-1}$ are replaced by the pseudo-values $m_{n-1} + c\ s_{n-1}$ and $m_{n-1} - c\ s_{n-1}$, respectively, while the pseudo-values for the remaining values are the values themselves. The new estimate of the robust mean m_n will be the mean of the pseudo-values, while the new estimate of the robust σ (sn) will be their σ divided by the square root of the constant *b*, which compensates for the downweighting of the extreme values. At $c = 1.5$, $b = 0.736$ (Analytical Method Committee, 1989). The estimated parameters rapidly converge to the robust mean and standard deviation.

Analytical methods used by the participating laboratories

To comment on the results, a brief description of the main analytical techniques employed may be useful. Alkalinity measurements are affected both by systematic errors related to equipment and the determination of the inflection point, and by random errors. The methodological aspects are more important, particularly for low values. Aspects related to errors associated with the kind of titration used (automatic titrator or manual burette) are discussed by Rodier (1984), APHA (1989) and Kramer *et al.* (1986).

The alkalinity of a water sample is a measure of its capacity to neutralize strong acids. In natural water, it generally corresponds to measurement of the bicarbonate concentration, as the inorganic carbon system is the dominant contributor to alkalinity and, if pH is below 8.3, carbonate concentration is negligible. In theoretic terms, the alkalinity is equivalent to the amount of acid necessary to reach the inflection point of the titration curve between bicarbonate and carbonic acid + carbon dioxide. A further problem arises from the fact that the equivalence pH of the alkalinity titration depends on the CO_2 concentration at this point, which is a function of the total concentration of the carbonate system. Consequently, the equivalence point of the alkalinity titration depends on the alkalinity to be determined (Stumm & Morgan, 1981; Kramer *et al.*, 1986).

Fixed end point titration

Some laboratories use a fixed pH as the end point of the titration, detected either potentiometrically or using a dye as an internal indicator. Apart from the equipment used, the alkalinity values depend on the pH value chosen as the end point. Differences due to the adoption of different end points are clearly systematic, and they may be important at low alkalinity levels. The use of different colorimetric indicators clearly means the adoption of different end points, adding further to the errors related to the different perception by the operator of the variation in color. For instance, in the case of colorimetric titration with methyl orange indicator, an uncertainty of 0.02 to 0.09 meq l^{-1} can be caused by different perceptions of colour change (Asbury *et al.*, 1989). Precision of colorimetric titration may be improved by using a color-comparison titration, or by performing a correction based on blank measurements, as suggested by Rodier (1984).

An improved single end-point alkalinity measurement has been proposed by Henriksen (1982), considering a titration to pH 4.5: the measured alkalinity ($MA_{4.5}$, in μeq l^{-1}) is corrected for the amount of acid used from the equivalence point to pH 4.5, estimated at 32 μeq l^{-1}, and corrected further for the variation of the equivalence pH with alkalinity using the equilibrium constant for the bicarbonate/carbon dioxide system:

$$TA\ (\mu eq\ l^{-1}) = (MA_{4.5} - 32) + 0.646\ (MA_{4.5} - 32)^{0.5}$$

Direct detection of the equivalence point

The detection of equivalence point is necessary to assure that the selected end point is correct. Recording the pH of the solution after each addition of acid, makes it possible to draw the titration curve and to detect the equivalence point. An example is shown in Fig. 3, where the identification of the inflection point is made easier if the first derivative of the curve is considered. In practical terms, such measurements require the use of an automatic burette and software which records and elaborates signals relating to acid addition and pH measurements of the solution analyzed. To determine alkalinity levels in atmospheric deposition and in acid-sensitive waters, the use of an automatic titrator is highly recommended.

Alternatively, it is possible to continue the titration well after the equivalence point and to extrapolate its value from a number of measures of the hydrogen ion concentration or of some related variables, such as the pH or the electric conductivity of the solution.

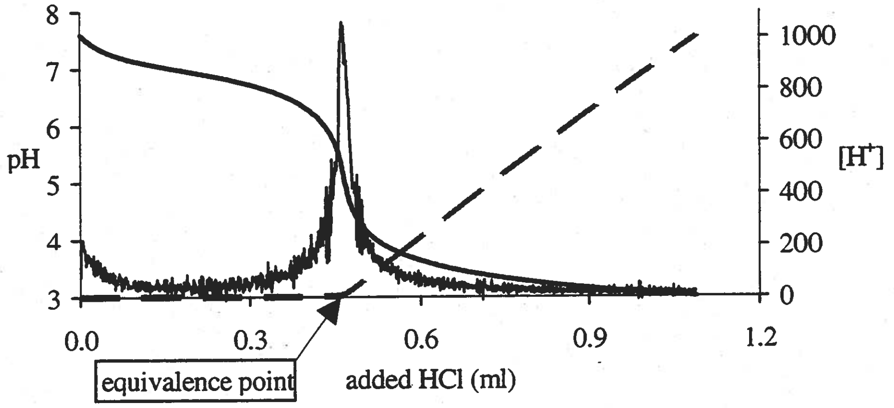


Fig. 3. Example of titration curve with HCl 0.05 N; dark solid line repres ents pH; dark broken line represents hydrogen ion concentration (μeq l^{-1}), and the thin light line represents the first derivative of pH.

Gran's titration

The method described by Gran (1950, 1952) consists in a stepwise titration, with pH measurements after each 5-10 additions of titrant acid in the pH range 4.5-3.5 (Midgley & Torrance, 1979). The equivalence point is then detected transforming the pH data (between 4.5 and 3.5) into functions and plotting against the volume of titrant added (x, in ml). The regression lines then intersect the x-axis at the equivalence point (x_0). The most used Gran's function (Fig. 4) is:

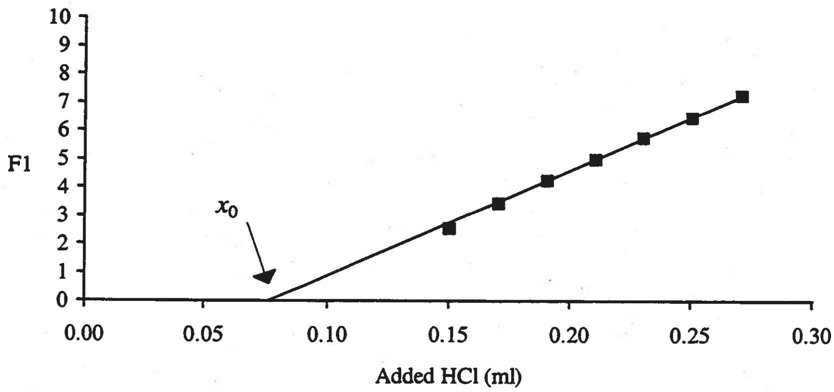
$$F_1 = 10^{-pH} (V + x)$$

where V is the volume of the sample in ml. Total alkalinity (TA, μeq l^{-1}) is then obtained as:

$$TA = x_0 N / V$$

where N is the titrant concentration (eq l^{-1}).

Fig. 4. Example of Gran's F1 function. x_0: intercept on the x-axis. Data points are collected between pH 3.5 and 4.5



In principle, Gran's titration can be performed using a manual burette and direct reading of volumes added and pH of the solution, in practice an automatic burette is needed, preferably with software facilities. Furthermore this technique is relatively time consuming for routine analyses (10-15 minutes).

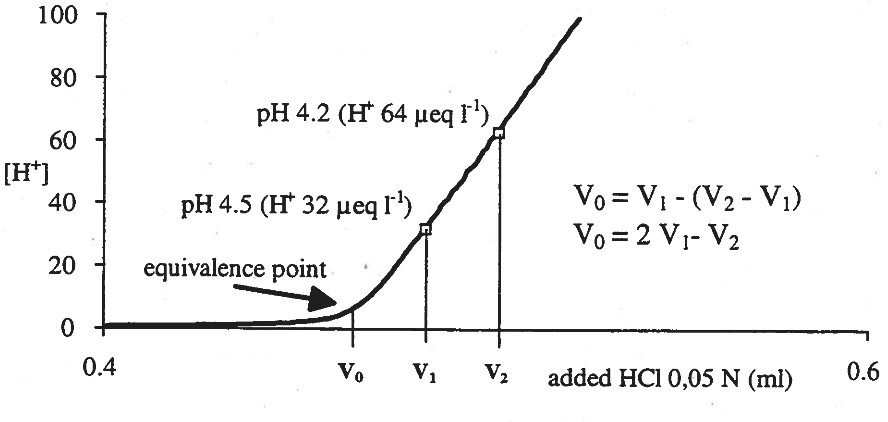
Two end points titration

At first, titration is performed up to a pH of between 4.3 and 4.7. The volume of acid added (V_1) and the first end point pH are recorded. The pH is then reduced by exactly 0.3 units, and the total amount of acid required (V_2) is measured (Fig. 5). Because this change in pH corresponds to an exact doubling of the hydrogen ion concentration, the equivalence point can be obtained by a simple extrapolation (A.P.H.A., 1981; Rodier, 1981):

$$TA = (2\,V_1 - V_2)\,N / V$$

This method can be considered as a Gran's titration performed with two pH and volume readings, expressly chosen to simplify the calculation. An automatic burette and a continuous record of pH improves the repeatability of the method.

