Convention on Long-range Transboundary Air Pollution

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

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Proceedings of the 21th meeting of the ICP Waters Programme Task Force in Tallinn, Estonia

October 17-19, 2005

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Abstract

Proceedings of presentations of national activities to the 21th meeting of the ICP Waters Programme Task Force in Tallinn, Estonia, October 17-19, 2005. Contributions on the following themes are presented: Estonian water quality and lake ecology, trends and status of S and N, biological response to recovery, heavy metals and POPs, ICP Waters and the EU Water Framework Directive. Reports and publications from the Programme are listed.

4 keywords, Norwegian	4 keywords, English
1. Overvåking	1. Monitoring
2. Ferskvann	2. Surface waters
3. Forsuring	3. Acidification
4. Internationalt samarbeid	4. International cooperation

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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 21th meeting of the ICP Waters Programme Task Force in Tallinn, Estonia, October 17-19, 2005

Prepared at the ICP Waters Programme Centre
Norwegian Institute for Water Research
Oslo, April 2006

Preface

The International Cooperative Programme on Assessment and Monitoring of Rivers and Lakes (ICP Waters) was established under the Executive Body of the Convention on Long-Range Transboundary Air Pollution at its third session in Helsinki in July 1985. The Executive Body accepted Norway's offer to provide facilities for the Programme Centre, which has been established at the Norwegian Institute for Water Research, NIVA. Berit Kvæven at the Norwegian Pollution Control Authority (SFT) leads the ICP Waters programme. SFT provides financial support to the work of the Programme Centre.

The main aim of the ICP Waters Programme is to assess, on a regional basis, the degree and geographical extent of the impact of atmospheric pollution, in particular acidification, on surface waters. Twenty-two countries in Europe and North America participate in the programme on a regular basis.

ICP Waters is based on existing surface water monitoring programmes in the participating countries, implemented by voluntary contributions. The monitoring sites are generally acid-sensitive. The sites are representative for waters with low acid neutralising capacity (ANC) and low critical load levels, given the distribution of these characteristics in all waters surveyed in the region. The ICP site network is geographically extensive and includes long-term data series (more than 20 years) for many sites. The programme conducts yearly intercalibrations on chemistry and biology.

At the annual Programme Task Force, national ongoing activities in many countries are presented. This report presents national contributions from the 21th Task Force meeting of the ICP Waters programme, held in Tallinn, Estonia, October 17-19, 2005.

Oslo, April 2006

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Contents

1. Introduction

The International Cooperative Programme on Assessment and Monitoring of Rivers and Lakes (ICP Waters) is a programme under the Executive Body of the Convention on Long-Range Transboundary Air Pollution. The aims of the programme are:

- To assess the degree and geographic extent of the impact of atmospheric pollution, in particular acidification, on surface waters;
- To collect information to evaluate dose/response relationships;
- To describe and evaluate long-term trends and variation in aquatic chemistry and biota attributable to atmospheric pollution.

The national contributions on ongoing activities presented to the ICP Waters Task Force meeting October 2005 are thematically grouped:

i. Introductory presentations on water quality in Estonia
ii. Water chemistry – trends and status of S and N
iii. Biological response
iv. Dynamic modelling / Critical loads (no contributions to the proceedings)
v. Heavy metals and POPs
vi. ICP Waters and the EU Water Framework Directive (WFD)

Introductory presentations were made on water quality of Estonian rivers and on principles of lake ecology classification in Estonia (Chapter 2 and 3).

The presentations on Al and Si concentrations in Czech lakes, trends in water chemistry in Swiss alpine lakes, the monitoring program in the Csórrét Reservoir, long-term trends in water chemistry of Kola North lakes and the national report of ICP-W activities in Latvia were grouped under 'Water chemistry – trends and status of S and N' (Chapter 4 to 8).

The presentations on recovery of fish and chemistry in Lake Saudlandsvatn and on recovery on invertebrates in the Saudland area were grouped under 'Biological response' (Chapter 9 and 10).

The theme 'Heavy metals and POPs' was addressed in two presentations, i.e. effects of metals and organic micropollutants on brown trout in Lochnagar, and multimedia modelling of POPs (Chapter 11 and 12).

The relation between ICP Waters and the EU Water Framework Directive was addressed in three presentations, i.e. on possible new classification methods for implementation of the WFD in UN-ECE monitoring programme, the UK perspective on acidification and the WFD, and on the design of monitoring of water quality in Hungary with regard to implementation of the WFD (Chapter 13 to 15).

Reports and publications from ICP Waters are presented in Chapter 16.

2. Monitoring of Estonian rivers

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The purposes of the national monitoring of rivers in Estonia is collection of hydrological, hydrochemical and hydrobiological data for assessment of rivers' status, monitor and prognosis changes, analyse reasons for changes in connection of human and natural processes for implementation of protection measures in catchment area.

The national monitoring programme of rivers started in 1992. Earlier years mostly control of pollution impact to recipient was carried out with insufficient frequency, the other impacts as agricultural and background monitoring were investigated through special investigation projects by scientific institutions irregularly. Also important indicators – total nitrogen and phosphorus were not analysed.

At present by national monitoring sub-programme monitoring is carried out in 60 stations for chemical status of rivers (one station per 750 km²), in 37 hydrological stations (one station per 1200 km²) and biological monitoring of rivers is organised on the rotation principle (during 4-5 years all rivers are monitored). The sub-programme of monitoring of inland water bodies ensures the output of monitoring of the compliance of surface water quality with international requirements and with the requirements set out in Estonian legislation, annual reviews of the hydrological, hydro-chemical and hydro-biological status of rivers (by river catchment areas; whereas surveys of hydro-biological processes should be carried out during a longer period of time and in different catchment areas); The requirements of the monitoring and information network EUROWATERNET, established by the European Environment Agency, in arranging national monitoring of transboundary water bodies and international lakes The river monitoring stations of chemical status can be:

- Transboundary water stations
- Reference stations – background
- Pollution load – impact stations (loads into big lakes and sea, HELCOM)
- Representative catchments (representative impact of big pollution source, region)
- Small agricultural catchments (less that 25 km²)
- Water quality of springs and impacts (Nitrate Directive)
- Stations of water special use (Fish-rivers, raw water etc)The chemical monitoring can be carried out ob the base of two programmes:
- I programme – 12 times per year, temperature suspended solids, pH, O_2, BOD_7, COD_{Mn}, NH_4, NO_2, NO_3, N-total, PO_4, P-total, SO_4, Cl, Si, colour, heavy metals, phenols, oil products
- II programme – 6 times per year, additionally HCO_3, SO_4, Cl, Ca, Mg, Na, K, Si, hardness, Fe
- in special stations HOCl, NH_3 and clorophyll-a

The samples are analysed in 4 chemical laboratories, additionally there is a central laboratory for determination of heavy metals, hydrocarbons, phenols etc. All laboratories have a quality assurance programme.
The river water quality status is estimated according to river water quality classification established in 1998 which is at present on revise for taking account all requirements of EC Water Framework Directive. The classification of rivers has worked out and on the preparation of the legislation. The main change is classification of different types for dissolved oxygen content and phosphorus.

The main problem in Estonia is high content of nutrients in rivers. There has been observed decreasing trend for nitrogen due to changes of land use and decreasing agricultural production since the 1990s, but phosphorus content is on the same level, causing changes in N/P ratio and deterioration of water quality and blue-green algae blooming in big lakes and coastal waters. According to the data in 2004, 54% of river stations didn't respond to the good water quality standards of total nitrogen (3 mg N/l) and 39% of stations for phosphorus good status level (0,8 mg P/l).

The sampling and analyzing of heavy metals in rivers is carried out once in year, only in HELCOM PLC-Water measuring year once in month in big rivers for more exact load calculation. The main reason for that is absence of heavy metal sources in Estonia and most of analyses are lower than chemical detection limit.

3. Some principles of ecological quality classification in Estonian lakes

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Estonian lake typology, corresponding to the WFD requirements

The ecosystems of Estonian lake types are very diverse. According to Aare Mäemets' typology (1974, 1976, 1977), eight lake types can be found in Estonia: oligotrophic (8% of the lakes), semidystrophic (6%), dystrophic (6%), eutrophic + hypertrophic (36 - 37 %), mixotrophic (36 – 37%), siderotrophic (0.2 %), halotrophic (1.4 %), and alkalitrophic (2.6%). This typology is based on the natural accumulation type and differs in principle from the typologies that could be found in the literature between 1950s and 1990s. These typologies are strictly based on the trophic state. Under the term "accumulation type" is considered to be complex phenomena of factors mainly influencing the matter circulation of the lakes. For instance, inflow of seawater, (influence sulphate and chloride ions) as well morphometrical features are the main factors forming specific matter circulation in halotrophic lakes. The same situation can be described in alkalitrophic lakes, where the main factor is calcareous input or in siderotrophic lakes, where mainly high content of dissolved iron creates different matter circulation from the other lake types. A specific complex of fauna and flora and a certain matter and energy circulation characterizes each lake type. Aare Mäemets worked out his classification on the basis of data from 1951-1970. For practical reasons Mäemets' typology is difficult to use because it is too complicated and comprehensive.

Ott & Kõiv (1999) modified this typology taking into account the changes in the nature during the past decades, also some new principles. 12 types without subtypes were distinguished. The lakes are grouped in a more generalized form.

Very soon after the last published issue, WFD gave new requirements for typology and since simplicity, practicality of the system is needed, this last Estonian version was remodified again (Nõges & Ott, 2003). At the moment, the number of types is reduced to eight – two large lakes (Peipsi and Võrtsjärv) as separate types and six small lakes. The latter typology is presented on the table 1. Still some uncertainties remained for the typology. The most important, still not decided problem is with mixotrophic, prevailing lake type. Part of these belong to the second, part to the third group. Karst lakes have temporary character, in which water can be found mostly on spring. This type is still not classified.

***Table 1**. Estonian WFD typology for small lakes.*

Type	Type N	Alkalinity, mg/l	Colour (1-10 arbitrary scale); Pt-Co °	Depth
Alkalitrophic	1	$HCO_3 \geq 240$	-	-
Shallow, light, medium alkalinity	2	HCO_3 80-240	<8; <100	not stratified
Deep, light, medium alkalinity	3	HCO_3 80-240	<8; <100	stratified
Dark, soft water	4	$HCO_3 \leq 80$	>7; ≥100	-
Light, soft water	5	$HCO_3 \leq 80$	<8; <100	-
Coastal lakes	6	Located close to the sea		<2 m

Frequency of values of main limnological characteristics in Estonian small lakes

The distribution of values on the frequency dendrogram is in the most of cases right shifted (alkalinity, Secchi disc visibility, dissolved organic compounds, nutrients; see Fig. 1-5). Generally Estonia have hard-water lakes, but the range of values is relatively wide (Fig. 1.).

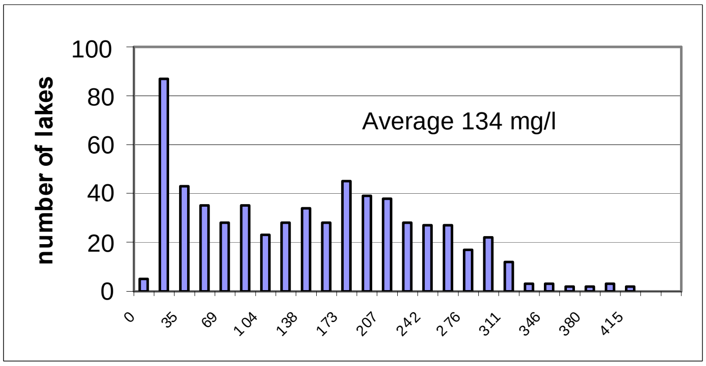

Figure 1*. Frequency of total alkalinity (HCO3, mg/l) in Estonian small lakes.*

Due to large territory covered by forests, bogs and swamps water is mainly yellow- coloured with high content of humic compounds (Fig. 2).

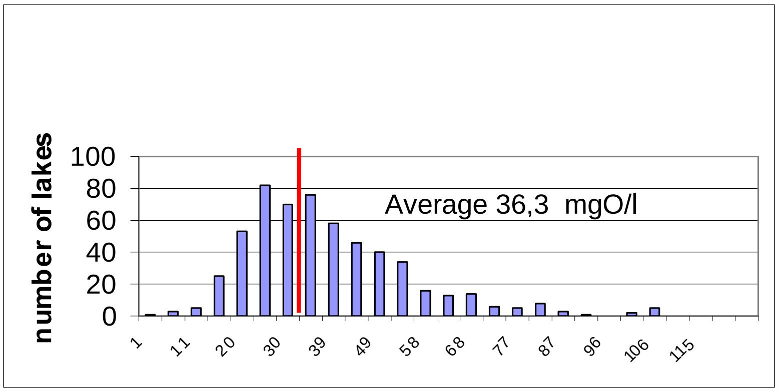

Figure 2*. Frequency of chemical oxygen demand (dichromatic oxygen consumption, mgO/l) in Estonian small lakes.*

Water transparency is related to high content of humic matters being only 1.9 m by Secchi disc visibility (Fig. 3). Light climate is mainly affected by dissolved organic compounds, on the second place is phytoplankton and on the third particulate matter.

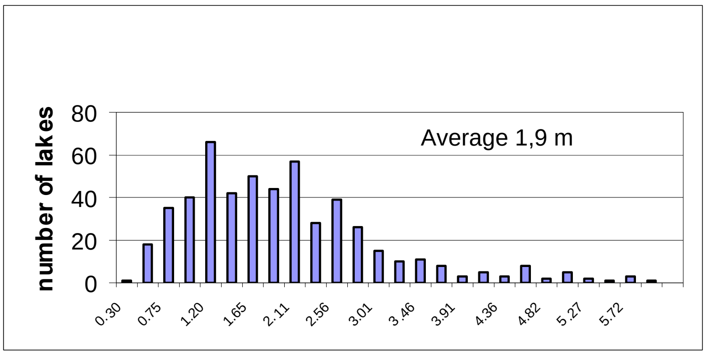

Figure 3*. Frequency of water transparency in Estonian small lakes (Secchi disc visibility, m).*

pH values in the lakes have very dynamic character depending on activity of photosynthesis. During warm day in summer values can rise some units during several hours in soft-water lakes. Therefore for a long-term estimation of the ecological status pH is not very informative or it should be measured very often for achieving good results. The lowest values in Estonian lakes have been measured in the lakes located in the sandy forest, but intense water feeding occurs from the raised bogs. Values can be even close to 3. Generally pH is relatively high due to high content of hydrocarbonates (Fig. 4).

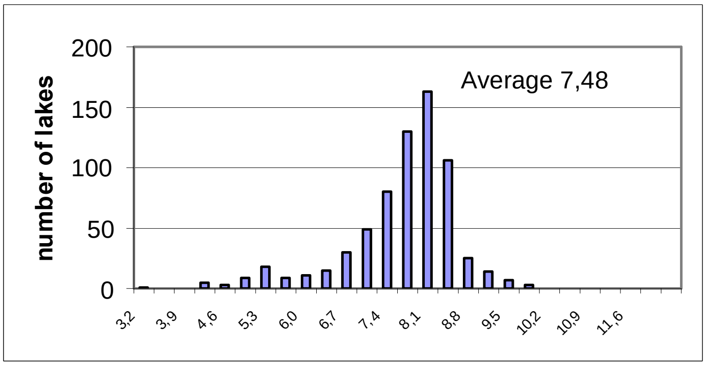

Figure 4*. Frequency of pH in Estonian small lakes.*

The ratio of main nutrients is not balanced in Estonian small lakes. Nitrogen content is on much higher level than phosphorus (Fig. 5-6). This ratio has trend to diminish during last years.

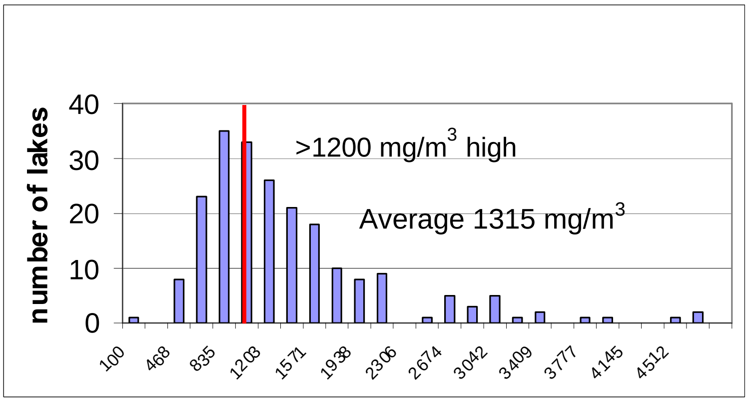

Figure 5*. Frequency of total nitrogen in Estonian small lakes.*

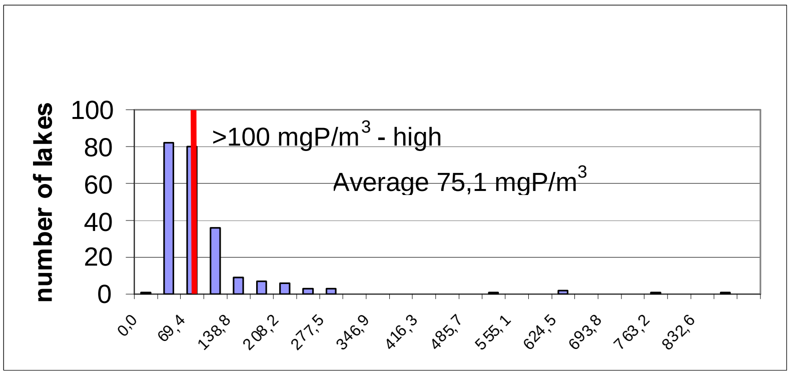

Figure 6*. Frequency of total phosphorus in Estonian small lakes.*

Estonian lake classification corresponding to the WFD requirements

Reference conditions and sites should be distinguished in order to classify properly lake ecological quality. Land-use in the catchment area is one of the aspects for selecting the conditions. Values for the lake types N 3 and 5 (see table 1) are presented on the table 2.