Fig. 5. Titration curve of the same solution presented in Fig. 3, performed with two end points, and extrapolation to the equivalence point (APHA, 1981; Rodier, 1981). Unit: µeq l^{-1}. V_0: inferred volume at the equivalence point, V_1: added volume at the first end point, V_2: added volume at the second end point.



Conductometric titration

This method is based on the high specific electric conductivity of the hydrogen ion (Britton, 1934; Vollenweider, 1962). The addition of a strong acid to a buffered solution does not significantly increase its conductivity, as hydrogen ions react with bicarbonate to produce carbon dioxide, and the specific conductivity of the anion added (usually chloride or sulphate) is close to that of the bicarbonate ion. At the equivalence point, both hydrogen ion and the anion of the titrant acid are free to contribute to conductivity. The equivalence point is detected by plotting the conductivity of the solution *vs* the added volume of acid (x) after the equivalence point, and detecting the intercept point on the x-axis.

Results and discussion

The results obtained (Fig. 1) reflect the great number of methods used, and show a high dispersion. The tendency in general is to overestimate the concentration, mainly in samples with lower alkalinity. The Youden plot (Fig. 2) clearly shows the prevalence of systematic errors, either in the whole set of data or when considering a single analytical technique.

The results of these intercomparison exercises confirm the good reliability of alkalinity methods which extrapolate the equivalence point, such as the Gran's titration (Midgley and Torrance, 1979), the two-end points (APHA, 1981; Rodier, 1981) and the conductometric titration (Britton, 1934; Vollenweider, 1962). The mean values of the results obtained using these technique are not significantly different from each other (t-test, $p<0.01$), nor are their standard deviations different (F-test, $p<0.01$). For the lower values, the conductometric titration gave even better results, but it was only used by three laboratories.

Contrarily, all other methods gave a significantly higher standard deviation. As expected, the colorimetric titration using bromochresol green or methyl orange as internal indicators, and the potentiometric titration to a fixed end point, also gave a significantly higher mean value. The Henriksen's (1982) correction was applied to the data submitted by the 15 laboratories using a pH value of 4.5 as the fixed end point (Fig. 6).

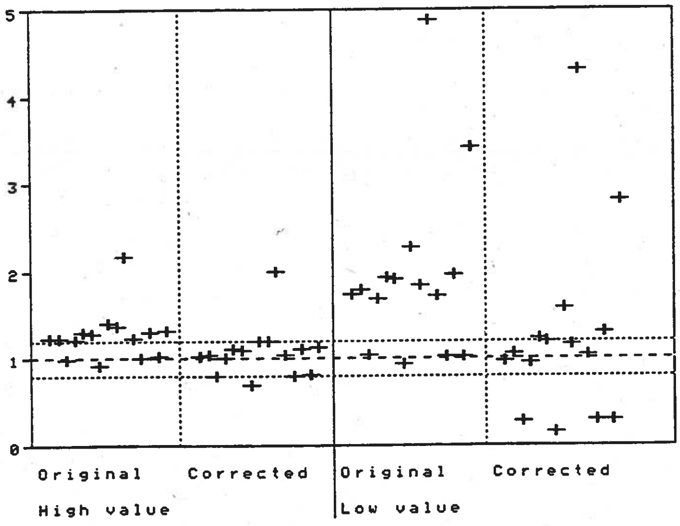


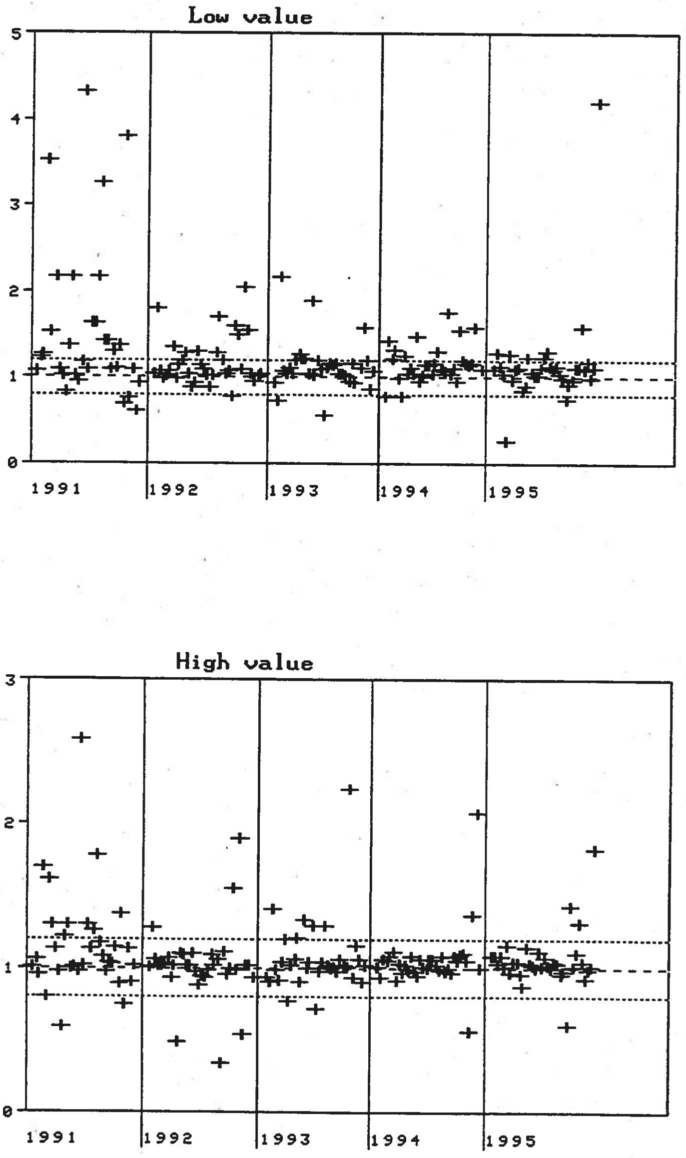
Fig. 6. Distribution plot of obtained data which used a pH value of 4.5 as the fixed end-point before ("Original") and after ("Corrected") the application of the Henriksen's (1982) correction. Unit: target value.

The results were good for the high values, but the laboratories using a fixed end point titration obtained a high dispersion for the low values, probably because of an excessive amount of the acid aliquot added. Consequently, this technique is not recommended for such low alkalinity values.

Surprisingly, the results obtained by using the potentiometric titration with direct equivalence point detection show a significantly higher dispersion with respect to the optimal methods. This is probably due to the difficulty in choosing the optimal amount of acid to add in each step of the titration.

The intercomparison exercises represent an important tool to improve the analytical quality and to verify the suitability of techniques to a given sample. Results from the 34 laboratories which participated in the five exercises, show a decreasing dispersion from year to year (Fig. 6).

Fig. 7. Distribution plot of the alkalinity value for the 34 laboratories participating in five exercises. Dotted lines indicate expected values ± 20%. Unit: expected value. Extreme outliers are not shown.



On the one hand, 12 of the 15 laboratories which used colorimetric methods during the first exercise improved their results after introducing the potentiometric titration with extrapolation of the equivalence point during the second or third year. Similarly, the three laboratories, which in 1991 used potentiometric titration with a fixed end point, introduced an extrapolation technique in 1992. On the other hand, the precision of the values obtained by the 16 laboratories which used an extrapolation technique in all the exercises (Table 3) improved, in particular in the lower values.

Table 3 Standard deviation of the alkalinity values obtained by the 15 laboratories which participated in the five exercises using potentiometric titration with extrapolation of the end point.

Exercise	Low value		High value	
	σ	robust σ	σ	robust σ
1991	0,730	0,199	0,128	0,092
1992	0,276	0,161	0,237	0,067
1993	0,274	0,163	0,159	0,148
1994	0,242	0,203	0,054	0,054
1995	0,162	0,140	0,149	0,083

Conclusions

In this paper, alkalinity was considered because of the large errors associated with the determination of low values. The participation in the five intercomparison exercises allowed a general improvement in the results which was evident only if the laboratories which participated in all the five exercises are considered. Contrarily, the results obtained in different laboratories with different techniques are poorly comparable. Part of the dispersion of the results is explained by the fact that some titrations consider different end point pH values, however, calibration and other random errors increase the dispersion of the results. The most reliable techniques were those which extrapolate the equivalence point, such as the Gran's titration, the two-end points and the conductometric titrations. The least satisfactory results were those obtained from single end point titration, using a dye as indicator. The results of these intercomparison exercises suggest that the use of an automatic titrator and the adoption of a two end points titration are sufficiently precise for the analysis of rainwater and poorly buffered water. In the case of single end point titration, with either automatic or manual titration, Henriksen's (1982) method is recommended because it corrects for the excess acid used to reach the end point pH in relation to the equivalence point.

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Acidification of ground waters at an area influenced by a chemical fertiliser plant

by Cecilia Iordache[1] and Stanescu Valentin[2], [1]Research and Engineering Institute for Environment, Spl. Independentei nr. 294, Bucharest, Romania, [2]Analist service SRL, Busharest, Romania.

Introduction

The main characteristics of the Romanian surface and ground waters are pH values of 6.8 -8.6. In recent years, the development of the monitoring system, should focus on the decreasing water alkalinity, both of ground and surface waters, directly correlated with local pollution sources. The change in the acido-basic balance influences other water characteristics such as the micro element contents.