WFD classification is still not completed, but the main features are selected. We use 5 abiotic, 3 phytoplanktic and macrophytic, as well as 5 zoobenthical parameters (table 3).

Some principles were used giving final decision of the ecological quality: a) minimal used number of parameters is 7, b) all parameters have equal weight, c) final score is decided by limit 2/3 of used total number of characteristics, it means that 2/3 of values should fall into concrete quality class or higher. Estonian version of the classification does not use the WFD requisition, also known as principle "one out, all out", where final score should be decided as the lowest level of parameters met during the analyses.

Table 2. *Land-use in the catchment area of reference sites.*

Parameter	Value
Population density, inhabitants/km^2	0 – 6
Urban areas, %	0
Forest and other natural areas, %	56 – 100
Agricultural land, %	0 – 5

***Table 3**. Description of parameters used in Estonian WFD classification (Ott, 2005).*

Parameter	Units, description, comments
Secchi disc visibility	m; is not used in lake type N 4.
pH	Is not used in soft water, dark coloured (type N 4, acidotrophic and dystrophic) lakes
Total phosphorus	mg/m^3; average from the water column
Total nitrogen	mg/m^3; average from the water column
Metalimnion range	m; metalimnion is defined as decrease of temperature or oxygen content 1.5 units per m in the water column. Is used in types N 1, 3, 5.
Concentration of chlorophyll a	mg/m^3; average from the water column
Phytoplankton compound quotient	Index is based on species number of indicator taxa, average from the water column
Phytoplankton community	Community is divided into 3 three indicative versions on the basis of dominating species.
Macrophyte association	Char - Communities dominated by charophytes, with vascular plant species. ElPo - Communities of elodeids and pondweeds, rooted in sediment and often abundant though with several species present, often including nymphaeids and some aggressive charophytes. CanNym - Dense communities of nymphaeids and or canopy forming poorly rooted plants like Lemna trisulca. This community may persist despite large phytoplankton densities. Iso - Communities dominated by isoetids (Isoetes, Lobelia). Mosses may also be present. Sphag - Communities dominated by Sphagnum, occurring in extensive swards. Alg - Low biomass, communities with aquatic mosses, filamentous desmids and zygnematales.
Number of macrophyte taxa	Number of hydrophyte species (species without emergent plants)
Macrophyte abundance	Macrophyte abundance PVI - plant volume infested on 0-5 scale 0 – without plants 1 – some visible plants 2 – ca 25 % 3 - ca 25-50 4 - ca 50-65, main parts of plants extend to the surface of the water 5 - >65, dense plant cover and extend to the surface
EPT index for macrozoobenthos*	Ephemeroptera, Plecoptera, Trichoptera taxa richness in the littoral on May. Is used for lake types N 2, 3, 4, 5, on four substrate types
Shannon’s diversity of macrozoobenthos species*	Shannon’ index is based on information of abundance and species richness. Is used for lake types N 2, 3, 4, 5 on four substrate types
British Average Score Per Taxon (ASPT)*	Sum of tolerance values of indicative macrozoobenthos species. Is used for lake types N 2, 3, 4, 5 on four substrate types
Acidity index for macrozoobenthos*	Is used for lake types N 2, 3, 4, 5 on two substrate types
The number of macrozoobenthos taxa*	Is used for lake types N 2, 3, 4, 5 on three substrate types

* Original descriptions of the corresponding indices: Armitage *et al.*, 1983; Johnson, 1999; Lenat, 1988

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4. Are inverse changes in Al and Si concentrations in lakes recovering from acidification interrelated?

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We investigated long-term trends of Si (essentially orthosilicic acid) concentrations in five glacial lakes in the Bohemian Forest, Czech Republic that are recovering from acidification. Our results show higher mobility of Si in spite of lower atmospheric deposition of acids. Si increased by 0.95 to 1.95 µmol yr-1 (36 to 51 %) during the period 1986 – 2004 and with increasing pH. Increases were caused by higher release of Si from the catchment to the aquatic environment. A change in soil solution conditions due to a sharp decrease of acidic deposition has led to strong decline in Al mobility and to great decreases of dissolved Al, especially Al3+. The increase of Si may be related to: 1) unblocking of the inhibitory effect of dissolved Al on weathering of aluminosilicates, 2) biogenic opal (phytoliths) dissolving faster, and/or 3) lower Si precipitation as secondary aluminosilicates in soil. The change in Al speciation on the dissolution rate of biogenic silica is critical. A lack of change in Si at sites outside central Europe may be explained by small or any decline in mobility of dissolved Al. The effect of long-term increase in temperature was probably minor.

From: Veselý, J., Majer V. and Kopaček J., 2005. Are inverse changes in Al and Si concentrations in lakes recovering from acidification interrelated? HESS 9(6), 699-706

5. Water chemistry trends in 20 Swiss alpine lakes between 1980-2004

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5.1 Introduction

Trend analyses can provide important information of the geographic extent of acidification and recovery of lakes and streams (Skjelvåle, 2003). It is known that in the last 20-25 years there has been a substantial reduction in the emissions of sulphur and nitrogen oxides (Fig. 1). As a consequence there has been an improvement of the quality of atmospheric deposition. In fact, in the last 20 years there has been observed a decrease in sulphate deposition and therefore also in acidity deposition in many European sites (Schöpp et al. 2003). The aim of this presentation is to verify if theses deposition trends get reflected in the trends of surface water chemistry. Trend analyses were performed on the key variables involved in acidification and recovery processes: alkalinity (Gran alkalinity), pH, sulphate, nitrate, base cations (calcium + magnesium).

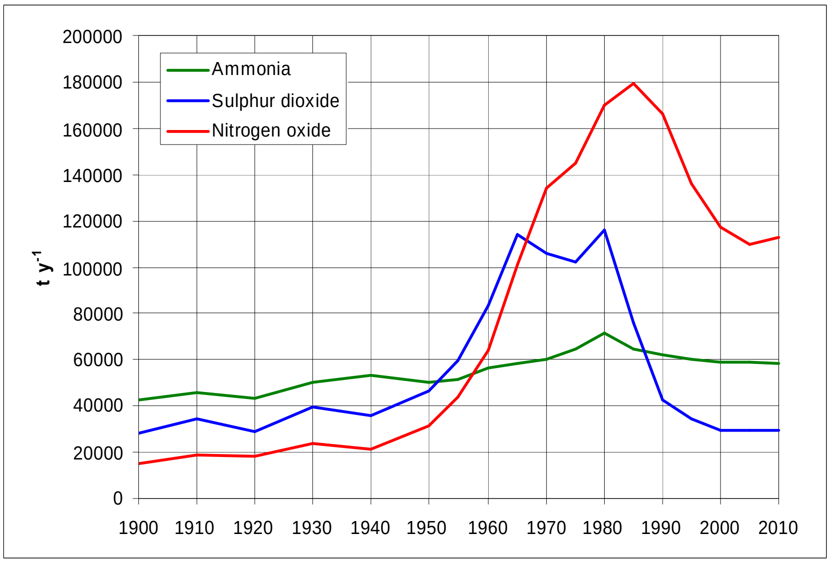

Figure 1 *Annual sulphur bioxide, nitrogen oxides and ammonia emissions in Switzerland from 1900 to 2010 (BUWAL, 2005)*

5.2 Study site

The study area is located in the Central Alps in the northern part of Canton Ticino, Switzerland (Figure 2). In order to study the influence of transboundary air pollution, the selected freshwater systems were selected in remote areas far from local pollution sources. Precipitation in this region is mainly determined by warm, humid air masses originating from the Mediterranean, passing over the Po Plain and colliding with the Alps. Since the study area's lithology is dominated by base-poor rocks especially gneiss, its freshwaters are sensitive to acidification. For the monitoring programme 20 alpine lakes were chosen. The lake's watersheds are constituted mainly by bare rocks, with vegetation often confined to small areas of alpine meadow. The selected alpine lakes are situated between 1690 m and 2580 m of altitude and are characterized by intensive irradiation, a short vegetation period, a long period of ice coverage and by low nutrient concentrations. The catchment areas vary between 16 and 289 ha, the lake areas between 0.4 and 16.7 ha and the maximum depths between 5 and 70m.

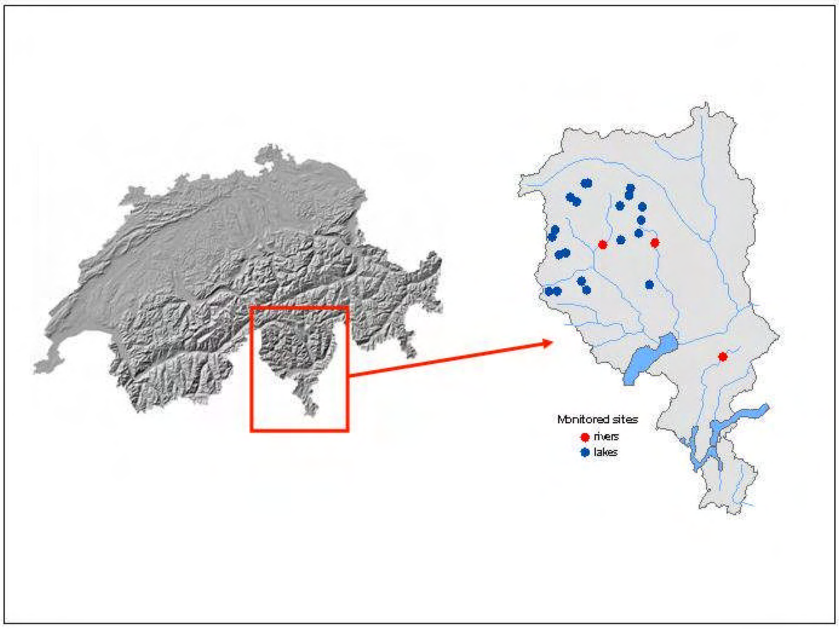

Figure 2 *Study site*

Ranges of the average chemical parameters of surface waters measured twice a year (beginning of summer and beginning of fall) in the 20 alpine lakes are shown in table 1.

Table 1 *Average main chemical parameters in surface waters of the 20 monitored lakes in the period 2000-2004.*

Parameter	**Ranges of average values**
Cond. (20 °C)	7.8-15.7 $\mu S\ cm^{-1}$
pH	5.2-6.9
Alk	-0.010-0.067 meq l^{-1}
Ca^{2+}	0.50-2.40 mg l^{-1}
Mg^{2+}	0.07-0.24 mg l^{-1}
Na^{+}	0.18-0.54 mg l^{-1}
K^{+}	0.12-0.43 mg l^{-1}
SO_4^{2-}	1.08-3.67 mg l^{-1}
NO_3^{-}	0.12-0.47 mg N l^{-1}
Cl^{-}	0.09-0.21 mg l^{-1}
Reactive soluble P	<4.3 μg P l^{-1}
SiO_2	0.37-1.22 mg l^{-1}
DOC	0.14-0.66 mg l^{-1}
total Al	12.8-100.9 $\mu g\ l^{-1}$

5.3 Methods

Trend analyses were performed on the key variables involved in acidification and recovery processes: alkalinity (Gran alkalinity), pH, sulphate, nitrate and base cations (calcium + magnesium). The analyses covers the period 1980-2004 and surface water data from the beginning of summer and the beginning of autumn were utilized. For the trend analyses the same approach as described in the 15 year ICP-water report (Skjelvåle, 2003) was used: simple linear regressions to calculate the trend slopes for each monitoring site. In addition two sided t-tests for the null hypothesis that the slope equals zero (i.e. no trend is present) have been calculated for each site and the null hypothesis was rejected for p-values below 0.05.

5.4 Results and discussion

5.4.1 Sulphate trends

Sulphate, beside nitrate, is the main acid anion of acidic deposition. Trends in sulphate concentrations were significant in 18 out of 20 lakes. In 17 lakes the trend was negative, reflecting the reduction of sulphur oxide emission in the atmosphere. In 2 lakes no significant trend was found and in 1 lake the trend was positive. The absence of decreasing sulphate concentrations in 4 lakes may be attributed to increased weathering of sulphur containing rocks, resulting from climate warming (Rogora, 2004) or leakage of old sulphate stored in the catchment. In fact, all of these 3 lakes are characterized by relatively high sulphate concentrations (mean 2000-2004: 2.98-3.67 mg l^{-1}). The median sulphate reduction rate was -0.79 μeq l^{-1} yr^{-1}. The rate was therefore smaller than previously reported for the Alps (-1.8 μeq l^{-1}, Skjelvåle (2003)). The decrease started at the beginning of the eighties, quickly after the beginning of the improvement of the air sulphur oxides concentrations, suggesting a fast chemical response of the lakes. The thin soil and the relatively small sulphur storage, typical for high altitudes, surly contributed to the rapidity of the response.

5.4.2 Nitrate trends

For nitrate 14 sites showed a significant trend.: in 12 lakes a negative and in 2 lakes a positive trend was observed. However, the median nitrate reduction rate was low (-0.11 μeq l^{-1} yr^{-1}). Interestingly, the median nitrate trend was 7 times lower than the sulphate trend, although the emission reductions of SO_2 (ca. 100 teq a^{-1}) and NO_x (ca. 90 teq a^{-1}) in Canton Ticino were estimated to be in the same range (SPAAS, 2003). However, the fact, that in Canton Ticino the decrease in NO_x concentrations in the atmosphere (0.4 μeq m^{-3}) is four times smaller than the decrease of SO_2 concentrations (1.6 μeq m^{-3}) may indicate that NO_x concentrations are influenced by air masses coming from the Po Plain. In addition, those air masses are also enriched with ammonia from livestock and cultivated lands. In fact, from the 80's to nowadays no trend in deposition of N compounds could be observed (Mosello et al., 2000). Differently, increasing nitrogen trends are found in rivers (Mosello et al., 2001) and reveal the presence of increasing nitrogen saturation in soils or the effect of recent climate warming on soil mineralization, causing increased nitrate leaching. Both phenomena, transboundary air pollution and increased nitrogen leaching from soils, may explain the difference between trends of Swiss nitrogen emission into the atmosphere and nitrate concentrations in alpine lakes.

5.4.3 Basic cations trends

Base cations (Ca^{2+} and Mg^{2+}) are mobilised by weathering and cation exchange reactions that neutralise acids in the watershed. They respond indirectly to changes in sulphate and nitrate. Without other base cation influencing phenomena, with decreasing acid anions (mainly sulphate) concentrations, base cations are expected to decrease. However, in the last few years an increase of the occurrence of alkaline rain episodes (probably due to climatic effects) were observed and it is likely that calcareous Saharian dust, rich in base cation, are responsible for it (Rogora et al. 2004). Enhanced weathering rates, resulting from recent climate warming may also contribute to increased base cation concentrations (Rogora, 2004). As reported elsewhere for European alps (Skjelvåle, 2003), for Ca^{2+}+Mg^{2+} no regional trend could be observed. Trends were significantly negative in 8 and positive in 6 lakes. The median rate was low: -0.08 μeq l^{-1} yr^{-1}. The absence of a global base cation trend may be explained, as mentioned before, by the fact that base cations are here controlled by both base cation decreasing and base cation increasing mechanisms.

5.4.4 Alkalinity trends

When rates of Ca^{2+}+Mg^{2+} decline are equal, or nearly equal, to rates of sulphate and nitrate decline, than recovery (increasing alkalinity and pH) is prevented. Subtracting the median acid anions trends (-0.79 and -0.11 μeq l^{-1} yr^{-1}) from the median base cation trend (-0.08 μeq l^{-1} yr^{-1}) we obtain a figure (0.82 μeq l^{-1} yr^{-1}) that suggests a positive alkalinity trend at our study site. In fact, we could find a significant positive alkalinity trend in most lakes (19). Differently, than from what reported in Skjelvåle (2003) a very clear regional increasing alkalinity trend could be observed. The median rate was 0.80 μeq l^{-1} yr^{-1} and its 90% confidence interval ranged between 0.32 and 1.08 μeq l^{-1} yr^{-1}. In Figure 3 the average alkalinity values in the 80's were compared with the average values between 2000 and 2004. It appears that alkalinity increased in most lakes. The average increase was 0.012 meq l^{-1}. In the 80's 4 lakes were acid (today 2), 14 were sensitive to acidification (today 13) and 2 had low alkalinities but were not acid sensitive (today 5).

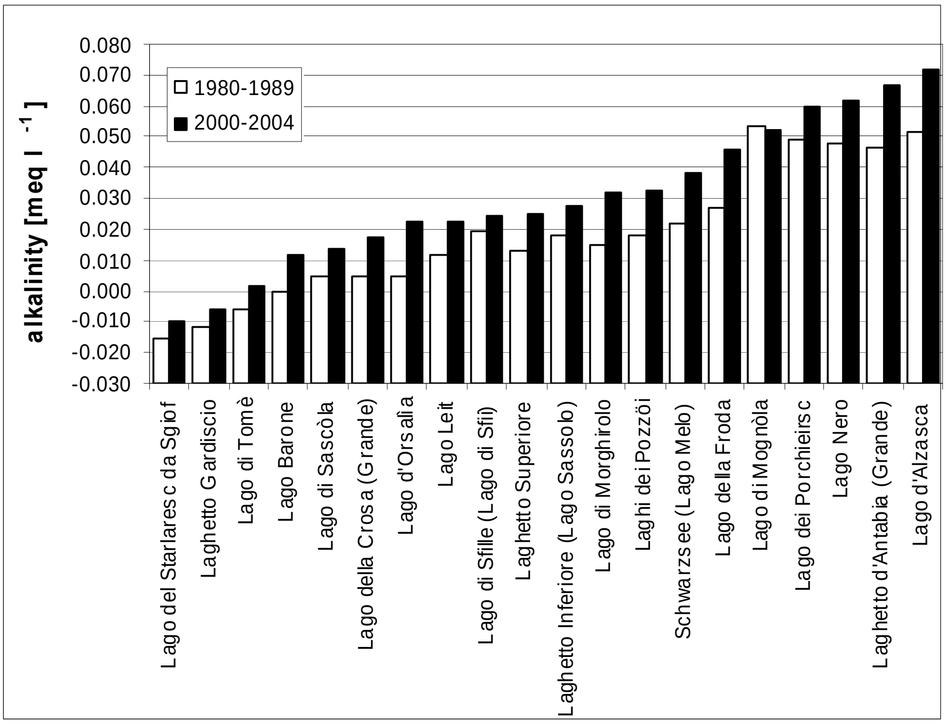

Figure 3 *Average alkalinity in the 80's and between 2000 and 2004.*

5.4.5 H^+ trends

As expected from the increase in alkalinity, for H^+ a significant decreasing trend was observed in most lakes (18). The median rate was -0.04 μeq l^{-1} yr^{-1}. The pH improvement becomes evident when plotting the average pH of the 80's and the years 2000-2004 (Figure 4). The pH increase was on average 0.3. In the 80's 8 lakes had an average pH<6, while nowadays only 3 lakes have pH values that are critical for aluminium dissolution.

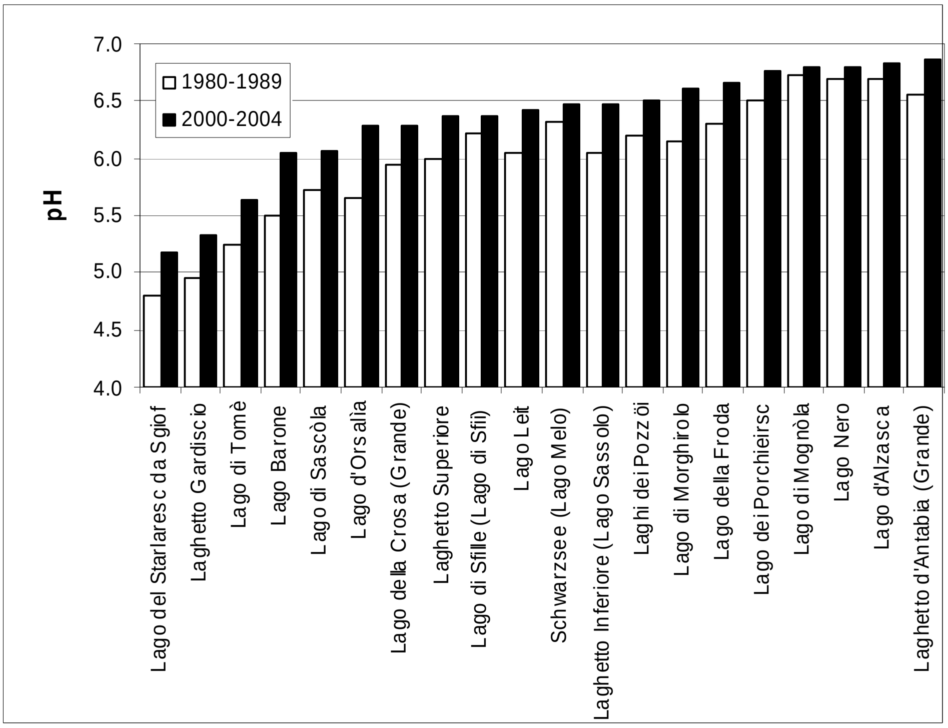

Figure 4 *Average pH in the 80's and between 2000 and 2004.*

5.5 Conclusions

The trend analyses revealed that the reduction of SO_2 emission caused significant decreasing sulphate and H^+ trends and increasing alkalinity trends in most lakes. Differently, the reduction of NO_x emissions was not reflected in the lakes chemistry. The reason is probably the transport of air masses enriched with NO_x and NH_3 from the Po plain to the Alps.

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6. Summary of the 36 months monitoring program results of Csórrét-reservoir, ICP site in Hungary

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Introduction

The Csórrét-reservoir is located in the Mátra-hill in Hungary. The reservoir was built in 1973 for supplying the nearby villages with drinking water. Csórrét-reservoir is relatively small, its total volume is 1 million m^3, its area is 13 ha, and its watershed is 6.8 km^2. The reservoir has five feeding creeks. The reservoir is free from any direct anthropogenic pollution, only the airborne pollution can reach it. The Csórrét-reservoir has the lowest alkalinity in Hungary; hence, this is the most sensitive surface water to airborne acidification.This paper presents some selected results of the 36 months monitoring program that was carried out on Csórrét-reservoir.

Materials and Methods

The monitoring program started in May 2002 with monthly sampling frequency. The reservoir and its feeding streams were sampled as well. The samples from the reservoir were collected in 40 m distance from the dam at the water intake facility. Five depths were sampled with a submersible pump (depth are relative to the bottom): T4: 1 m (bottom), T3: 3.5 m, T2: 7.0 m, T1: 10.5 m, T0: surface (14-16 m). The streams were sampled at a fixed section between 10-50 m from the mouth of the stream. Temperature, pH, dissolved oxygen, electric conductivity, redoxi-potential, photosynthetically active radiation (PAR) were measured in situ. The samples were analyzed for the following conventional parameters: KOI_{ps}, NH_4^+, NO_2^-, NO_3^-, organic nitrogen, SO_4^{2-}, Cl^-, alkalinity, Ca^{2+}, Mg^{2+}, Na^+, and K^+. The total and dissolved concentrations of metals (Hg, Cd, Pb, Cu, Cr, Ni, Al, Zn, Fe, and Mn) were determined by atomic absorption spectrophotometry.

Results

Temperature

The maximum depth of Csórrét-Reservoir is 22 m, average depth is 10 m. The reservoir is wind-protected, deep, dimictic lake with two turnovers yearly. The thermal stratification starts in April and ceases in October. The maximum temperature difference among epi- and hypolimnion is 10-12 °C. The thickness of epilimnion is about 7 meters, the metalimnion is 2-3 m, the hypolimnion starts at 9-10 meters depth.

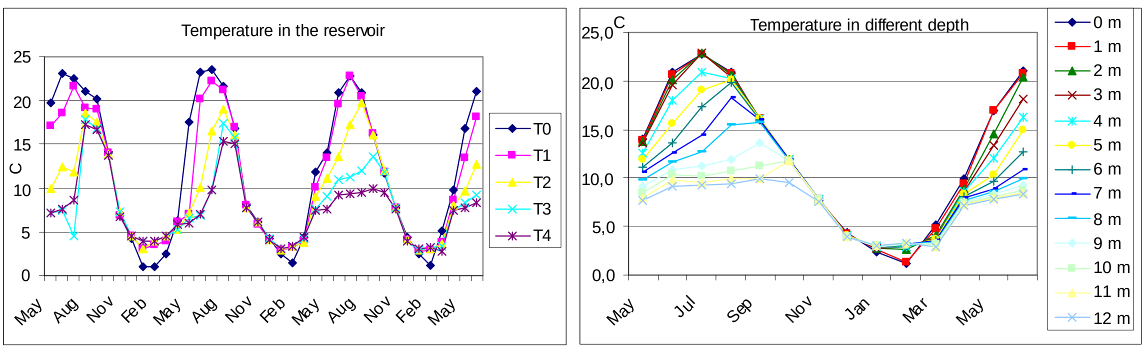

Figure 1. *Temperature in the reservoir*

Alkalinity

The alkalinity of the reservoir varies between 0.5-0.8 mekv/L, in most of the year. Alkalinity decreased rapidly at several times during the investigation period. All of these decreases can be connected to a hydrometeorological event. During snowmelts, the main part of the water of the reservoir is replaced with snow-water. Snow-water has no alkalinity, and it can not dissolve any buffering compounds from the frozen soil, consequently it decreases the alkalinity and pH of the reservoir. Similar phenomenon can take place, if a large amount of rain falls within a short time. In dry periods, the alkalinity increases slowly, but continuously.

The alkalinity of the reservoir is basically determined by the feeding creeks (Fig. 2/b). The reservoir is fed by five creeks, however creeks No. 2, 3 and 4 contribute 80% of total runoff, hence thesethree creeks determines the alkalinity of the reservoir. The alkalinity of these creeks is 0.8-1.2 mekv/L during most of the year, and the lowest value ever measured was 0.3 mekv/L at the time of heavy flood. Consequently, it is not probable, that the alkalinity of reservoir decreases below this value, as for this a very huge amount of low-alkalinity rainwater should fall into the reservoir (many times more, than the total volume of the reservoir), but it is not probable in this climate zone. Alkalinity decrease caused by acid rain is not expectable, because the watershed is so large compared to the surface of the reservoir (~70 fold), that the effect of acidic and alkalinity-free rainwater falls directly into reservoir is negligible.

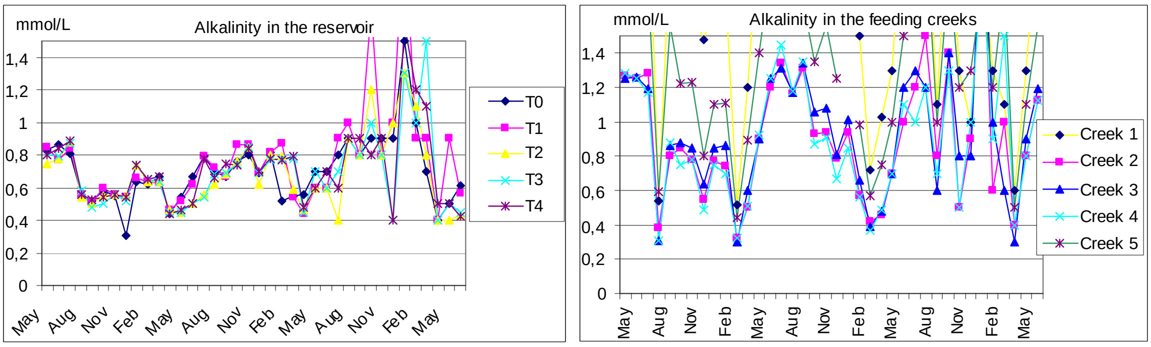

Figure 2. *Alkalinity of the reservoir, alkalinity of feeding creeks*

pH

The pH of the reservoir varied between 6.5-9.5 in the study period. The pH value that evolves at the beginning of spring (pH=7.3-7.7) can be considered as the typical value of the reservoir. The pH has two typical patterns. At snowmelts and after heavy rains, pH (and the alkalinity) decreases. The scale of the decrease can reach 0.5 pH unit, but it does not mean the risk of acidification.

In summertime, pH has a typical vertical profile. In the epilimnion, the pH can reach 9.0-9.5 units. Oppositely, in the hypolimnion pH can decrease down to 6.8-7.0. After the autumn turnover, the pH of the reservoir is homogenous, and the present value this time will peculiar at wintertime. The first remarkable pH change is caused by the snowmelt.

Biological processes determine the typical summer pH-profile. Measurement of photosynthetically active radiation (PAR) showed, that the compensation depth (PAR is only 1% related to surface PAR) is about 7 meters. This correlates well with the depth of epilimnion, and this depth is the border of the high and low pH level in the water. From the surface, down to the compensation depth, there is enough light for photosynthesis, and photosynthesis dominates over decomposition. In the epilimnion, significant algal activity can take place, that causes pH increase. According to chlorofill measurements and microscopic investigations, this algal activity takes place in the Csórrét-reservoir. It is important to declare, that the “high algal activity” in the case of Csórrét reservoir means oligotrophic state, but due to the low buffer capacity, it can increase the pH up to this high (9.0-9.5) level. Below the compensation depth, the decomposition processes are dominant due to the lack of light. Decomposition processes causes 0.5-1.0 unit pH decrease in the reservoir, however it has never decreased below 6.8. During the autumn turnover pH of the hypolimnion increases, and in the cold water the decomposition processes are so slow (or stopped), that it can not cause further pH decrease.

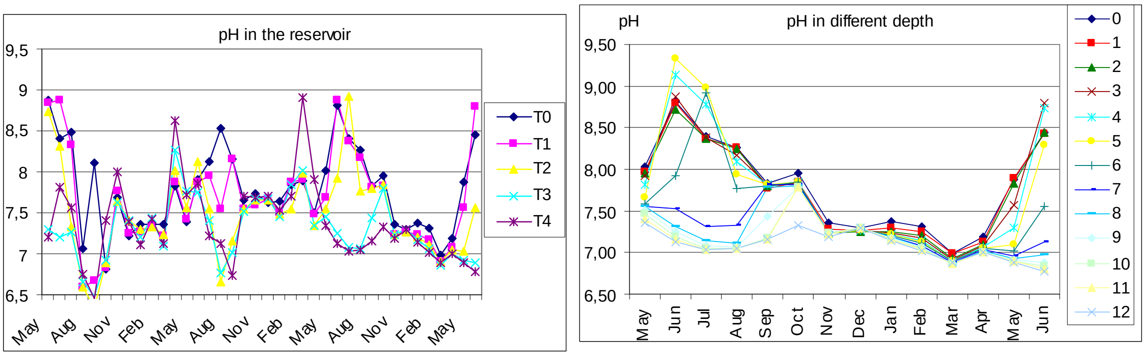

Figure 3. pH in the reservoir

Dissolved oxygen

The vertical oxygen profile is shown on the figure 5. At spring turnover, the dissolved oxygen concentration increases up to 8-9 mg/L in the whole water body (~80-90% saturation). At the time of summer stratification, oxygen has a typical vertical profile. In the epilimnion, the concentration remains high, the saturation can reach 90-100%, moreover for short periods over saturation can occur due to the algal activity. In the hypolimnion, there are no oxygen productive processes taking place, contrary the decomposition processes consume oxygen. Due to the thermal stratification, there is no oxygen supply from the surface, hence in the hypolimnion a continuous oxygen concentration decrease occurs. The minimal oxygen concentration level can be measured at the end of August, with 0.0-1.0 mg/L concentration. Thus, an anaerobic condition evolves at the bottom of reservoir, that influences other water quality parameters. At the autumn turnover oxygen concentration of the water is around 6-7 mg/L. In winter, when the reservoir is ice-covered, and the water is isolated from the atmosphere, the oxygen concentration decreases slowly in whole water body.

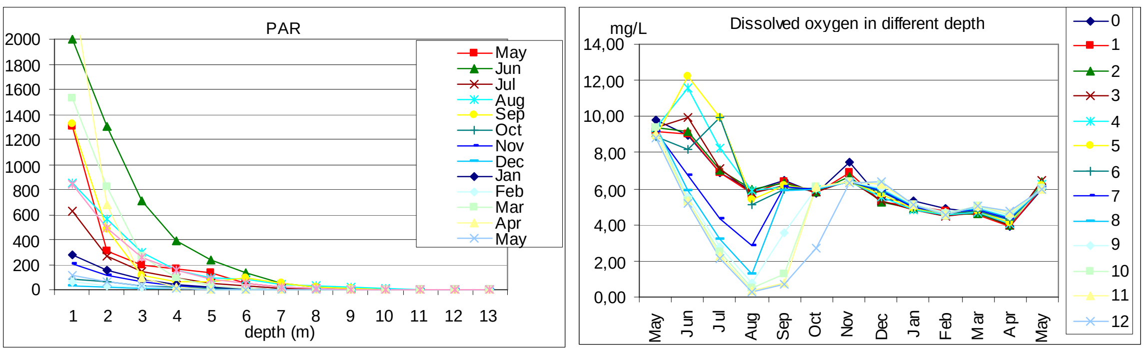

Figure 5. Photosyntetically active radiation in the reservoir, dissolved oxygen in the reservoir

Iron and manganese

The total iron concentration in the reservoir is 100-150 μg/L, in most of the year. In July-August, in the bottom layers an significant iron concentration increase occurs, up to 1000 μg/L level. The ratio of the dissolved and particulate forms is about 50-50% (Fig.6.). After autumn turnover, the iron peak in the hypolimnion collapses, and the concentration falls down to the "normal" 100-150 μg/L. The concentration changes of total manganese are very similar to iron. In most of the year, its concentration is between 50-100 μg/L. At the end of summer, it can be as high as 800-1500 μg/L. Differently from iron, the manganese is present dominantly (90%) in dissolved form. The high iron and manganese concentrations at the end of summer is in strong relationship with the thermal stratification, and with the results of biological processes taking place in the water. It was already discussed, that in the bottom layers, at the end of summer anoxic-anaerobic conditions evolve, which results in reductive conditions. The sediment contains a large amount of iron and manganese, "usually" in oxidised form. The oxidised Fe(III) and Mn(IV) compounds are badly soluble in the water, hence their concentrations are low in the water, as the particulate iron and manganese compounds settle down in lack of mixing. Due to the anaerobic conditions, the iron and manganese compounds reduce to Fe(II) and Mn(II) form, which are well soluble. According to this process, the sediment releases lot of iron and manganese as "internal load". In the autumn turnover, the bottom hypolimnion is re-oxygenated, the reduced iron and manganese compounds are oxidised back to bad soluble Fe(III) and Mn(IV) forms, and precipitates and settles down. That is why the summer peaks collapses rapidly at autumn.

The role of the feeding creeks in the summer iron and manganese peaks was investigated also. It was found, that the iron and manganese concentration is low in the whole year, and they are present predominantly in particulate (oxidised) form. The high peaks in the reservoir did not depend on the iron and manganese concentration of creeks. The creeks contribute to these peaks with loading iron and manganese containing alluvium into the reservoir, preparing the possibility of internal load. These end-summer peaks are unfavourable for drinking water producing, however these processes are natural in deep lakes, like the Csórrét-reservoir.