This paper presents the acidification of ground water as a result of the "Navodari" chemical plant activity, and correlates this data with the physiochemical characteristics of the soil.

The source of acidification of water

During the technological flow of producing sulphuric acid, the "Navodari" fertiliser plant uses ordinary pyrite as a raw material either extracted in Romania or imported. Pyrite usually contains important quantities of impurities such as Zn, Cu, Pb, As, Ni, Co, Cd. Following the burning of pyrite, residual gases are released into the atmosphere through a 30 m high furnace. The gases contain important quantities of SO_2 but also ash with Cu, As, Pb, Zn, Mn and other micro-elements. To analyse the actual level of pollution around the chemical plant water samples were collected from groundwater sources at 7 monitoring points. The level of ground water was between 1.8 - 2.5 m.

Soil samples were also collected at 0 - 10 cm level close to the monitoring points.

Results and discussion

Table 1 shows the ground waters and soil sampling points and the distance and direction from the pollution source, as well as the water and soil pH. The soil close to the chemical plant has a great buffering capacity, however, following the emission of SO_2 over a long period of time, its pH became acidic, up to a value of 3.8 - 4.0, at a distance of 300m from the evacuation tower (the source of residual gases). The soil pH within the plant varied between 4.21 -5.62.

The water pH varied between very large limits (2.90 - 7.63). The lowest values were recorded in the water samples taken from the installations of sulphuric acid where the soil pH showed minimal values., These values are probably determined by the losses of sulphuric acid from installations.

Table 1.

Sampling	Distance (m)	Direction	Soil pH	Water pH
H - 43	375	E-SE	4.69	7.63
H - 95	540	N-NE	5.62	6.11
H - 55	210	N-NE	4.32	2.90
D - 1	160	NW	4.43	3.40
D - 2	400	N-NW	4.63	7.15
H - 68	475	NE	5.42	7.21
C - 15	150	SE	5.21	7.17

The diagrams in Fig. 1 - 6 show contamination with micro-elements coming from residual gases, dissolved into the soil due to acidification. We have to mention that the minimal values of the analysed micro-elements are higher than the allowable values for groundwater. The determined values for Al, Cu, Mn, Zn are in direct relation with decreasing water pH. For Cd and Pb there were no noticeable high values with variations of pH.

Conclusions

There are only a few ground water sources within the area influenced by the "Navodari" fertilising plant and only a few sampling points. To assess the impact of the fertilising plant on the ground waters, there are a few sampling points for monitoring within the plant.

The results of the soil and water analyse in the area of sampling points showed local acidification and contamination of water by micro-elements influenced by distance and sampling location from the pollution source (evacuation tower for residual gases). Although there was no noticeable direct correlation between the level of acidification and the contamination of water by Pb, Cd, Zn, there were higher concentrations of these contaminants in the soil samples that had higher levels of pH.

This result may be a warning about the possibility of a greater contamination of waters in the area, in the future.

Fig. 1 Zn concentration in groundwater and soil

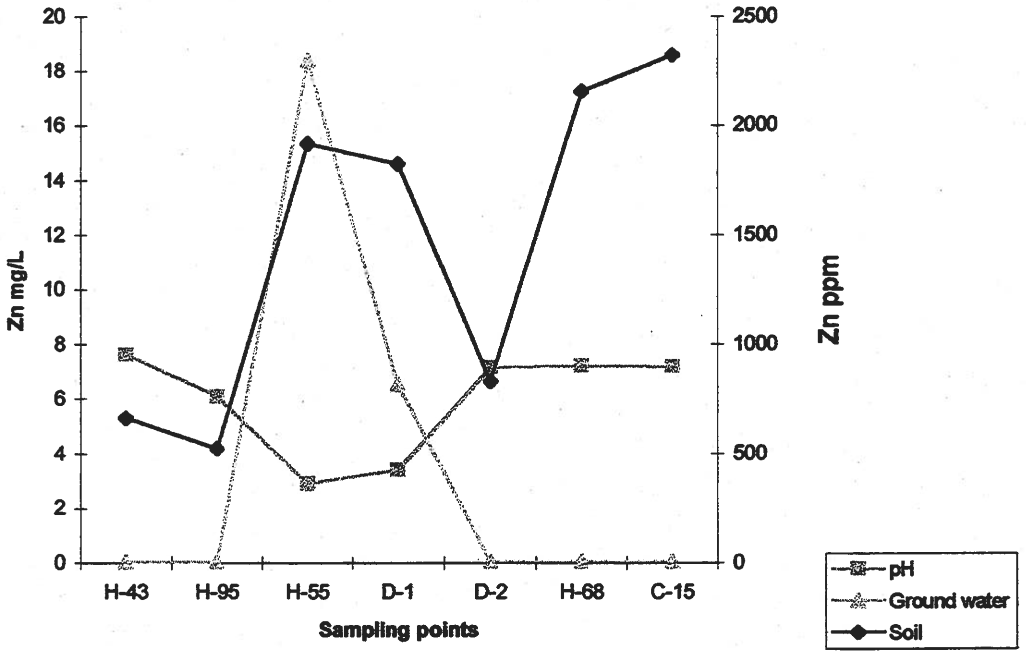


Fig. 2 Mn concentration in ground water and soil

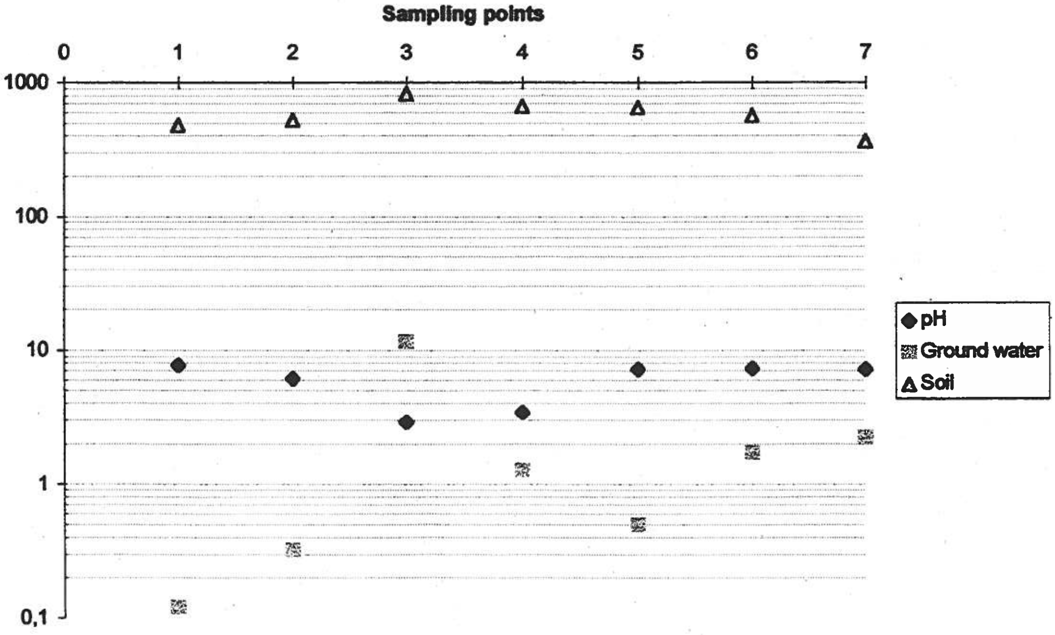


Fig. 3 Cd concentration in ground water and soil

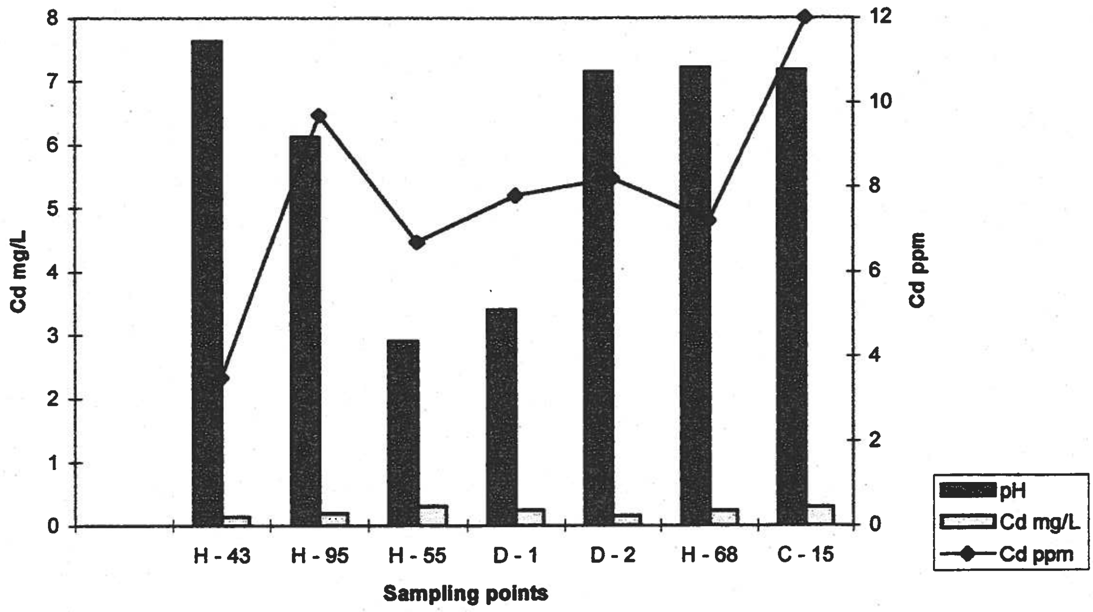


Fig. 4 Cu concentration in ground water and soil

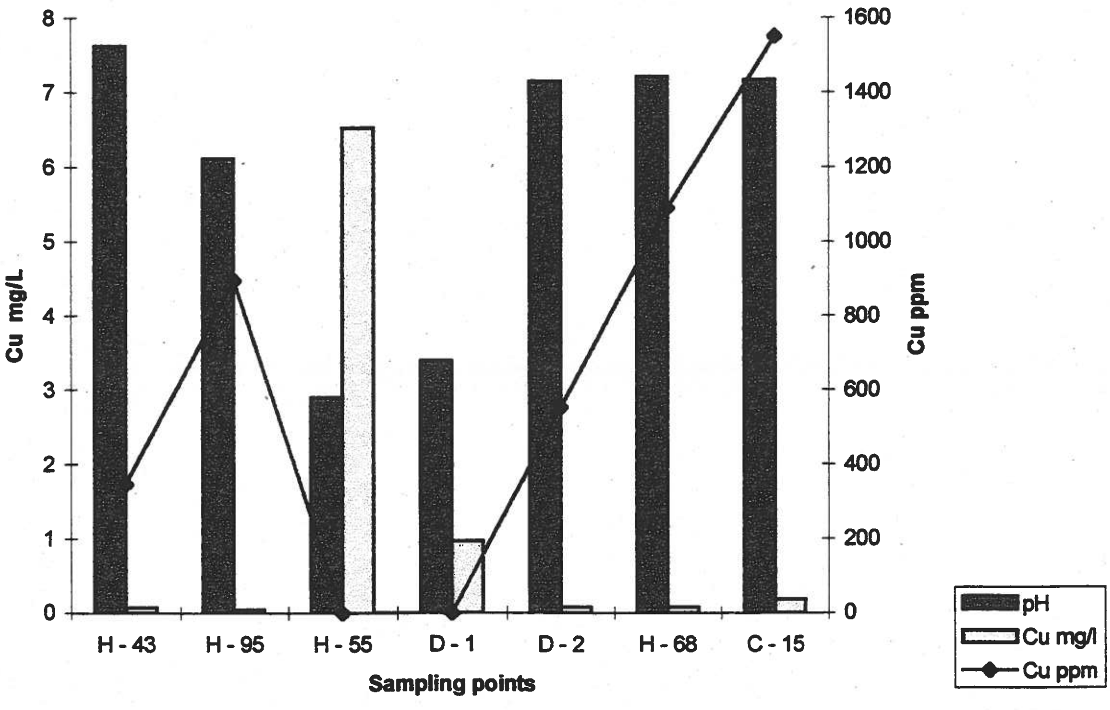


Fig. 5 Pb concentration in ground water and soil

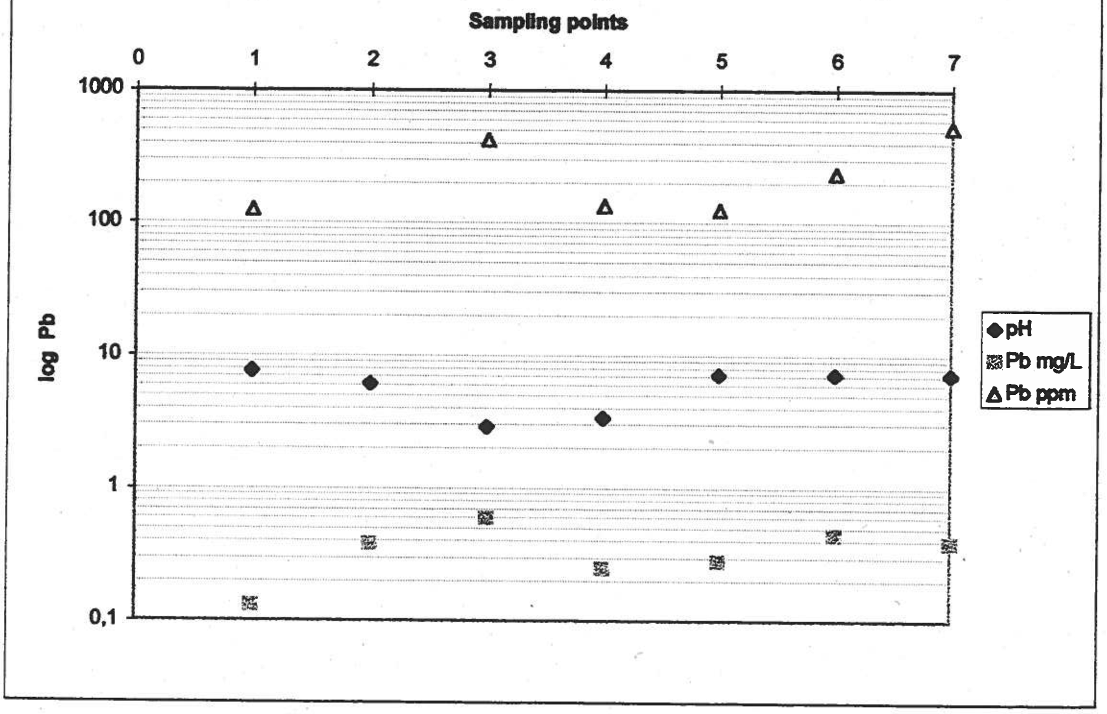
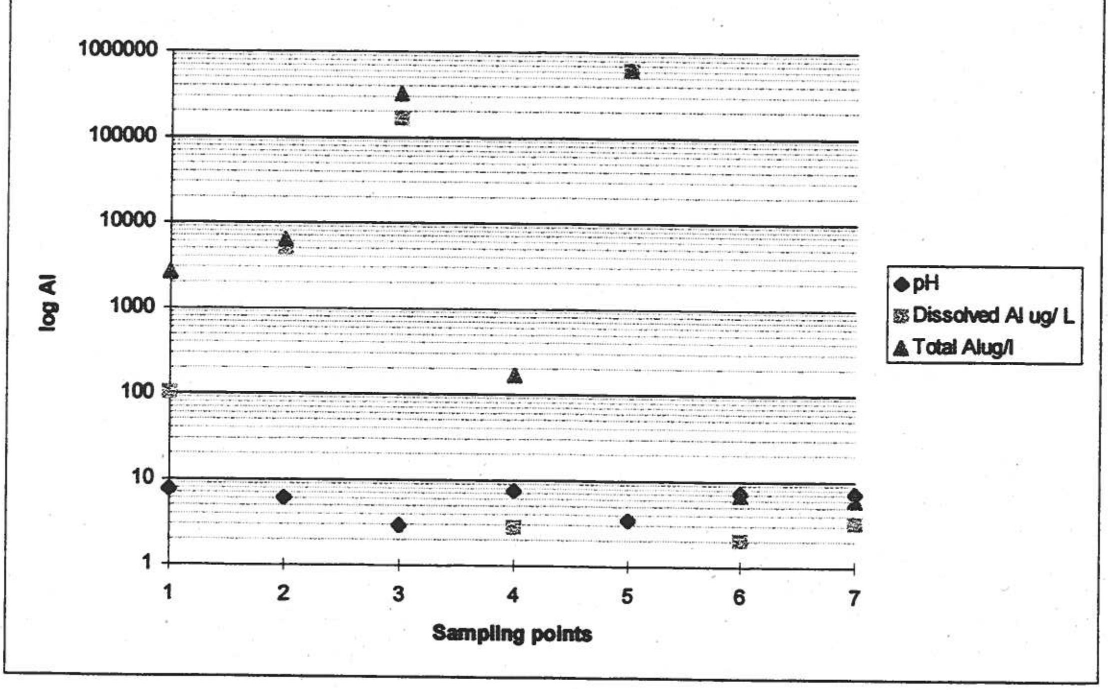


Fig 6 Disolved and total aluminium concentration in ground water



Trends in the acidification of the Danish ICP monitoring locality, the headwater moorland stream Skærbæk

by Søren E. Larsen, Nikolai Friberg and Aage Rebsdorf, Department of Streams and Riparian Areas, National Environmental Research Institute, DK-8600 Silkeborg, Denmark.

Introduction

In Denmark, the dominating calcareous soils and, consequently, alkaline freshwater in general prevent serious freshwater acidification from atmospheric deposition. In the western part of the peninsula Jutland (Fig. 1) the soils are sandy, and long-term acidification of some streams (Rebsdorf *et al.*, 1991) and lakes (Rebsdorf, 1983; Wium-Andersen, 1987; Rebsdorf & Nygaard, 1991; Jacobsen, 1992; Riis & Sand-Jensen, 1998) has been documented.