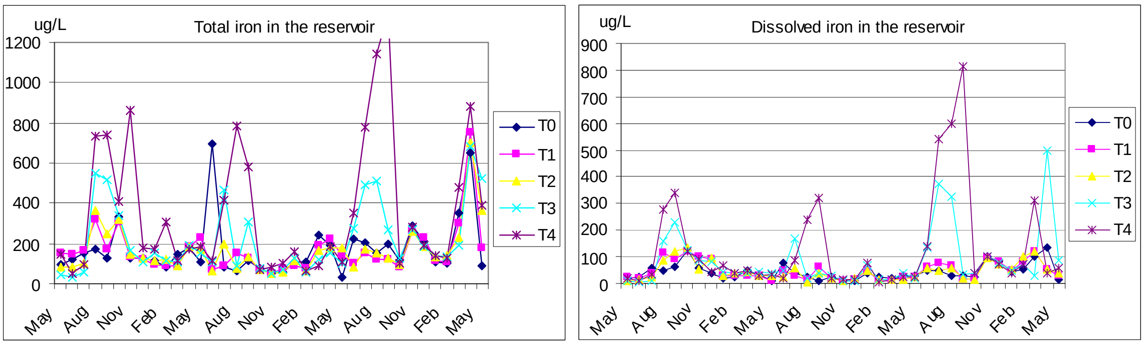

Figure 6. *Total and dissolved iron in the reservoir*

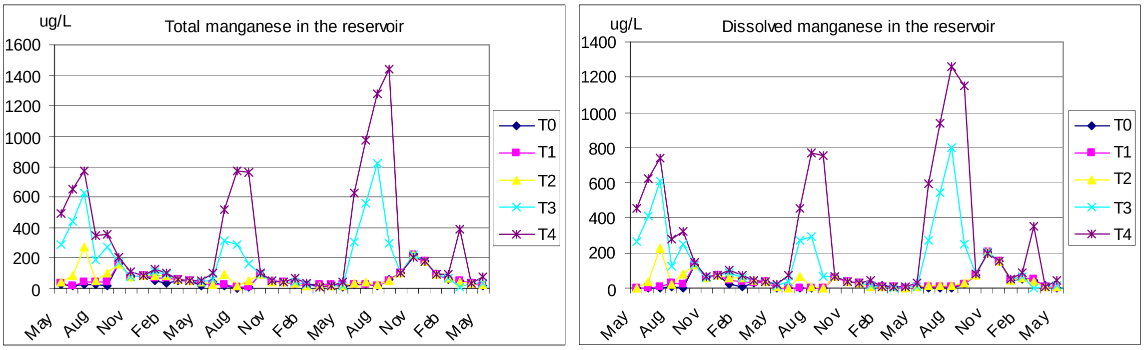

Figure 7. *Total and dissolved manganese in the reservoir*

Summary
The Csórrét-reservoir has the lowest alkalinity (0.5-1.0 mekv/L) in Hungary. Rapid alkalinity decrease occurs after snowmelts, and heavy rains (significant water change). The alkalinity of the reservoir is determined by the alkalinity of the feeding creeks. As the lowest alkalinity of the creeks was 0.3 mekv/L, it is not presumable, that the alkalinity of reservoir can decrease below this level.

The pH of the reservoir varies in wide range: 6.8-9.5. From autumn, to spring the pH is equal in the whole water body, typically with 7.3-7.8 value. In summer, the epi- and hypolimnion differs. The pH of epilimnion can increase up to pH 9.5, due to the pH increasing effect of algal activity. In the hypolimnion the decomposition is the dominant process, which decreases the pH down to 6.8, which is the lowest measured value in the 36 months monitoring program. It can be concluded, that the Csórrét-reservoir is not really endangered by airborne acidification, however natural biological processes cause the “acidification” of reservoir.

The oxygen supply of the reservoir is good, however at end of summer, in the bottom layer anaerobic condition evolves, which affect other water quality parameters, like iron and manganese.

The total iron and manganese concentration of reservoir is low in most of the year, while at the summer stratification in the hypolimnion high iron and manganese peaks evolve, due to the internal load. These peaks collapse after ceasing anaerobic conditions after autumn turnover. The high iron and manganese peak is not desirable for drinking water producing, but this is natural phenomenon in deep lakes.

7. Long-term trends in water chemistry of Kola North lakes, Russia

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Russia

Within the "Survey Lakes" project in the Kola North, Russia, lake investigations are done with a five-year interval. The region has received anthropogenic deposition of sulfur and other pollutants from the copper-nickel metallurgical plants "Pechenganickel" and "Severonickel" for many years (Moiseenko, 1994).

To analyze long-term changes of water chemistry and acidification, 6 lakes with different levels of deposition of pollutants were chosen. The lakes have different sizes, geological and landscape characteristics of their catchment areas. A brief description of the lakes is provided in Table 1. Keudsherjaur and Moncheozero lakes are located in a distance of 10 km: the first one is close to the "Pechenganickel" plant, the second one is close to the "Severonickel" plant. These lakes are located in areas with locally high deposition of pollutants. The distance between the plants and other lakes is more than 80 km.

Table 1 *Description of the investigated lakes and its catchment.*

Lake	Latitude	Longitude	Square of the lake, km^2	Catchment area square, km^2	Region	Forest-covered area, %	Swamp-covered area, %	Rocks, forming the catchment area
Keudsherjaur	69^o 10'	30^o 11'	4,7	10,3	Forest-tundra	52	22	Basalt
Moncheozero	68^o 00'	32^o 50'	38,6	590,0	Taiga	58	10	Jaspilite, basalt traps
Tulpjavr	69^o 06'	32^o 41'	3,12	26,0	Forest-tundra	40	15	Schist
Dolgoe	69^o 28'	31^o 54'	0,7	12,8	Tundra	11	13	Gabbro
Glubokoe	67^o 18'	34^o 15'	1,7	99,2	Taiga	56	28	Gneissoid granite
No-Name	68^o 06'	34^o 01'	0,05	0,8	Taiga	59	21	Diorite

Parameters such as pH, sulphates, organic anion (A), alkalinity (Alk), sum of cations (S Cat.), copper and nickel concentrations (as reflection of copper-nickel productions) and aluminum concentration were investigated. Quality control of the measurements of water chemistry was done by international intercomparison (Hovind, 2001). Were calculated acid neutralizing ability of water (ANC), critical loads (CL) and their exceedings (CLex) (Henriksen et al., 1992). Figures 1 to 3 shows the trends in these parameters for the last 15 years.

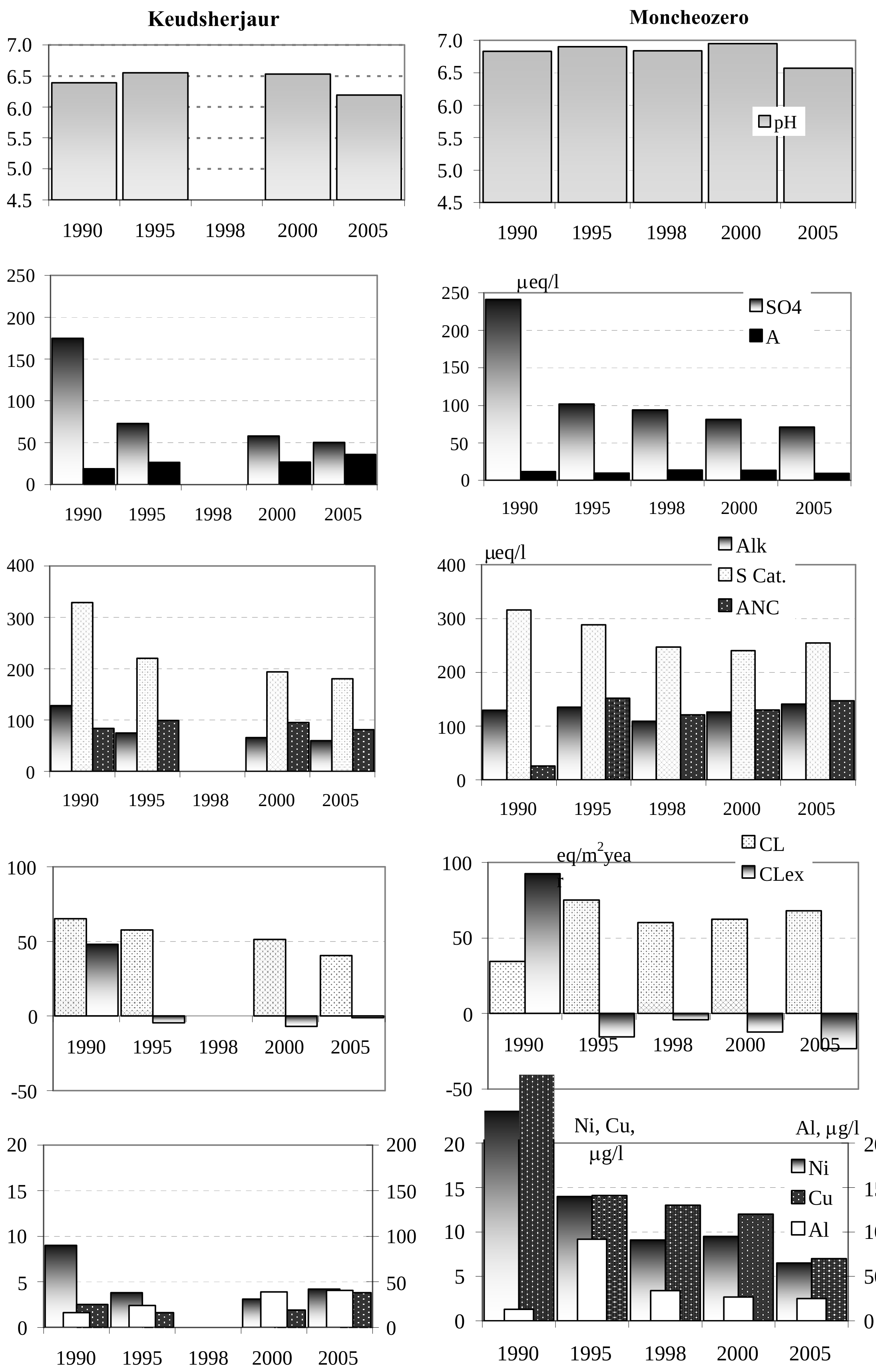

Figure 1. Dynamics of parameters of Keudsherjaur and Moncheozero lakes.

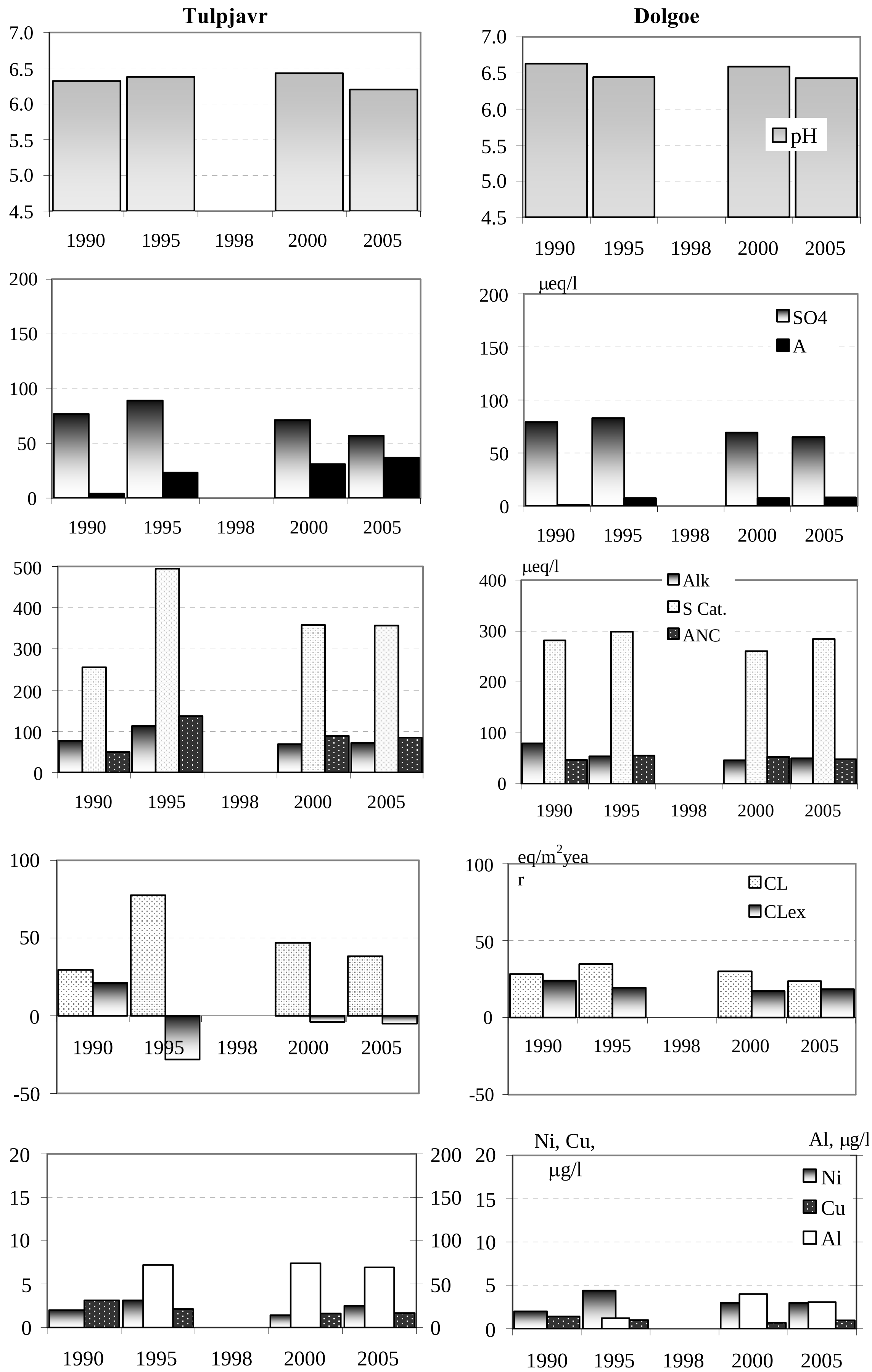

Figure 2. Dynamics of parameters of Tulpjavr and Dolgoe lakes.

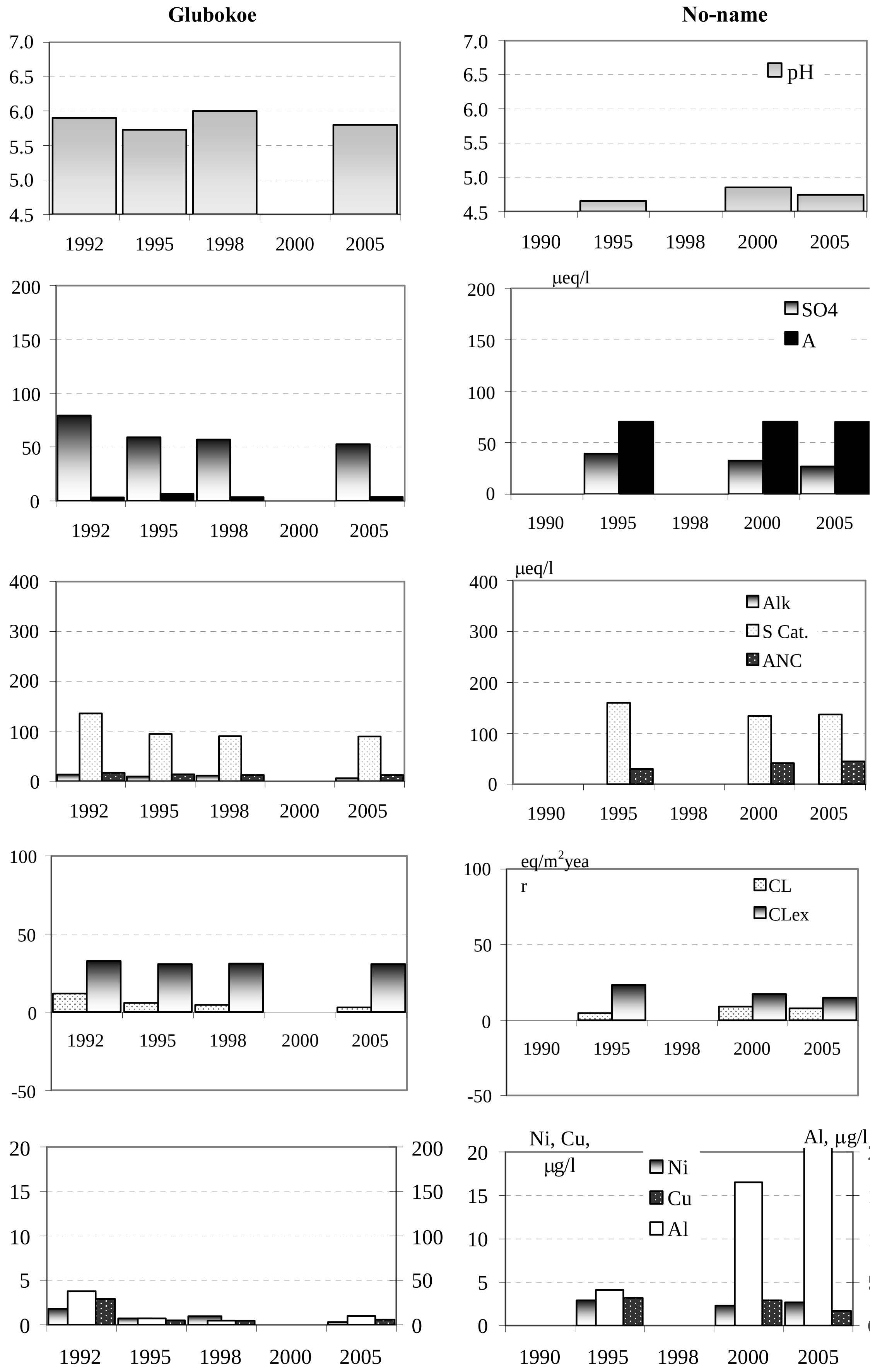

Figure 3. Dynamics of parameters of Glubokoe and No-name lakes.

In the lakes located within 10 km of the plants, that received the highest loads of pollutants (Keudsherjaur and Moncheozero) we can conclude that there appeared to be a tendency of improvement of water chemistry (figure 1). This is indicated by the decreasing concentrations of sulphates, nickel and copper in the lakes. After 1995, the critical load was no longer exceeded because of the decrease in sulphate. At the same time, the sum of cations has decreased and, accordingly, salt contents. For Keudsherjaur lake which is average (in size) but with very small catchment area (Table 1) the decrease in sum of cations was significant (44 %). Additionally, calcium has decreased from 0,37 to 0,33. At Moncheozero, the sum of cations has decreased 19% only. But, there is a positive fact: in the 1990 water of these lakes were sulphates-calcium, and since 1995 they were hydrocarbonate-calcium, more natural for waters forming at catchments formed by rocks of basic contents.

Other lakes, located far from plant pollution, are situated in areas that are vulnerable to acid precipitation (Figure 2 and 3). Vulnerability of lakes Glubokoe and No-Name is determined by geological structure of their catchment areas, which are represented by acid formations (table 1). Although catchments of lakes Tulpjavr and Dolgoe are formed with rocks, similar to basic content and geologically are rather stable to acid precipitation, their vulnerability is determined by important role of atmospheric precipitation, and it provides chloride-sodium water chemistry and low biological productivity of catchments of the tundra and forest tundra regions.

Proceeding from values of acid neutralizing ability of waters of these lakes (fig. 2 and 3), the lake Tulpjavr (forest tundra region) has the least stability to acidification, in less degree – the lake Dolgoe (tundra region). However, geological conditions of taiga region lakes (Glubokoe and No-Name) in greater degree determine water vulnerability, than increase of zonal stability to acidification. It is proved by values of critical load exceedings.

Nonetheless, we can notice decreasing of sulphates, nickel and copper contents in waters (beyond dependence of water chemistry forming in lakes located far from plants), that points at decreasing of regional sulphates and metal load at the area of Kola North. Despite of it there is no increasing of pH tendencies (fig.1,2,3). This effect can be explained by the following. First, we should notice, that extremely low pH values of the waters of No-Name lake is determined by low buffer capacity of waters and acidification by substances of humic nature (color of waters in average is 130oPt). Increasing of organic anion concentration (Keudsherjaur, Tulpjavr and Dolgoe lakes cases) buffer the potential increase of pH due to a decrease in sulphate. Regional after-effect of this fact may prove out in decreasing of calcium and magnesium concentrations (as a result of their accumulation by humus at the catchment area) and in increasing of aluminum migration. So, decreasing loads of air pollution on Kola North, Russia has led to recovery of water chemistry in lakes close to the pollution sources and further away from the pollution sources.

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8. Report of national ICP-Waters activities in Latvia, 2004/2005

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In 2004/2005, the ICP-Waters programme works continued at five sites: L.Jugla- Zaki, Amula – mouth, Sesava – mouth, Zvirbul stream and Tulija – Zoseni (Figure 1).

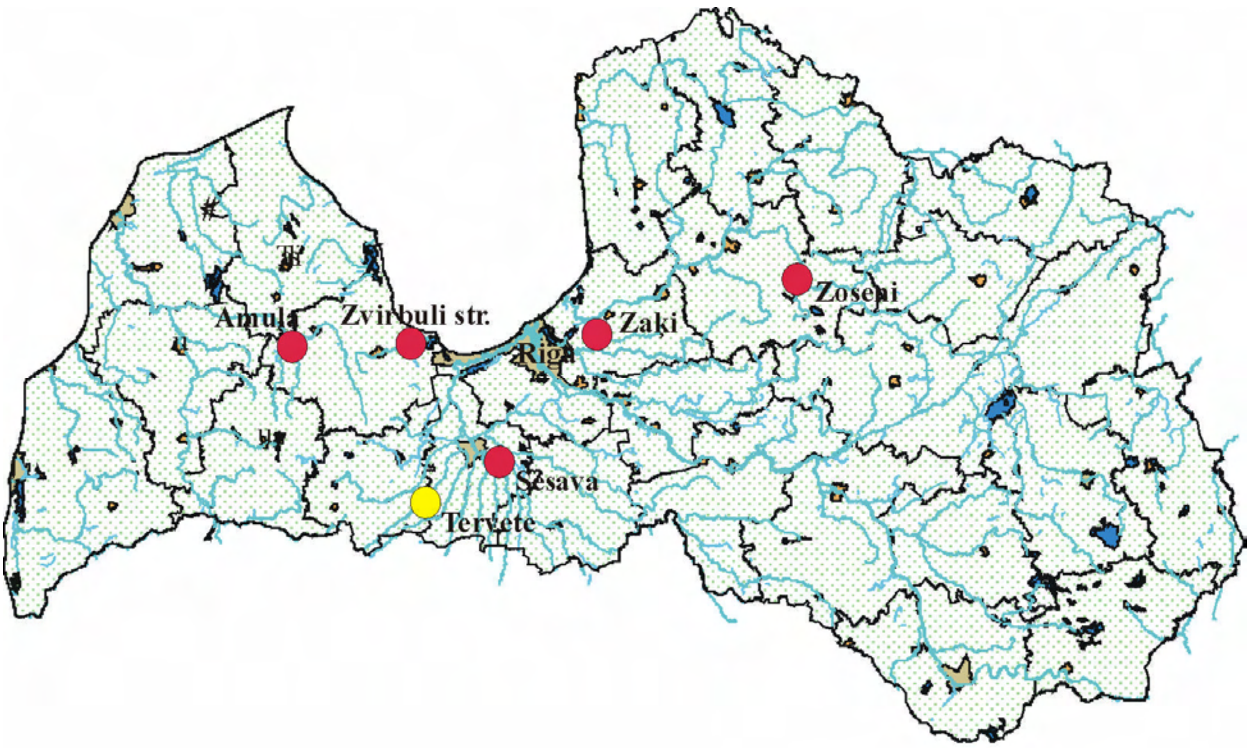

Figure 1. ICP-Waters sites in Latvia

The 2004/2005 activities focussed on:

- QA/QC of sampling and analysis;
- Working out and implementation of national legislation compliant with the Water Framework Directive
- Carrying out new measurements under the ICP-W programme for the implementation of the forthcoming Directive relating to heavy metals;
- Carrying out feasibility studies on rivers to incorporate new stations in the ICP-W network
- Assessment of the measurement results from the ICP-W sites using the water quality objectives under WFD.

Summary of the results

1. The laboratory participated in a hydrochemical intercomparison 0418 exercise held by NIVA. The results were fairly good (within the limits accepted), except for alkalinity in one sample (accuracy of 56%). The reason for the "omitted value" may be that the alkalinity values in our routine measurements were higher than in the intercomparison sample.
2. Under the ICP-W programme for 2004, Hg measurements were carried out. The results showed Hg concentrations below the detection limit at the ICP-W sites.
3. Due to a restructuring within the Ministry of Environment of Latvia, the Latvian Environment, Geology and Meteorology Agency has been formed. The Agency is responsible for the implementation of FWD that includes inter alia characterisation of the water bodies and specific reference conditions; identification of pressures; implementation of monitoring. For this purpose, results of long-term measurements from the ICP-W sites were used. The results are summarized in Table 1.
4. In 2003/2004, the feasibility studies on 5 Lielupe basin rivers were carried out to incorporate a new station instead of the Sesava-mouth site, because this station had not met the ICP-W requirements(the water quality values are in excess of the type specific reference conditions) (Figure 2). The station Tervete that is upstream of the village of Tervete has been included in the 2005 ICP-W monitoring programme (Figure 1).

Results and activities

For Latvian rivers, 6 water body types have been identified following the WFD requirements. The ICP-W site types are show in Table 1.

Table 1 *Characteristics of Latvian rivers*

River	Type	Characteristic of type	Reference conditions				
			O2, mg/l	**BOD5, mg/l**	**Ptot, mg/l**	**Ntot, mg/l**	**N-NH4, mg/l**
Tulija	1	Rapid rhitral small river	>8	<2	<0.04	<1.5	<0.09
Amula and Tervete	3	Rapid rhitral medium river	>8	<2	<0.05	<1.8	<0.09
Sesava and L.Jugla	4	Slow potamal medium river	>7	<2	<0.06	<2.0	<0.16

Figure 2 shows annual mean concentrations for the type specific reference conditions. According to those, the ICP-W sites, excluding Sesava, may be incorporated in the national water quality network as the reference sites.

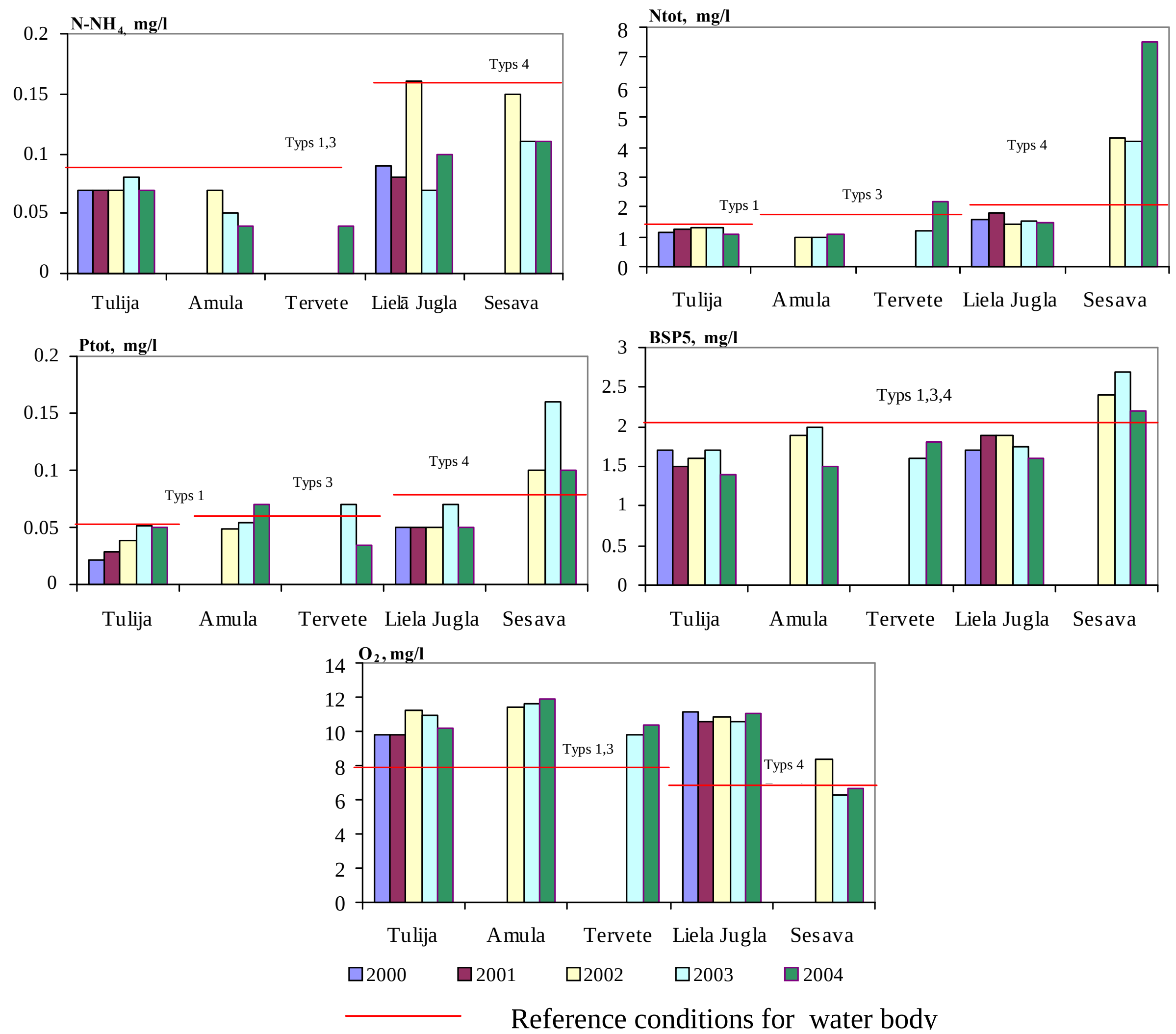

Figure 2. *Annual mean concentrations at the ICP-W sites, 2000-2004 (single measured values for Tervete)*

The measurement results had been used in national and international reports and research papers:

- N.Kadikis, S.Stivrina, P.Berga and T.Ambalova "Assessment of Acidification and Related Long-term Trends at ICP-W Sites in Latvia", Nordic Hydrological Programme Report No48
- M.Frolova, I.Lyulko and I.Dubakova "Assessment of the Long-range Transboundary Air Pollution in Latvia, 1985-2003", 8th International Global Atmospheric Chemistry (IGAC) Conference Handbook
- N.Kadikis "Metodology of Environment monitoring, way from observational data to information, LHMA experience", Latvian University 62 conference's handbook (in Latvian)
- Lyulko (Ed.) "Air Quality and its Impact on the Environment, 2003", Riga, 2004 (in Latvian)

Future Activities

- 2004 data reporting to the ICP-W data base;
- Participation in intercomparision events;
- Cooperation with ICPs in EMEP and the WFD relevant activities;
- Establishing a surface water quality network under WFD, including ICP-W sites.

9. Lake Saudlandsvatn, South Norway, a lake under recovery from acidification

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During the 1900s large areas of southern Norway were affected by acid deposition, with widespread acidification of lakes and damage to fish populations (Overrein *et al*., 1980; Hesthagen *et al*., 1999). Acid deposition reached its peak in the late 1970s and declined by about 70% (sulphur) and 20% (nitrogen) since the mid-1980s (Aas *et al*., 2004). Acidified lakes have shown substantial recovery, with increasing pH, acid neutralising capacity (ANC) and lower concentrations of labile aluminium (Skjelkvåle *et al*., 2001, 2003).

Here we report data on acidification and recovery of water chemistry and of brown trout (*Salmo trutta*) in Lake Saudlandsvatn in southernmost Norway during the 29-year period 1977-2005. The lake has over the years been followed in different projects, like the SNSF-project (1977-79), The Norwegian Pollution Control Authority (SFT) Monitoring Programme for Long Range Transported Pollutants (1980 to present), and the ANC-Recovery Project, financed by the Norwegian Research Council (2001-2003).

We have investigated the relationship between water chemistry and the abundance of brown trout (*Salmo trutta*) in Lake Saudlandvatn and its inlet and outlet stream. The lake population was sampled with benthic gill-nets every second year from 1977 to 2005. From 1977 to 1995, the sampling was carried out by a SNSF-gillnet series (Rosseland *et al.,* 1980), while from 1997 to 2003 with Nordic multi-mesh gill nets (Appelberg *et al*., 1995). Both gill nets series catches fish with about equal efficiency (Jensen and Hesthagen, 1996). During the 1970s and early 1980s the lake was highly acid, with pH less than 5.0, sulphate concentration around 140 µekv./L and an ANC between -30 and -20 µekv./L (Figure 1). In spite of this, the lake supported a relatively dense population of brown trout, with CPUE-values (Catch Per Unit Effort; numbers per 100 m^2 gill net area per night) ranging between 16-18 specimens (1977-83), Figure 2. Later, their abundance declined gradually to nearly extinction in the early 1990s (CPUE = 2 in 1993). Chemical recovery following reduced deposition of sulphur became evident in the 1990s, when pH rose to about 5.5. In the late 1990's, the brown trout population also started to recover, and by 2003 and 2005 it had achieved a higher density than in the late 1970s (CPUE = 24 and 34, respectively), Figure 2.

Both the inlet and outlet brook are used as spawning brooks, and studies of egg survival has been performed in periods from 1977 while electrofishing for fry density has been performed regularly at time of test fishing since 1986. In Lake Saudlandsvatn, the success of not becoming a barren lake has clearly been due to a 4 m^2 spawning area in the outlet brook, acting as a refuge for survival in periods with marginal water quality when the inlet (major) spawning brook could not produce any recruits to the lake. The development in the abundance of 1+ fish obtained in Lake Saudlandsvatn was well explained by fry densities (0+) in the inlet and outlet stream one year earlier (year of hatching). An increase in ANC from about 0 to 20 µeq L^{-1} gave a pronounced increase in CPUE-1+. There was also a positive correlation between fry densities (age 0+) in the inlet and outlet stream each autumn and ANC. The density of brown trout fry in these sites increased significantly when ANC rose from about 10 to 20-30 µeq L^{-1}. Thus, the recruitment strength in the tributary streams reflects the abundance of fish in the lake itself.