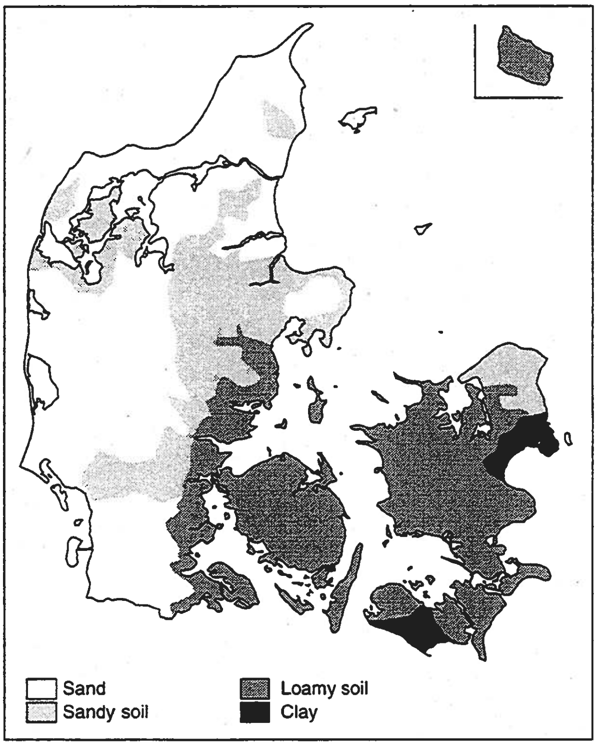


Fig. 1. Soil map of Denmark.

Recently, very acidic short-term pulses with pH-values as low as 3.7 have been detected in some Danish coniferous forest streams. These acidic situations are primarily attributed to acidic deposition, although exaggerated by the specific acid soil conditions below conifers (Friberg *et al.*, 1998). In addition, groundwater acidification has been documented in western Jutland which is attributed primarily to nitrification of ammonium-containing fertilisers applied on the farmland (Pedersen, 1985; Overgaard, 1986).

In spite of the generally sufficient buffering capacity of the Danish soil and freshwater to counteract acidification, the above studies reveal examples of documented acidification both at isolated sites and more regionally in central and western Jutland.

Due to extensive agricultural activity in Denmark, with 65% of the total area in Denmark used for farmland and another 12% for forestry, it is in most cases difficult to separate the factors affecting the acid-base status of streams and lakes, and to specifically quantify the contribution from atmospheric deposition. Only in small, isolated sites with minor human disturbances such as water bodies in heather and nature reserves is it possible to exclude other human acidifying effects than atmospheric deposition.

The catchments of most Danish streams are directly influenced by land use practices such as agriculture or forestry, even in the upstream parts. The upper part of the catchment area in one small stream, the Skærbæk, is an exception. Consequently, this stream was chosen as the Danish locality in the International Co-operative Programme for Assessment and Monitoring of Acidification of Rivers and Lakes (ICP-Waters). The stream drains a sandy moorland catchment without agriculture in the upper sections, but possibly with a slight influence from forestry (see Table 1). In the two periods 1976-1980 and 1986-97, chemical analyses was regularly undertaken at a site (henceforward denotes Site 1) in Skærbæk which had low alkalinity and was therefore believed to be sensitive to acidification from atmospheric deposition.

In the period 1987-97, analyses was also undertaken at a site (henceforward denotes Site 2) downstream Site 1. The stream at Site 2 was partly influenced by agriculture (see Table 1) and the alkalinity was higher. Consequently, Site 2 is probably insensitive to atmospheric acidification. For this reason, Site 2 was chosen as a reference site to the more acidified Site 1. In a previous study (Rebsdorf *et al.*, 1991), acidification at Site 1 was documented by trend analysis during the period 1976-1988.

The intent of this paper is to illustrate the long-term acid-base development in Skærbæk from 1976 to 1997.

In addition, the invertebrate fauna is shown to illustrate the relationship between acidity and invertebrates at the acidic Site 1 and the neutral Site 2.

Study sites

Skærbæk is a first order stream located in an uncultivated, sandy area in central Jutland. It flows into the River Salten Å, which in turn flows into the River Gudenå, which eventually flows into the sea (Kattegat) at Randers Fjord. The vegetation mainly consists of grass (*Deschampsia flexuosa* (L.) Trin.) and heather (*Calluna vulgaris* (L.) Hull) and a few solitaire spruce trees. Minor parts of the catchment consist of natural wetland and coniferous plantation (predominantly *Picea abies* L.) (Table 1). The dominating submerged macrophytic vegetation was *Potamogeton polygonifolius* Pourret in scattered patches.

Two sites at Skærbæk stream have been monitored (Fig. 2).

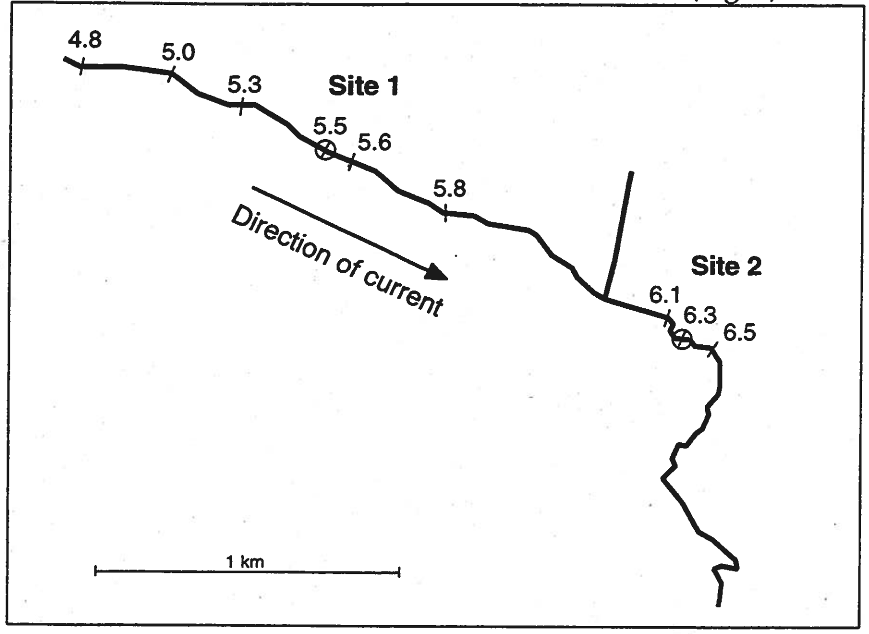


Fig. 2. pH-gradient in Skærbæk stream February 4, 1987.

The upstream site (Site 1) is situated about 2 km upstream the second site (Site 2). The catchment area at the upstream Site 1 (SK 110B in the ICP data base) has previously been estimated to 3.6 km^2 (Brusch, 1989; Rebsdorf *et al.*, 1991).

However, measurements of discharge and precipitation, and knowledge of evaporation (precipitation data from Department of Atmospheric Environment, National Environmental Research Institute, evaporation data from Department of Agricultural Systems, Danish Institute of Agricultural Sciences) give an area of about 1.9 km^2, according to the following calculations.

The mean precipitation during 1990-92 was 804 mm and mean evaporation 460 mm. This gives a mean discharge of 344 mm during 1990-92. The mean discharge in period 1990-92 was measured to be 21 l s^{-1} or 662.256 m^3 a^{-1}.

This results in an area of

$$\frac{662.256\ m^3a^{-1}}{\frac{344}{1000}m^3m^{-2}} = 1.9\ km^2 .$$

Downstream at Site 2 (SK 038F in the ICP data base), the catchment area was estimated to be 5 km^2 using the same method as described above. This is about 2 km^2 less than estimated by Brusch (1989).

Because of the new catchment area estimates, the distribution of the different types of land cover was revised (Table 1) in relation to the previous estimates by Brusch (1989), who found a greater contribution from forest and farmland and a smaller contribution from heather and wetlands at the two sites.

Table 1. Catchment characteristics of the two sites in Skærbæk.

	Site 1	Site 2
Catchment area (km^2)	1.9	5
Grid reference (UTM)	526360 E, 6215550 N	527825 E, 6214870 N
Dominant soil type	Sand	Sand
Estimated vegetation (%) in the catchment:		
Heather and grass	80	45
Coniferous forest	10	30
Wetland	10	5
Agricultural land	0	20
Period of monitoring	1976-97*	1987-97

*) No regular measurements 1980-85.

Methods

Chemical analyses

Regular monthly samples of stream water were collected around noon in 1 or 2 litre polyethylene bottles, which were completely filled and transported to the laboratory within a few hours, where they were stored overnight at 2-4° C in the dark. The following day pH, alkalinity and conductivity were measured after temperature was held constant at 25° C. Alkalinity and pH were measured using a standardised Radiometer PHM 64 Research pH meter during the period 1976-1990, and by using a Radiometer 85 Precision pH-meter after 1990. Alkalinity (both positive and negative values) was determined by Gran titration (Mackereth *et al.*, 1989). Conductivity was measured by a Radiometer conductivity meter (CDM 83) at 25 ± 0.1°C. The major cations (Ca, Mg, Na and K) were measured by flame atomic absorption spectrophotometry. Nitrate was determined from 1976-1992 by an automated flow injection method (Tecator 5012). Chloride was measured from 1976-1992 by potentiometric titration. In the same period, sulphate was determined by a method according to Mackereth *et al.* (1989). After 1992, nitrate, chloride and sulphate were measured by ion chromatography (Shimadzu Ion Chromatograph HIC 6A). Total nitrogen was transformed into nitrate by persulphate oxidation (Danish Standards Association, 1975) and the nitrate was then measured by flow injection. Ammonium was measured spectrophometrically by the indophenol blue method (Danish Standards Association, 1975). Dissolved organic carbon was measured with a Shimadsu TOC-5000 Total Organic Carbon Analyser. True colour was measured by the platinum method of Danish Standards Association (1992).