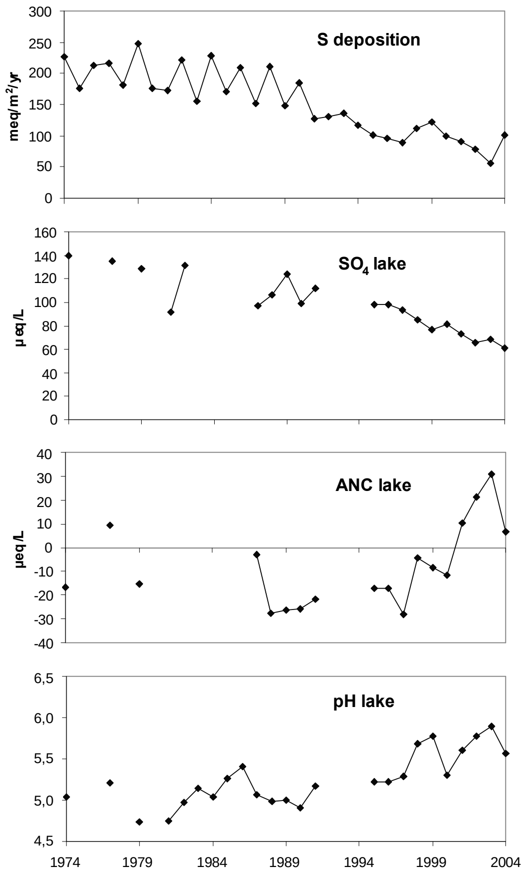

***Figure 1**. Calculated SO_4 deposition at Birkenes (Aas et al., 2004), measured SO_4 concentration, calculated ANC and measured pH in the outlet of Lake Saudlandsvatn.*

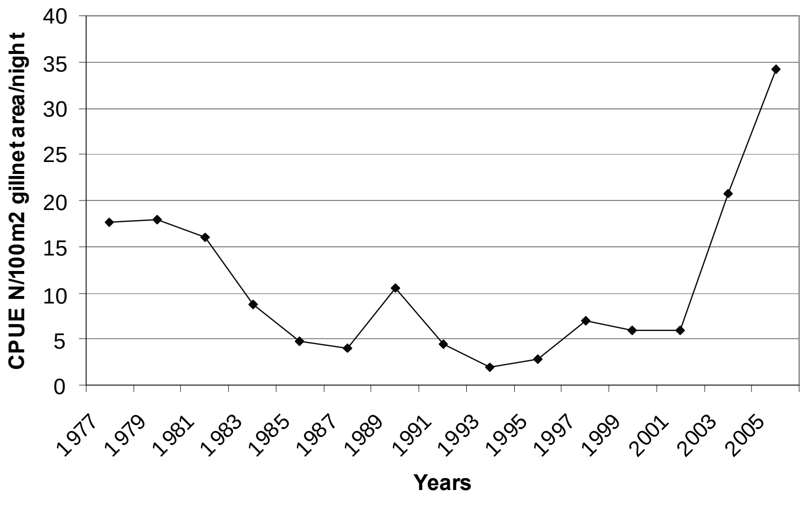

***Figure 2**. Catch of brown trout (as CPUE) in Lake Saudlandsvatn in the period 1977-2005.*

The reason for the decline in the abundance of brown trout in our study lake is therefore to a large extent due to recruitment failure.

The fish population size (measured as CPUE) showed significant lag times to changes in water chemistry (measured as ANC) both during the acidification phase and the recovery phase. In the late 1970s, although the lake had low pH and ANC levels, the trout population in the lake was still strong. This occurred despite the fact that the recruitment in both the inlet and outlet streams had failed. During the 1980s the pH and ANC levels in the lake began to increase, whereas the trout population showed a slow decline that resulted in nearly complete extinction of the population by the early 1990s. Then in the 1990s and through 2003, the pH and ANC continued to increase, but only after 1999 the trout population began to recover. When modeling the ANC for Lake Saudlandsvatn, the data thus indicated that the lag time in population response to changes in water chemistry in Lake Saudlandsvatn was more than 10 years, Figure 3.

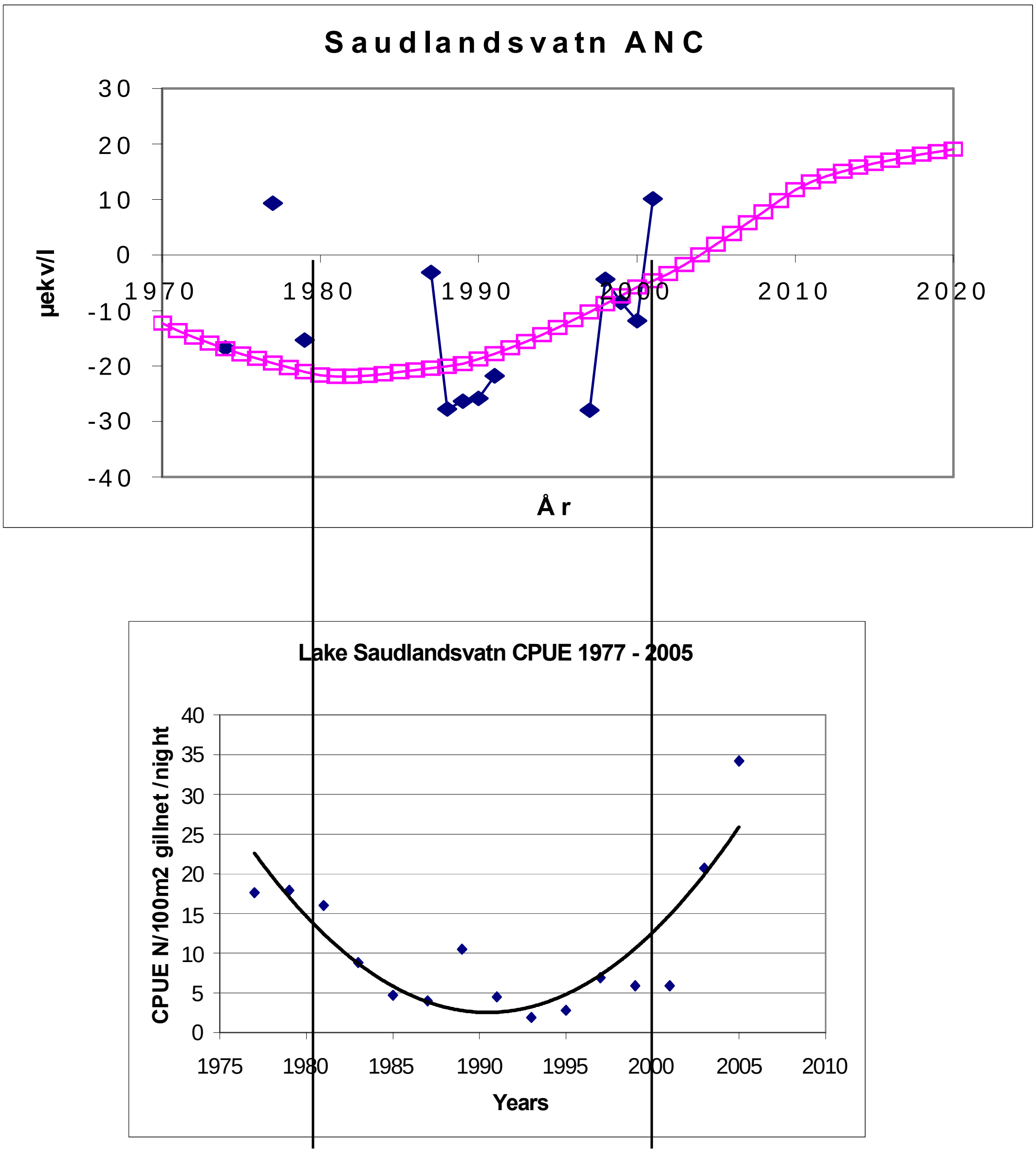

Figure 3. *A simulation by MAGIC of the ANC in Lake Saudlandsvatn (upper), and the corresponding CPUE of brown trout in the period 1977 – 2005 (lower).*

Based on the CPUE in 2003 and 2005, one might be led to think that the brown trout population in Lake Saudlandsvatn has fully recovered relative to the results from late 1970s. The rapid increase in catch since 2001 is also in agreement with the increased invertebrate recovery in Lake Saudlandsvatn, see Fjellheim and Raddum (this Report). However, by looking at the year-class distribution, it is evident that it is one single year class (hatched in 2002) that makes up the high CPUE in 2003, and still dominates in 2005, Table 1. Also the lack of older fish indicates a biased population structure.

Another sign of existing water quality problems in Lake Saudlandsvatn is indicated by the representation of the vulnerable life history stage “postspawners” (older fish that have spawned before). Rosseland *et al.* 1980 reported lack of postspawners in Lake Tveitvatn as a first sign of a declining population of brown trout going from stunted (over populated) to barren during the process of acidification. This phenomenon was probably due to an increased sensitivity of postspawners to acidic waters, demonstrated by Rosseland and Skogheim (1987). By looking at the age composition in Lake Saudlandsvatn and their maturation status, it is evident that with one specimen exception, no postspawners have been present since 1987 (Table 2). This confirms the results from Lake Tveitvatn that the brown trout population in Lake Saudlandsvatn was going towards extinction. However, as the water chemistry improved during the process of recovery, the population structure of brown trout in Lake Saudlandsvatn seems to follow the same pattern on the way back to a healthy population, namely young recruits but with a lack of old postspawners.

Table 1. *Age composition of the brown trout catches in Lake Saudlandsvatn in the period 1977 - 2005.*

		Age							
		0	1	2	3	4	5	6	7
Years	1977	0	3	24	19	11	0	0	0
	1979	0	9	8	8	22	10	1	0
	1981	0	9	29	12	11	7	2	5
	1983	0	4	23	8	3	1	2	0
	1987	0	1	11	1	0	0	0	0
	1989	0	2	5	21	4	2	0	0
	1991	0	14	14	4	0	1	0	1
	1993	0	0	3	0	2	0	1	0
	1995	0	5	0	2	1	0	1	0
	1997	0	8	8	3	0	1	1	0
	1999	1	6	7	1	2	1	0	0
	2001	1	5	7	2	2	1	0	0
	2003	0	42	8	3	8	2	0	0
	2005	0	31	26	33	14	0	0	0

Based on the criteria for the FIB model (Rosseland *et al.* 2005, Raddum and Rosseland 2005), the brown trout population in Lake Saudlandsvatn can not be characterized as healthy. A continuous monitoring of the lake water quality and fish population is therefore highly recommended.

Table 2. *Numbers of brown trout being first time spawners (Recruit spawners) and trout that had spawned before (Post spawners), separated into male and females in the catches from Lake Saudlandsvatn in the period 1977 – 2005.*

	Male		**Female**	
Year	**Recruit spawners**	**Post spawners**	**Recruit spawners**	**Post spawners**
1977	12	7	15	3
79	2	13	15	14
81	12	3	17	14
83	7	5	5	2
87	3	4	2	3
89	13	0	16	0
91	10	0	5	1
93	3	0	3	0
95	3	0	3	0
97	5	0	3	0
99	5	0	7	0
2001	3	0	5	0
2003	13	0	10	0
2005	27	0	27	0

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10. Natural recovery of benthic invertebrates in Saudland area, south Norway

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Introduction

During more than one century, anthropogenic pollution has been a major threat to South Norwegian nature. In areas of low buffer capacity, freshwater life has been impoverished due to eradication of sensitive species. The supply of acidic compounds causes biological perturbations many levels of the lake ecosystem, impacting both flora and fauna (Gran et al., 1974, Sutcliffe and Hildrew, 1989, Hesthagen and Hansen, 1991). The critical limits of many invertebrate species are lower than that of fish (Haines 1981, Lien et al., 1996) and monitoring of benthic invertebrates has been an issue in the Norwegian multidisciplinary programme "Monitoring of long-range transported air pollution" since 1981. The first site to be included in the monitoring was located in the Saudland area in Farsund County, Southernmost Norway. The localities in this site has since then been monitored twice a year. The time series from the Saudland area covers at present a period of 24 years; the longest in Norway with respect to acidification and benthic invertebrates. This paper will mainly focus upon the changes in the benthic animal community during this period, with special reference to acid-sensitive species.

Materials and methods

Lotic samples were taken from the inlet of Lake Gjærvollstadvatn and inlet/outlet of Lake Saudlandsvatn (Figure 1). Both lakes are situated 106 m a.s.l. and surrounded by deciduous forests and farmlands. The bedrock is mainly composed of gneisses and granite, giving a low buffering capacity. The localities of the inlet streams were situated in riffle areas where the substrate is dominated by stones and gravel.

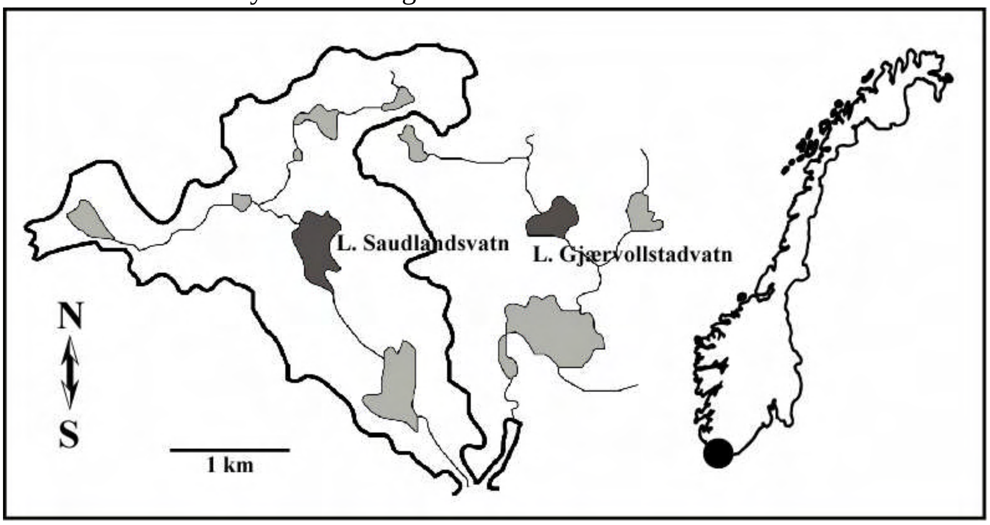

Figure 1*. Map showing the main localities and the sampling sites.*

The two lakes seem to have similar water chemistry. Around 1980 both lakes were acidified, pH varying between 4.75 and 5.0. The chemical recovery of L. Saudlandsvatn started around 1990 (B. O. Rosseland, this volume), giving an increase in pH from around 5.0 to 5.8. Brown trout (*Salmo trutta* L.) is the only fish species in the lakes, suffering high egg and fry mortality, bringing the populations close to extinction (B. O. Rosseland, this volume).

Qualitative benthic kick samples were collected in spring (May/June) and in autumn (October/November). We sampled three stations from the main inlet of each lake and the outlet river from Lake Saudlandsvatn. All samples were sieved through a net of 250 µm and later sorted and identified. Acidification scores were calculated according to Raddum et al. (1988) and Fjellheim and Raddum, (1990).

Results

The acidification scores (Figure 2) were low during the 1980's indicating severe damages to the benthic community. During this period small mussels, *Pisidium*, were the only sensitive animals found regularly (Figure 3), indicating a pH slightly less than 5.0 (Fjellheim and Raddum, 1990). From 1992 a gradual recovery was observed. The autumn community indicate a stronger improvement (r^2=0.87) than the spring community (r^2=0.74). Four acid-sensitive taxa played a major role in the recovery: the stonefly *Isoperla* sp., the caddis flies *Hydropsyche siltalai* and *Wormaldia occipitalis* the mayfly *Baetis rhodani* (Figure 3). Benthic animal diversity measured as EPT taxa richness (Lenat and Penrose, 1996 Wallace et al., 1996) increased from around 15 in 1984 and 1985 to above 25 in 2003 and 2004 (Figure 4).

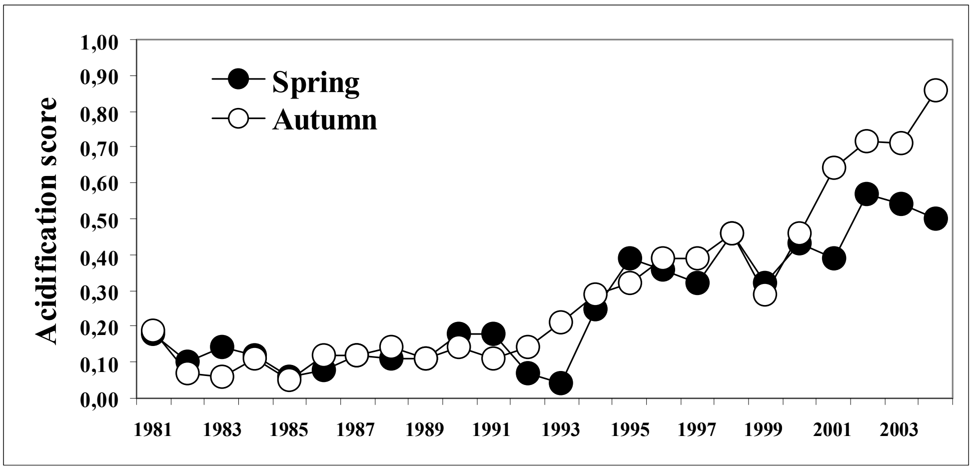

***Figure 2**. Mean acidification score for the Saudland area 1981 - 2004, based on the model of Raddum et al. (1988) and Fjellheim and Raddum (1990).*

Discussion

The dynamics of natural recovery of benthic fauna from acidification in lakes and rivers is, due to the short time-scale of emission control, a relatively new issue. Biological monitoring of Rivers Vikedal, western Norway, indicate that benthic animal recovery in the upper, unlimed river, started around 1993 (Fjellheim and Raddum, 2001). This finding is in line with the results from the Saudland area, indicating a response delay of a few years compared to the chemical recovery.

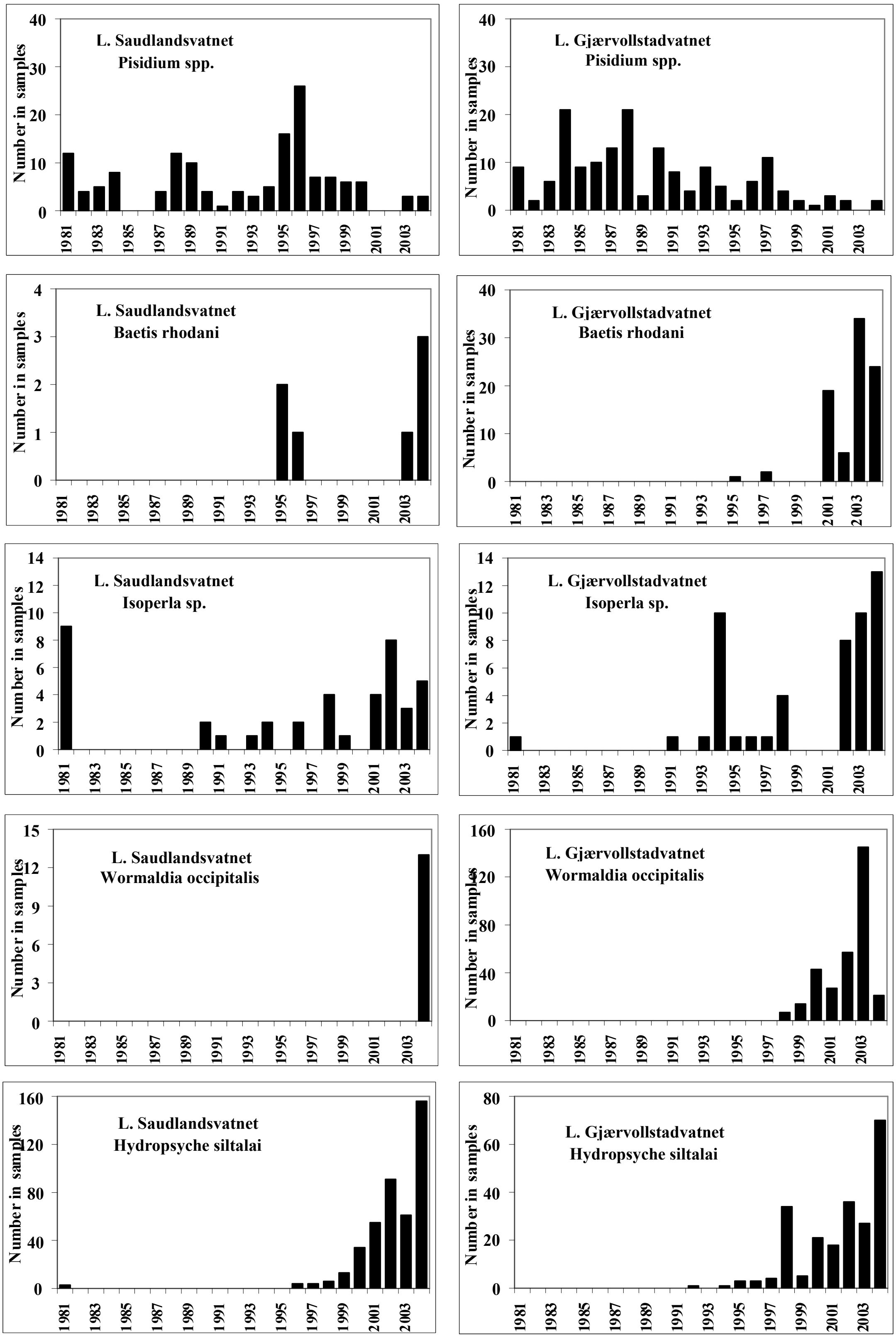

Figure 3. *Total numbers of acid-sensitive invertebrates recorded in samples from the Saudland area during the period 1981 - 2004.*

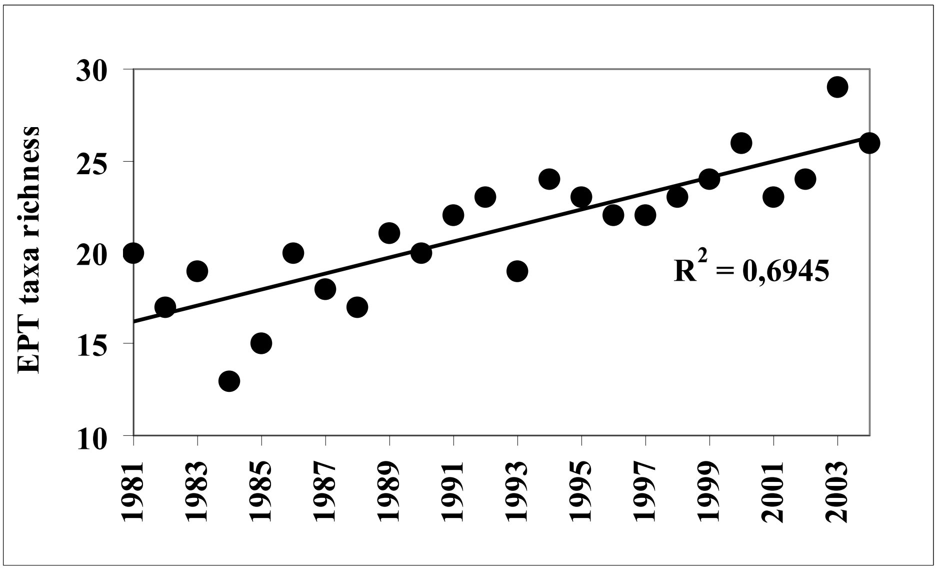

***Figure 4**. Development of the EPT taxa richness metric (Lenat and Penrose 1996) in the Farsund area during 1981 - 2004.*

The experience of recovery from acid stress is better in limed watersheds, both in Norway (Raddum et al., 1984, Fjellheim and Raddum, 1992, 2001, Walseng et al., 2001), as well as in other countries (Eriksson et al., 1983, Evans, 1989, Henrikson and Brodin, 1995, Bradley and Ormerod, 2002). Studies after liming Norwegian watersheds indicate that the recovery process depends on the situation of the catchments, lime dose, species and time. The most mobile invertebrates, like winged insects, recolonise the localities rapidly, while the responses of less active animals, like snails, generally are slower (Fjellheim and Raddum, 1995, Raddum and Fjellheim, 2003). Chemical data from several unlimed acidified watersheds indicate that a natural recovery starting in the beginning of the 1990’s (Skjelkvåle et al., 2001). This recovery was first observed in less impacted localities, like the lower part of the watersheds and tributaries of better water quality. We also have evidence for an earlier recovery of benthic invertebrates in rivers situated in less acidified rivers (Halvorsen et al., 2003).

During the 1980's, the benthic communities of the Saudland area was dominated by acid-tolerant species, like the caddis flies Polycentropus *flavomaculatus*, *Plectrocnemia conspersa*, *Neureclipsis bimaculata*, the mayflies *Leptophlebia vespertina*, *L. marginata* and the stoneflies *Leuctra hippopus*, *L. fusca* and *Nemoura cinerea*. Presence of small mussels (*Pisidium* spp.) indicated a pH slightly less than 5.0, which also were confirmed by water chemistry samples. Due to the wide distribution and high sensivity to acidification, the mayfly *Baetis rhodani* is a key indicator species in acidified localities in South Norway. The species was recorded in one sample during the winter 1981, a time of sampling not equivalent to the succeeding sampling dates. We therefore know that the species has recolonised.

Disappearance and recolonisation of sensitive species may be highlighted using dynamic conceptual models suggested by Posh et al. (2003) and MIRACLE (Modelling Invertebrate Recovery of ACidified Lotic/lentic Ecosystems, Raddum and Fjellheim 2002). As an example, Figure 4 presents the development of *Baetis rhodani* in the Farsund area during the chemical recovery of the surface water. The species was missing from the samples during 1981 – 1994. During this period, the critical limits were exceeded for an unknown amount of time, corresponding to t5 of Posch et al. (2003). The time lag from t5 to 1994, when the species was first encountered depends on the water quality and the dispersal rate. During the first years the populations were highly unstable, as reflected by low densities or the species missing from the samples. In 2001, *B. rhodani* exceeded the critical abundance t6 and has since then been found regularly. Assuming a satisfactory water quality, the populations will, according to the MIRACLE model, disperse (stage 3) into a pattern of natural fluctuations (Stage 4). The time to reach stage 4 will mostly depend on biotic factors (Raddum and Fjellheim 2002, Yan et al., 2003). The monitoring data presented in Figure 3 could similarly be interpreted in the same way as *B. rhodani*. At the start of the monitoring, the critical limit was exceeded for most species. Exceptions were the caddis fly *Hydropsyche siltalai* and the stonefly *Isoperla* sp., which both were close to extinction at the beginning of the monitoring.

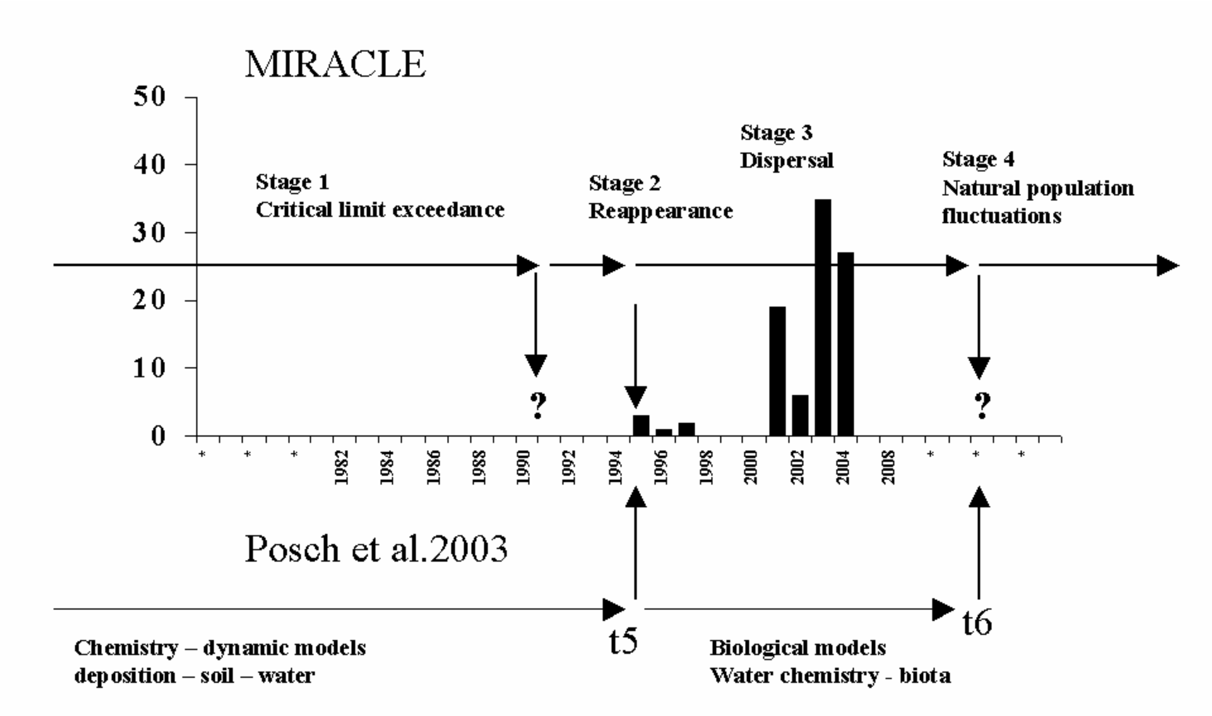

***Figure 4**. Recolonisation of the mayfly Baetis rhodani in the Saudland area, in the frames of conceptual models suggested by Posh et al. (2003) and Raddum and Fjellheim (2002).*

The development of the benthic animal diversity during the 1980s indicates that the critical limits of many species were exceeded prior to 1980. The increase in EPT richness during this period is probably a result of recolonisation of sensitive species. The faunal succession in the Saudland area is marked, but is still far from an endpoint. We expect a future faunal assemblage to be more diverse. As an example, the 2004 EPT taxa richness of the limed Rivers Audna and Ogna, both situated in the same region (Fjellheim and Raddum, 1995) was 39 and 44 (Fjellheim and Raddum, unpubl.). We expect highly sensitive taxa like the mayflies *Caenis* spp., *Cloeon* spp., the freshwater snails *Lymnaea* spp. and *Gyraulus* sp. to colonise the localities in the Saudland area in near future. The positive development of the communities of acid-sensitive animals is correlated to reduced air pollution resulting from the international sulphur acts from 1979 and onwards. During the period 1981 - 2003 annual national sulphur emissions in Norway was decreased from a total of 128 000 to 53 000 tons (Statistics Norway, 2004). Additionally, reduced emissions outside Norway contributed to a substantial reduction in long-range transported pollutants after 1980 (Skjelkvåle et al., 2001).

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11. The effects of multiple stressors from metals and organic micropollutants on the brown trout in Lochnagar, Scotland

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Extended abstract from: Rosseland et al. 2006.

To our knowledge, only two fish species have been found in Lochnagar; brown trout (*Salmo trutta*) and European eel (*Anguilla anguilla*). Based on literature, the brown trout were stocked in Lochnagar in 1851, and have been there ever since. The brown trout population in Lochnagar, has been indirectly monitored for the last 16 years by the Fisheries Research Services (FRS), Freshwater Laboratory, Pitlochry, Scotland, as a part of a National Monitoring Programme (Acid water Monitoring Network). Based on the electro fishing in the lake outlet stream, it is obvious that the stream population has gone through years with marginal water quality and/or physical challenging conditions, Figure 1. Several years with lacking year classes normally found at the stream localities, are indicators of stress. Typically is also the fact that it is the lowest stretch which is least affected, as both an improved water quality and probably also an increased water supply will be most abundant at lower stretches.

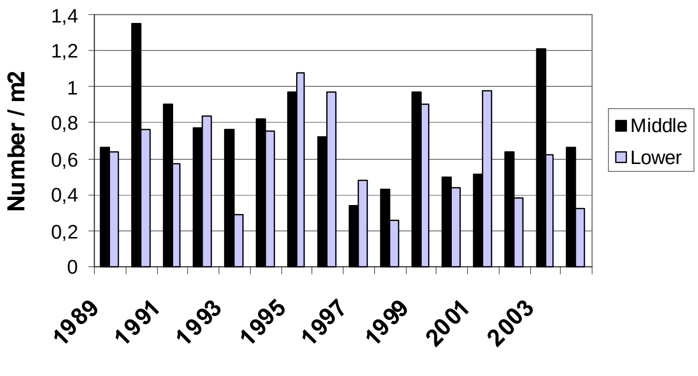

Figure 1. *Brown trout densities (all age classes) in two 50m sections of the outlet stream from Lochnagar. Data from: FRS, Freshwater Laboratory, Pitlochry, Scotland.After Rosseland et al. 2006.*

The data collected as a part of the EMERGE Project from 18 brown trout caught by fly fishing in the lake in July 2001 form the main basis for characterising the fish population in Lochnagar (Rosseland *et al.* 2003). From otolith age interpretation, it seemed that stagnation in growth took place already after an age of five years, Figure 2. The condition factor (CF) also indicated that the surplus energy for growth was lacking in older fish, as the CF fell from the same age as the growth ceased. This indicates either a high density (stunted) population, or a population stressed by marginal water quality at least in periods of the year. An increased metabolism due to compensatory mechanisms to maintain a normal ion regulation or enforced detoxification activities can reduce the surplus energy normally used for storage of energy (high CF) and growth.

Post-spawners of brown trout are more sensitive to acid waters than younger stages. As the brown trout in Lochnagar start to spawn at age 3, this might add extra to the cost of survival for the older fish in the population. Typically, some fish were not spawning every year.

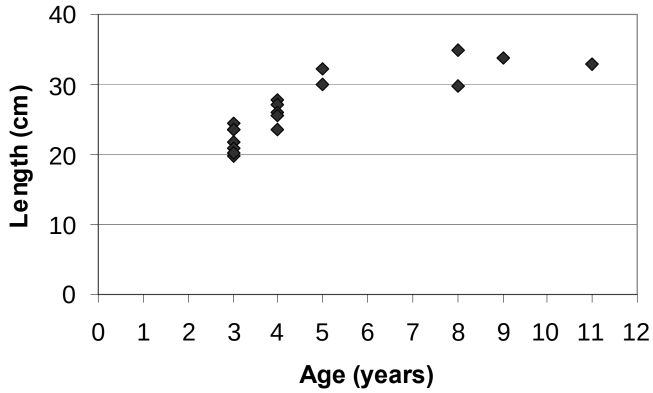

Figure 2. *The age and length of the 18 brown trout caught by fly rod in Lochnagar in July 2001. After Rosseland et al. 2006.*

Most of the brown trout had normal stomach filling at time of catch (from empty to full). The food reflected what the isotope analyses (δ^{15}N and δ^{13}C) showed, namely that none had sign of fish debris in the stomach, and that the invertebrates mostly represented herbivorous or soft bottom groups which also can inhabit the deeper part of the lake, Figure 3.

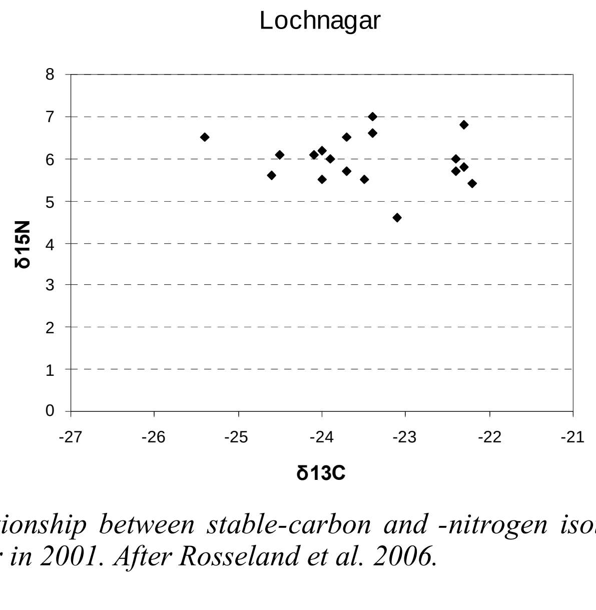

Figure 3. *Relationship between stable-carbon and -nitrogen isotope ratios of individual fish from Lochnagar in 2001. After Rosseland et al. 2006.*

Based on blood samples, the plasma concentration of the major osmotic ions Na and Cl was within the lower normal range for brown trout, indicating a successful osmoregulation at the time of sampling. As the ionic composition of the lake water is not as extreme as we find in other high mountain lakes, this has helped the brown trout in Lochnagar to maintain their osmotic homeostasis.

The metal accumulation on the gills, however, indicates that especially Al, Pb and Cd is high in Lochnagar, compared to other lakes studied, Figure 4. None of these metals, including Cr, Cu, Ni, Mn, Zn, Fe, As and Se, bio-accumulated on the gills as a function of age. The gills then represent an organ which bio-concentrate the metals, and provide a direct measure of the free and bio-reactive metal species available in the lake water. The specific level of Al on gill was 20 – 30 times higher than background level (2 µgAl/g gill wwt weight or 10 µgAl/g gill dry weight) for non-acidified lakes, but the amount was still within a level where brown trout can regulate its ion balance. For comparison, Atlantic salmon would have suffered ion-regulatory problems with the same amount of Al on gills.