Invertebrate methods

Semi-quantitative benthic invertebrate samples at Site 1 and 2 were taken with a standard handnet (25x25 cm opening, 0.5 mm mesh size). At each sampling site four standardized kick samples were taken on a diagonal transect across the channel at equal intervals of 25, 50, 75 and 100 % from one of the stream banks. Each kick sample was taken by kicking backwards twice about 40 cm (Kirkegaard *et al.*, 1992). The four samples were subsequently pooled, preserved in 96 % ethanol and processed in the laboratory. A time-series of invertebrate data from 1980 to 1996 exists for Site 1, only. The first invertebrate samples from 1980 and 1989 were taken using a slightly different method: Samples were taken by kicking in all available habitats and collected with a 1 mm mesh-size handnet and sorted in the field. However, they are included in this study because they are the only available results previously acquired. All invertebrate samples were taken in the spring (April/May).

Statistical trend analysis

Trend analysis of the time series of pH, alkalinity and concentrations of nitrate and sulphate was done by Kendall's seasonal test method with correction for serial correlation (Hirsch & Slack, 1984). This is a robust, non-parametric, site-specific, statistical test for monotone trends. It is robust towards missing values, values reported as "< detection limit", and non-normality. The number of seasons per year was 12, one for each month of the year. A statistical test was calculated for each season and these are combined to one overall test statistic if homogenous. Flow adjustment was done by applying LOWESS (LOcally WEighted Scatterplot Smotthing, see Cleveland, 1979). Since daily mean runoffs were only available for the period from 1989 to 1997, the time series of measurements during this period of time were analysed for significant downward or upward trends. Significant trends were estimated by the Sen slope estimator (Hirsch *et al.*, 1982). A significance level of 5% was used.

Results

The uppermost part of Skærbæk is acidic with pH values that gradually become more neutralised downstream (Fig. 2). The general chemistry is characteristic of sandy soils leaching low alkalinity freshwater, but rather rich in seawater salts due to the proximity of the North Sea and dominating westerly winds (Table 2). The nitrate concentration level is rather high at Site 2, which is undoubtedly caused by agricultural activity in the catchment (see Table 1).

Analysis of Site 1

Time series plots of all raw data measured at Site 1 from 1976 until 1997 are shown in Fig. 3.

All four series display the same pattern of sampling, with measurements during the late seventies then a gap until 1986, except for a single observation in 1984. There were only a few sulphate measurements in the period 1986-89.

Fig. 3. Time series plot of raw data measured at Site 1 during 1976-97.

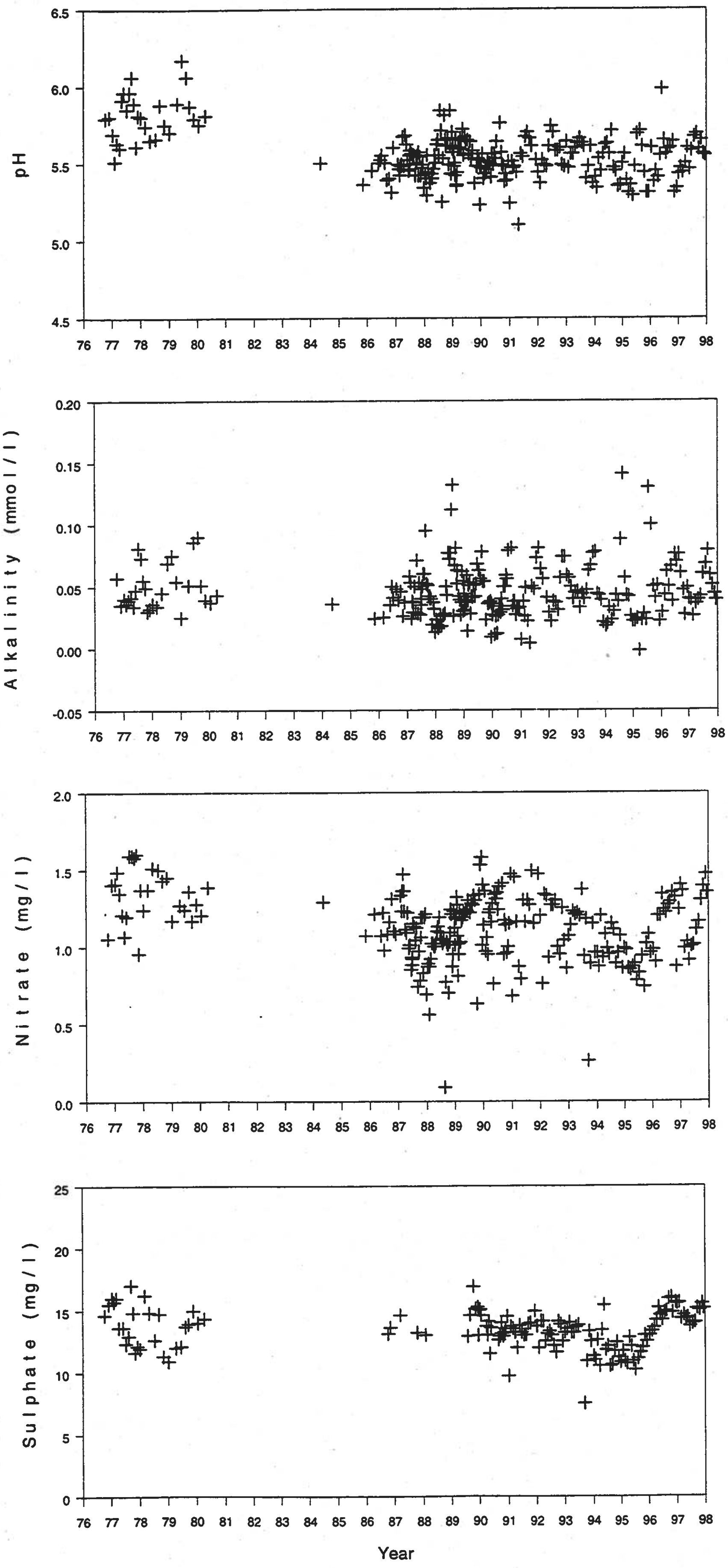


Table 2. Some physical and chemical characteristics of Site 1 and 2 in Skærbæk measured from 1992 through 1993. Mean values of measurements from monthly sampling (minimum/maximum values in parentheses). Bulk precipitation data is from the National Environmental Research Institute, Department of Atmospheric Environment (unpubl.). Excess sulphate is calculated as total sulphate minus sea-salt sulphate, *Excess sulphate = total sulphate (S) - 0.047 Cl* Hovmand *et al.*, 1992).

Parameter	Site 1	Site 2	Bulk precipitation
Discharge (l s^{-1})	21 (13,45)	57 (42,77)	
Temperature (°C)	6.9 (3.3,10.7)	7.3 (1.6,12.1)	
Conductivity 25° (mS m^{-1})	10.4 (7.7,11.2)	14.0 (10.8,14.8)	
pH	5.55 (5.37,5.74)	6.67 (6.34,7.09)	4.54*
Gran alkalinity (µeq l^{-1})	48 (21,78)	128 (54,210)	
Sulphate (mg l^{-1} SO_4)	12.9 (7.5,14.1)	16.9 (11.5, 18.8)	3.0
Excess sulphate (mg l^{-1} SO_4)	10.8	14.7	2.4
Calcium (mg l^{-1} Ca)	5.2 (3.5,10.6)	8.7 (6.0,13.6)	
Magnesium (mg l^{-1} Mg)	2.0 (1.6,2.3)	2.9 (2.3,3.3)	
Sodium (mg l^{-1} Na)	8.5 (7.3,9.6)	9.6 (8.3,10.3)	
Potassium (mg l^{-1} K)	1.2 (0.7,1.6)	1.4 (0.9,1.8)	
Chloride (mg l^{-1} Cl)	15.1 (12.3,16.5)	17.0 (13.9,18.0)	5.0
Total Nitrogen (µg l^{-1} N)	1373 (990,1880)	3015 (1940,3780)	
Nitrate (µg l^{-1} N)	1129 (290,1420)	2844 (1530, 3360)	680
Ammonium (µg l^{-1} N)	13 (4,61)	14 (0,90)	520
Dissolved organic carbon (mg l^{-1} C)	3.3 (1.2,17.9)	2.3 (0.8,9.0)	
True colour (mg l^{-1} Pt)	24 (4,51)	17 (2,33)	
Dissolved iron (µg l^{-1} Fe)	206 (40,760)	74 (0,210)	

*Calculated as the total volume weighted hydrogen ion concentration by weight, and thereafter transformed into a pH unit.

The values of pH during the period of 1976 to 1980 are higher than the measurements during the previous 12 years (1986-97). Thus there seem to be an acidification effect from 1980 to 1986, but no data can confirm this. The time series of pH are more or less constant during the period 1986-1997. If we restrict ourselves to the data from 1989-97, the LOWESS regression (see Fig. 4) shows a clear relationship between daily mean runoff and pH, with pH decreasing with increasing runoff. After adjusting for runoff (i.e. calculating the residuals between measured and LOWESS estimated pH) the time series of monthly average residuals show no statistically significant trend, but do show a tendency towards increasing values (*P*=9.3%) when applying Kendall's seasonal test. Test statistics for the 12 different months were not homogeneous since values in three of the months were decreasing, however not significantly. Residuals in the month of January are statistically significant (*P*=3.5%) with an increasing trend. The increase is estimated to be 0.04 pH units per year by the Sen Slope estimator.

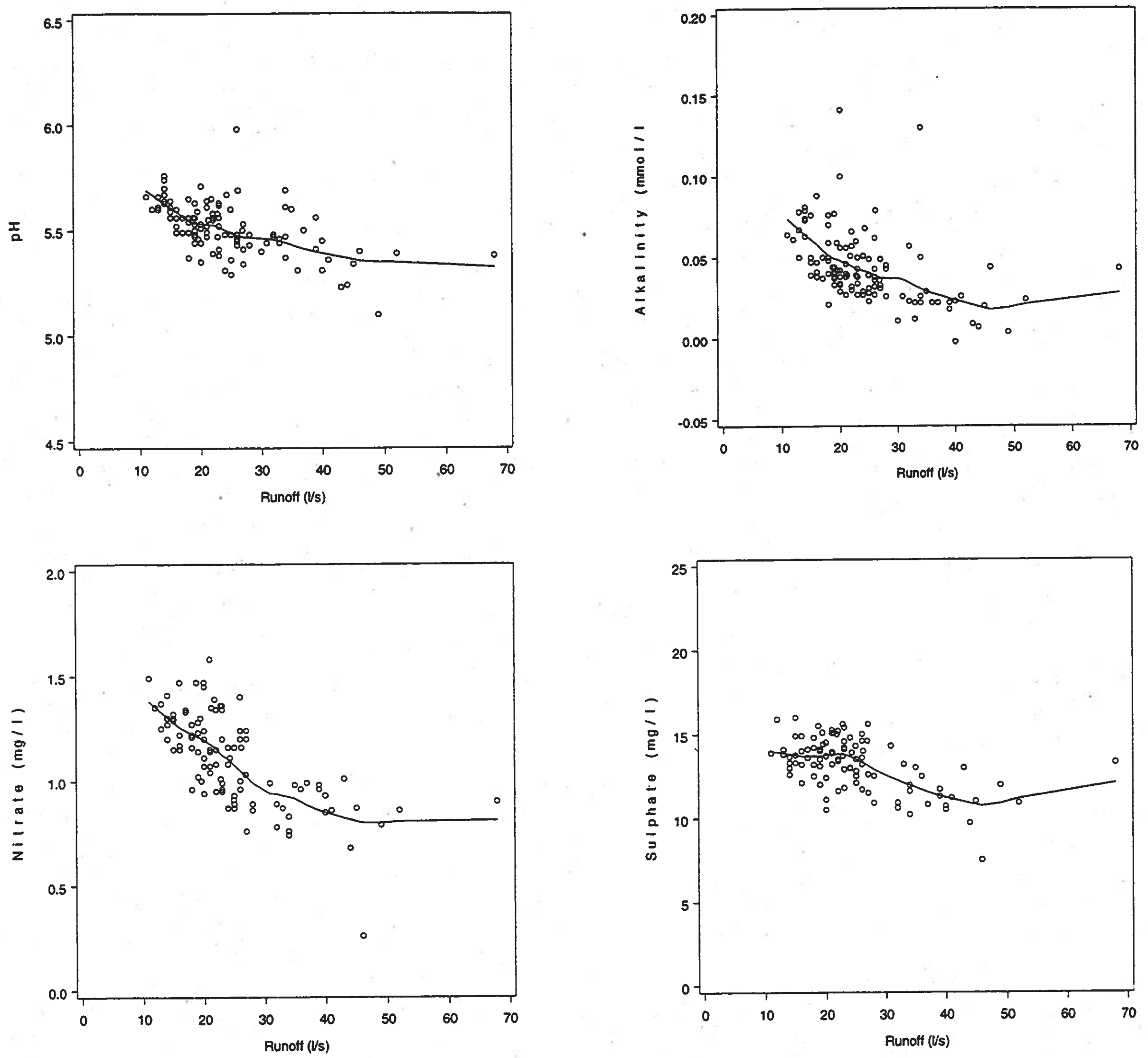
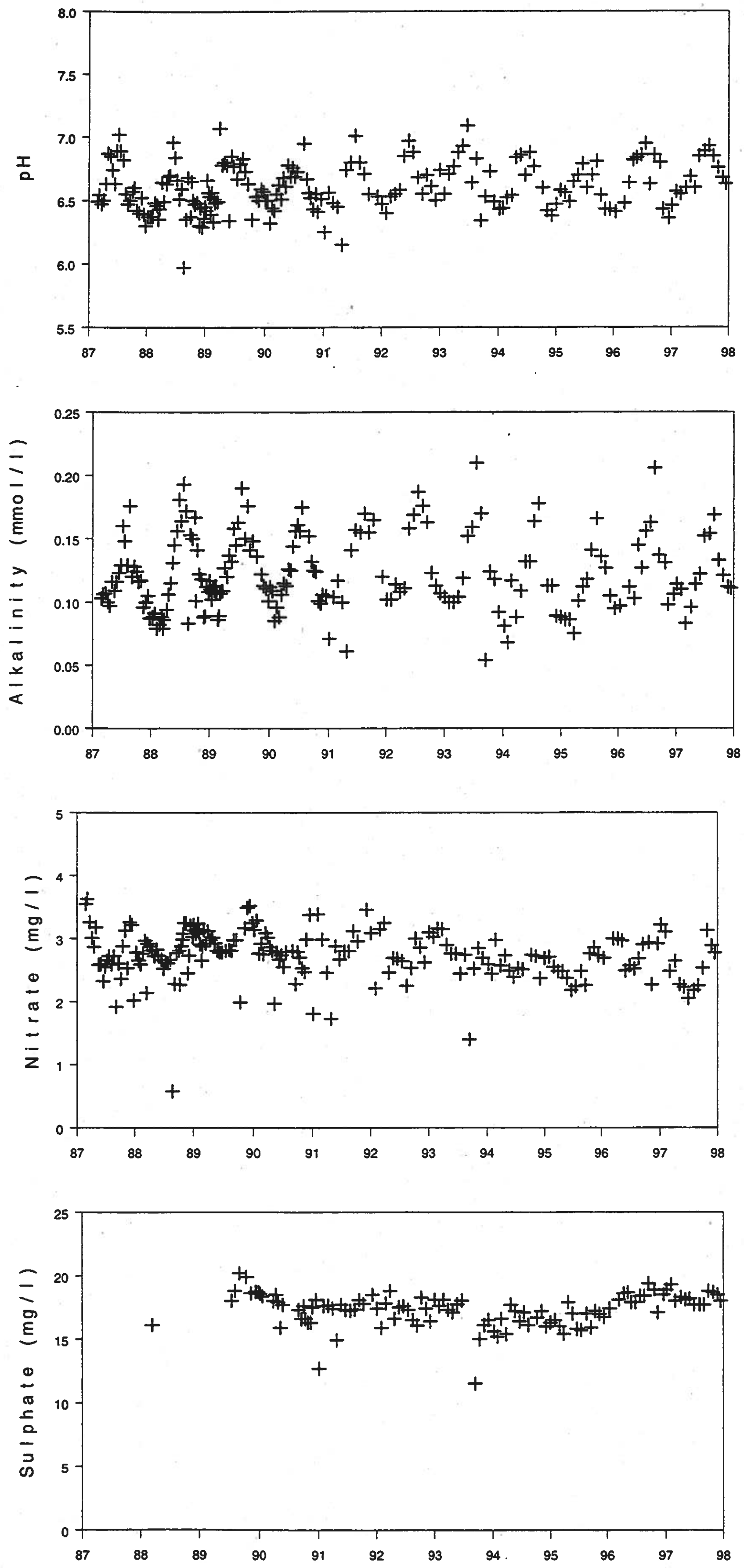


Fig. 4. LOWESS regressions.

The time series of alkalinity show no difference in the measurements during 1976-80 and 1986-97. A small rise in values is noticable during the last period (1986-97). After adjusting for the relationship (decreasing alkalinity with increasing discharge) between alkalinity and discharge (see Fig. 4) modelled by LOWESS, regression showed a positive (increasing) trend in the period 1989-97 (*P*=3.5%). The Sen slope estimator shows that alkalinity measurements increased by 0.0014 mmol l^{-1} per year. All months show a positive trend, but only February is significant at the 5%-level (*P*=3.5%). Measurements in February are estimated to increase by 0.0033 mmol l^{-1} per year.

Nitrate measurements in 1976-80 were higher than 1986-97. In the period 1986-97, nitrate measurements appeared to decrease until 1995 and then increase from 1995-96, and then decrease once again in 1997. For the time series restricted to 1989-97 there was a relationship between nitrate and discharge (Fig. 4), i.e. decreasing values of nitrate with increasing discharge. After adjusting for this relationship there are no significant trends during 1989-97.

Fig. 5. Time series of pH, alkalinity, nitrate and sulphate measured at Site 2 during 1987-97.



Sulphate measurements appeared to decrease from the period 1976-80 until the period 1989-97. During the period 1989-97 sulphate decreased until 1995, then increased almost creating a straight line until 1997, where measurements once again decreased. The LOWESS regression (Fig. 4) showed a relationship between decreasing sulphate values with increasing discharge. After adjustment, values showed no significant trends during 1989-97.

Analysis of Site 2

All raw data measured at Site 2 are shown in time series plots in Fig. 5. Measurements of pH, alkalinity and nitrate started in 1987. With the exception of a single observation in 1988, sulphate measurements began in 1989. Trend analysis will be performed on the data from the period 1989-97, analogous to the analysis of measurements at Site 1. Since no data on daily mean discharge are available for Site 2 during 1989-97, the discharges at Site 1 are used to adjust for discharge using LOWESS regression for the data at Site 2. Plots of LOWESS regressions between discharge and pH, alkalinity, nitrate and sulphate at Site 2 are not shown, but the regressions show the same type of relationships as observed for Site 1.

The time series of pH indicate small increase in pH values during the period 1987-97. Results of adjusted values in the trend analysis showed p-values had a tendency to increase during 1989-1997 (P=5.7%). Values measured in the month of October showed a significant increase (P=3.5%). The trend in October month is estimated to 0.04 pH-units per year.

The alkalinity measured from 1987-97 appeared to be either constant or to slightly increase (Fig. 5). The test for a monotone trend in the adjusted values shows no trend during 1989-97 in the overall time series in each monthly time series.

The nitrate time series showed a decreasing trend during 1987-95, and then increasing measurements during the second half of 1995 and throughout 1996. In 1997, the values of nitrate were once decreasing once again. The time series of the adjusted values have a significant decreasing trend in the period 1989-97 (P=4.9%) which was estimated to be -0.025 mg l^{-1} per year. The trend is not homogeneous within months, since three of the twelve months show an increasing trend, although not significant.

The time series of sulphate starts in 1989. The values decreased until the summer 1995, and then increased, similar to Site 1, from the summer of 1995 and through 1996. In 1997, the concentrations levelled off and decreased slightly. The trend test of adjusted values indicated no significant trends.

In Table 3, the five most numerically important species/taxa of the faunal composition from Site 1 and 2 is given. Faunal composition are clearly differen between the two sites. The most obvious differences were the presence of the amphipod *Gammarus pulex* L. and the dominance of taxa such as *Baetis rhodani*(Pict.) and *Ancylus fluviatilis*

Müll. at Site 2. At Site 1, *Leuctra hippopus* Kmp. dominated, followed by Simulidae.

Table 3. Faunal composition, expressed as the five most numerical important species at Site 1 and 2.

	Stream Skaerbæk	
	Site 1	Site 2
Faunal composition	1. *Leuctra hippopus*	1. *Gammarus pulex*
	2. *Simulidae*	2. *Baetis rhodani*
	3. *Sphaerium corneum*	3. *Limnius volckmari*
	4. *Nemurella picteti*	4. *Ancylus fluviatilis*
	5. *Leuctra nigra*	5. *Silo nigricornis*

Invertebrate samples from Site 1 have, throughout the sampling period from 1980 to 1996, been dominated by acid tolerant plecopteran species such *Nemoura cinerea* Retz., *Nemurella picteti* Klp., *Leuctra nigra* (Olv.) and *L. hippopus*, with Simulidae being the only other quantitatively important taxon.

There has been no major change in the number of taxa found at Site 1 (Fig. 6) during the sampling period except in 1980 where only 8 taxa was found. However, this could be attributable to the sampling procedure then employed and should not be over-emphasized.

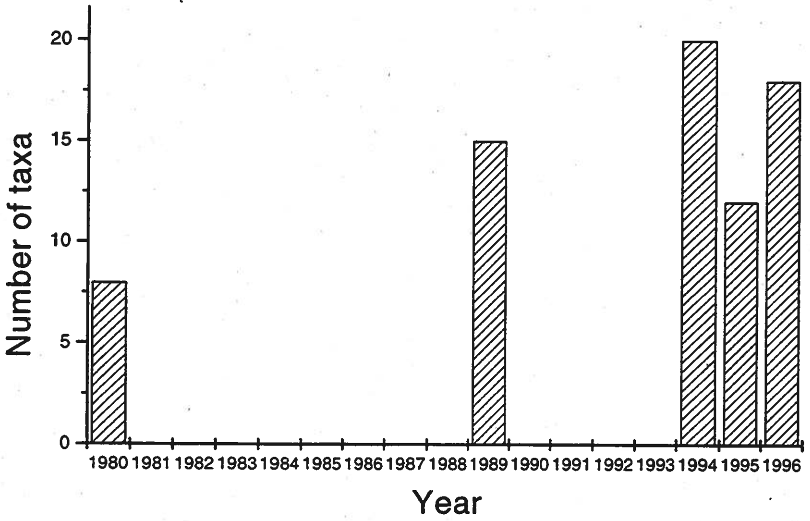


Fig. 6. Change in number of taxa found at Site 1 in the period 1980 - 1996.

Discussion

In a previous study (Rebsdorf *et al.*, 1991) acidification at Site 1 was documented by trend analysis over the period 1976-1988. In Fig. 3 this is clear by the two different levels in pH during 1976-80 and during 1986-88. The "Nine Year Report" (NIVA, 1997) documents an increasing trend in pH and alkalinity during the 5-year period 1986-90 at Site 1, and a decrease in sea salt corrected sulphate and base cations in the period 1990-95 at both sites. The decrease in sea salt corrected sulphate is in accordance with a considerable decrease in the atmospheric sulphur dioxide concentration and wet sulphate concentration in the precipitation from 1978 to 1992 (Hovmand et al., 1994) and a strong decrease in the atmospheric deposition of sulphur during 1985-1996 (NIVA, 1997).

Trend analyses of discharge-adjusted time series of pH, alkalinity, nitrate and sulphate measured at Site 1 and 2 during 1989-97 show a significant rise in pH at Site 2. Values of pH are also increasing at Site 1 but not statistically significant on a 5%-level. Alkalinity is increasing at Site 1. During 1989-97 nitrate is decreasing significantly at Site 2. This decrease might be related to changes in agricultural practices in the catchment, which at Site 2 is influenced partly by agriculture (see table 1). At both sites time series of nitrate and sulphate are decreasing from 1987 until summer 1995 (Fig. 3 and 5). From July 1995 until 1997 a clear rise in both sulphate and nitrate is seen at the two sites. Then in 1997 sulphate and nitrate are again decreasing.

The recent increase in the concentration of sulphate and nitrate at both stations contradicts the general decrease in the atmospheric deposition of sulphur and, to a certain degree, of nitrogen compounds. However 1995 and 1996 were extraordinarily dry, and especially the winters 1995/96 and 1996/97 were very dry. As a result the ground water table in the catchment has been lowered more than natural fluctuations could give rise to. A lowering of the ground water table means that oxygen penetrates to deeper horizons in the soil and thereby mediates oxidation of reduced nitrogen and sulphur compounds which were deposited since the last dry period around 1975-76 and now they leach to the stream water as an extra surplus to the concentration of sulphate and nitrate. The mentioned oxidation should also give rise to a weak decrease in pH. This decrease in pH could not be noticed in the time series.

Faunal composition at Site 1 was very different from that in most other Danish streams. In about 80% of 200 streams investigated in the National Monitoring Programme (Kronvang *et al.*, 1993), *G. pulex* and *Baetis* sp. were the dominant faunal elements. At Site 2, however, such species as *G. pulex; B. rhodani;* and *A. fluviatilis* were found to be dominating. The absence of these taxa from Site 1 is in agreement with findings on acid tolerance of several invertebrates made in Southern Sweden (Otto and Svensson, 1983) and Norway (Raddum and Fjellheim, 1984; Økland and Økland, 1986).

There has been no change in the invertebrate community composition at Site 1 in the study period from 1980 to 1996. Therefore, despite small improvements in water chemistry, pH is still to low for acid sensitive invertebrate species to colonise. However, if the trend continues and pH gets closer to 6, acid sensitive species will easily be able to colonise the upper reach of stream Skaerbak, either by upstream migration in the water or aerial dispersal from the neutral, down stream reaches.

Conclusion

The upstream and acidic site (Site 1) of the Danish ICP-stream which was acidified in the 1970ies and 1980ies seems to have stabilised about 1986 with a nearly constant (weakly increasing) pH up to 1997. According to the alkalinity time series there is a small positive trend in the alkalinity values in the latest 10 year period, so the stream seems to be recovering from an acid to a more neutral status. This tendency corresponds well with the decreasing sulphate concentrations (due to the decreasing anthropogenic sulphur deposition) during the same period. In 1995 and 1996 the sulphate concentrations increased again, and this phenomenon coincided with very dry years (1995 and 1996) giving rise to lower groundwater table allowing reduced sulphur compounds to be oxidised into sulphate which leached into the stream. In 1997 the concentrations of sulphate decreased again.

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