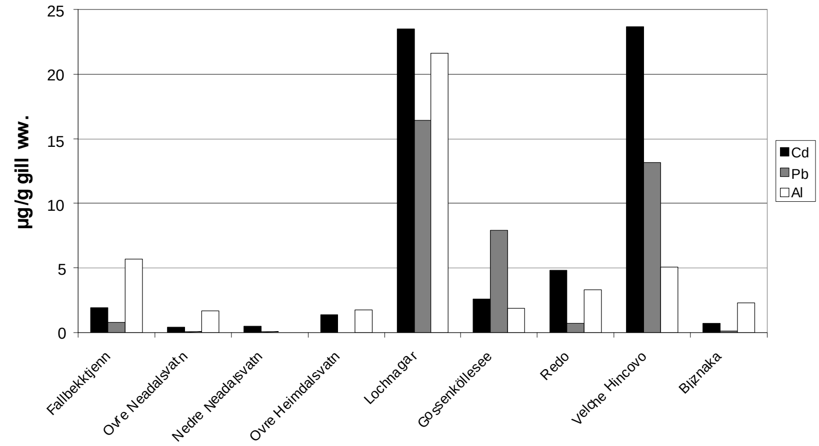

Figure 4. *Mean concentration of Pb and Cd on gills of salmonides in lakes from the EMERGE project. Adapted from Rosseland et al. 2006*

Analyses of the kidney showed clear bioaccumulation with size (length) and age of all metals analysed; Pb, Cd, As and Se. Compared to the levels in other EMERGE lakes, Lochnagar had the highest level of Pb and Cd (Figure 5), and the second highest of Se. Selenium, however, act as a protective metal by binding and detoxifying Hg and other toxic metals in fish. The high Se concentration in kidney from brown trout in Lochnagar and Velche Hincovo, the two EMERGE lakes with the highest load of Pb and Cd, can thus be an effect of that.

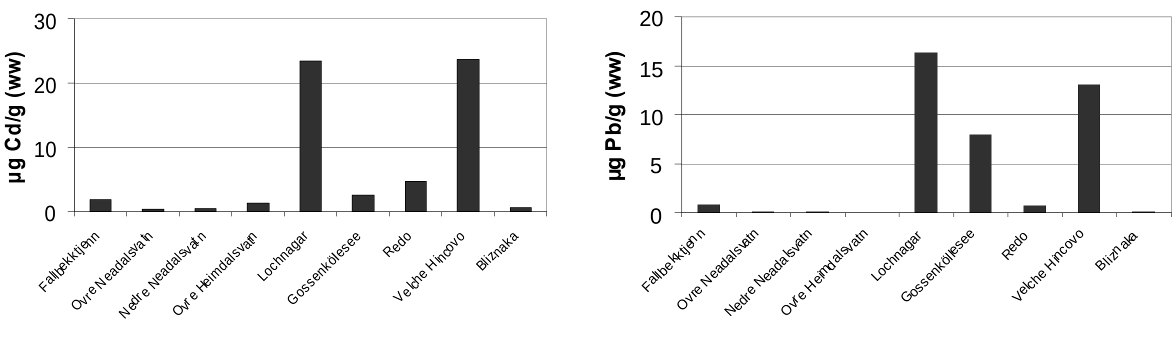

Figure 5*. Concentration of kidney cadmium (Cd) and lead (Pb) in standardized 250g brown trout from 9 EMERGE lakes. Adapted from Rosseland et al. 2006.*

Mercury is the only heavy metal that has both bioaccumulation and biomagnification properties. The brown trout in Lochnagar is a non-piscivorous population, but had the highest bioaccumulation rate of all non-piscivorous EMERGE and MOLAR lakes, including the piscivororus Arctic charr population at Spitsbergen (Lake Arresjoen), Figure 6. Although only one of the oldest brown trout exceeded 0,2 ppm Hg, old fish in Lochnagar will have a contamination level of Hg which are approaching dietary advise level given by WHO and US-

EPA. The high Hg accumulation must reflect a high Hg load to the lake catchment, as well as a high lake water concentration and metylathion rate.

Persistent Organic Pollutants (POPs) were in low levels when compared to other alpine lakes from EMERGE and MOLAR project which, in consistency with previous descriptions on the distribution of diffuse pollution by these compounds, is in agreement with the low altitude and relatively high annual average temperature of this lake. The concentration of "the new" POPs, belonging to the group of organohalogen pollutants widely used as flame retardants, namely polybrominated diphenyl ethers (PBDE), showed high concentrations in brown trout liver and muscle within the group of high mountain lakes which are characterized by having low amounts of these compounds. In fact, Lochnagar had the highest concentration of PBDE of all EMERGE lakes (Vives *et al.* 2004). The distinct high concentrations of these compounds in fish from Lochnagar reflect inputs from unknown local sources.

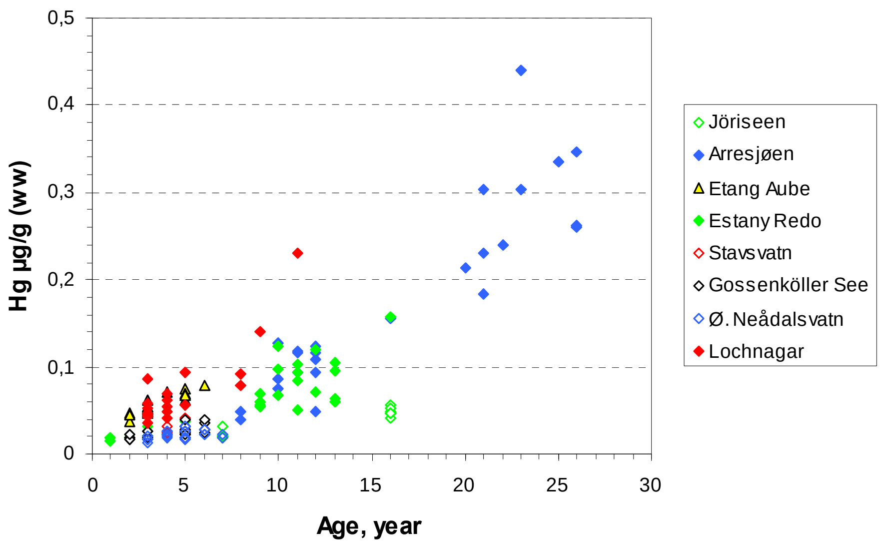

Figure 6. *Concentration of Hg as a function of age in brown trout from Lochnagar in July 2001, compared to the concentration in lakes analysed in the MOLAR project (Rognerud et al. 2002). From Rosseland et al. 2006.*

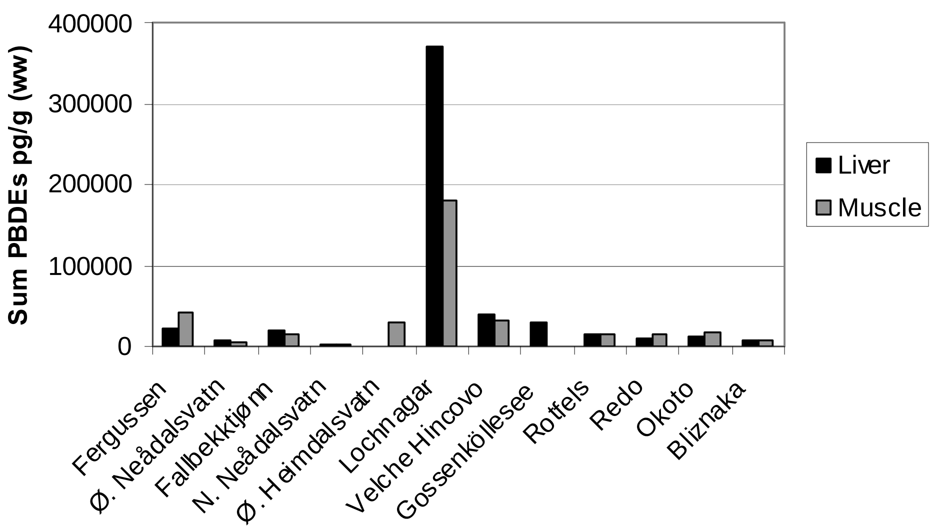

Figure 7*. Sum PBDEs in liver and muscle of salmonides sampled in the EMERGE project.After Rosseland et al. 2006.*

Histological examination of liver tissue of the brown trout in Lochnagar revealed clear signs of toxic effects. The liver had the highest frequency of melano-macrophages per mm^2 of liver when compared to brown trout populations in EMERGE and MOLAR projects.

Since no standard test fishing with series of gillnets in autumn have ever been performed in Lochnagar, we have no good data enabling us to characterise the population structure and year-class strength etc. in the lake. The data presented here on the level of pollution load and subsequent effects on the fish, however, are strong. These findings confirm that the pollution load of heavy metals and POPs to the brown trout in Lochnagar exceed critical levels for effects i.e. in liver tissue.

To be able to study whether the pollution loads have affected the population structure and critical parameters for sustainable production, standard test fishing with gillnet series following international protocols is highly recommended for Lochnagar.

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12. Multi-media modelling of POPs

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Multimedia models are simple generic mathematical models that can be used to evaluate the fate of semi-volatile organic compounds in the global environment. Several of such models are available, freely or upon request to their authors. Some are already used as regulatory tools or as part of regulatory tools (e.g. EUSES, Caltox (1997; Bonnard, 2002)). In the autumn 2005, the OECD expert group on multimedia modelling has presented a new model that could be used as a screening tool in the very early stages of risk assessments. The principles and conditions of uses of multimedia models are presented here. An example of application is given using the OECD screening tool.

Most multimedia models have only a small number of compartments (often less than 10) to represent the environment. The OECD Screening tool has 3: air, soil and seawater. Their properties are assumed to be homogenous so spatial or climatic differences are usually not represented in this type of models. Calculations are usually performed at steady state although some models perform dynamic calculations and can also distinguish between climate zones or periods. All multimedia models are based on mass balance calculations. The main processes usually represented include:

- exchanges between solid-gas-water phases
- advection by winds and water currents
- losses through degradation
- water and soil particles runoff
- deposition of particles
- washing out by rain…

The models simulate the emission of pollutants into air, soil and water. The proportions that are introduced in each of these compartments can usually be chosen by the model user (Mackay, 2001; OECD, 2004).

Multimedia models data requirements are usually low: Since compartment characteristics are set by the modeller, the user has only to fill in substance physico-chemical characteristics. The OECD screening tool requires that users enter only 5 values for each compound: the partition coefficient between octanol and water (Kow), the partition coefficient between air and water (Kaw derived from Henry law's constant) and half lives in air, water and soil.

The multimedia models outputs are the fluxes between, in and out of the compartments, the proportions of substance in each compartment and, often, the persistence of the substance in the global environment and its potential for long range transport. These two last outputs can be useful to assess substances in the framework of the Stockholm and the Aarhus Convention on POPs since both texts give persistence and potential for long range transport as criteria for substances to be classified as POPs (1998; 2001).

Multimedia models have several advantages: they are quick and easy to use. They allow systematic and rapid comparisons between substances on criteria set by international conventions. In contrast, field measurements are expensive, sometimes difficult to organise and cannot give any information on persistence and long-range transport prior to the release of the chemicals in the environment although they remain essential to increase understanding of chemicals fate in the actual environment. Moreover, it is difficult to compare field results for two different substances because their release history and location are generally different.

In order to evaluate substances with the OECD screening tool, one has first to set up a database containing their partition coefficients and their half-lives. The model is then run, which is straightforward. The results appear on 2 xy plots (Figure 1). Both use the persistence for the x-axis but two different long-range transport metrics are used for the y-axis. On the first plot, the characteristic travel distance is used. It represents the distance an air mass may travel from the pollution source before the concentration of the pollutant has decreased to C0/e, i.e. to 37% of its initial concentration C0. This can be of a few km or distances that are greater than the earth circumference for substances that have a large potential for long range transport. The second plot shows the deposition efficiency on its y-axis. This metric is an evaluation of a substance potential to deposit in cold areas, and thus a way to evaluate the potential for soil and water contamination in areas far from sources such as mountains or the arctic. Hence, the first plot will point out substances that are likely to be everywhere in the atmosphere or in water whereas the second will particularly pinpoint substances that may reach remote regions via the « grasshopper effect ».

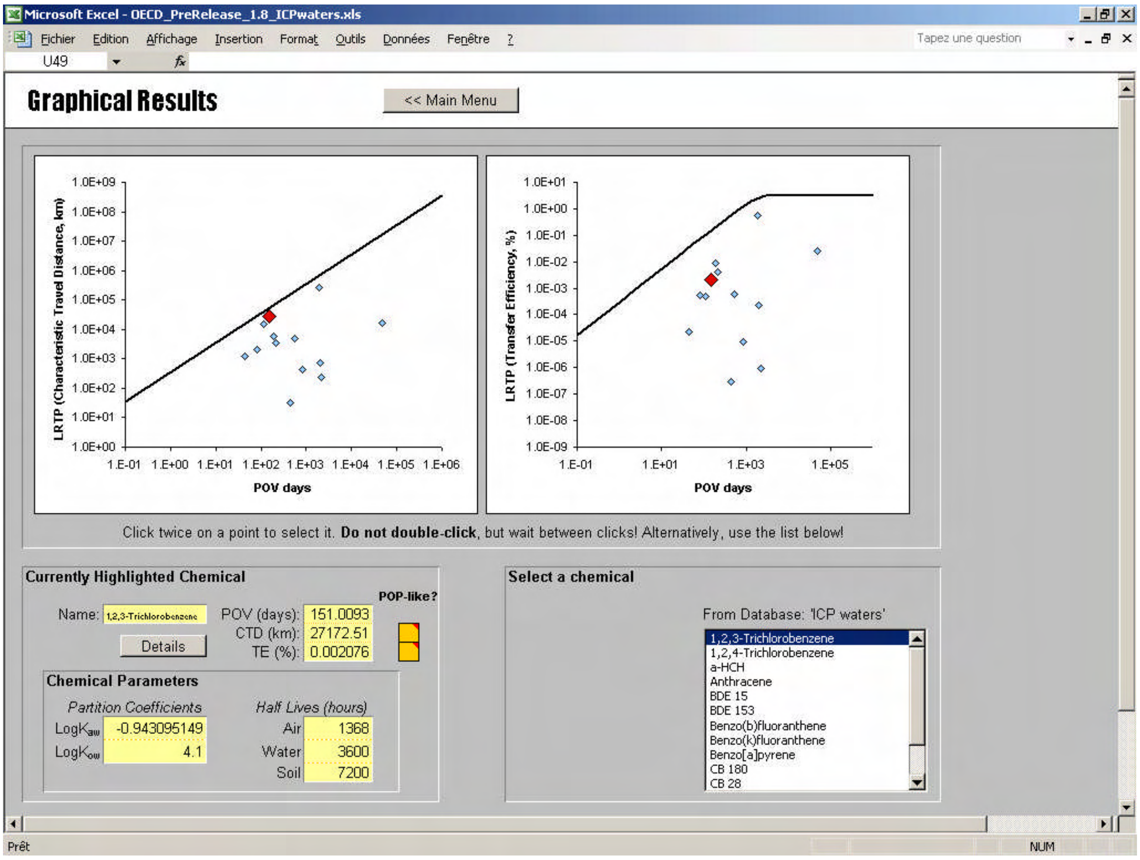

Figure 1 *Multimedia models*

On both graphs, the substances that have high potential for long range transport and long persistence in the environment can easily be identified since they appear in the upper right hand corner of the plot. These are substances for which further studies are required since they present characteristics that are likely to be unacceptable in the environment. Known POPs, such as PCBs, lindane and hexachlorobenzene are found in that part of the graph.

The OECD screening tool also evaluates the repartition of the emitted substances between the three compartments. One can thus evaluate whether a substance remains in the compartment in which it has been emitted or whether it may migrate toward another one, such as air for the most volatile substances, water for the most soluble and soil for the most lipophile.

There are uncertainties in multimedia modelling partly related to uncertainty in input data and partly to model structures. It is difficult to validate these models because they are generic but the trends they give fit with field observations. Model inter-comparison exercises have also been carried out and showed that the differences between models could be accounted for by different parameterisations (such as compartment sizes) or types of metric chosen for long range transport potential (e.g. characteristic transport distance vs. deposition efficiency) (Fenner et al., 2005; Shatalov et al., 2004).

These models therefore provide an easy way to assess large number of substances and could be used in order to perform initial screening for specific substances or for large batches of compounds. Knowledge of their repartition in the environment could help to set up field experiments as well as monitoring programmes and pollution prevention schemes.

13. New classification methods for the implementation of the European Water Framework Directive and possible use in the UN-ECE Monitoring program

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Introduction
In the current biological German water quality monitoring there does almost not exist any standard (16 states with 16 waterlaws, different sampling etc.) – the only exception is the Saprobic Index normation. The Water Framework Directive (WFD, European Union 2000) is a chance to harmonize biological monitoring in Germany – also for other purposes e.g. ICP-Waters Monitoring. The WFD is also a chance to bring back in mind degradations of waters other than organic wastewater pollution e.g. acidification.

WFD asks for new concepts of ecological classification of waters. Increasing monitoring requirements forces EU-Memberstates to reorganize their monitoring. This raises chances to find additional methods for biological indication and to standardize monitoring programs.

Activities in Germany
During the year 2004 have been tested some of the new biological WFD-classification methods at German ICP-waters sites of running waters. For three of the four WFD bioelements these methods contain metrics for the indication of acidification. For Macroinvertebrates, Macrophytes (mosses) and Diatoms special indices for such indication have been developed and were compared to the former used methods.
Type specific metrics are
Macroinvertebrates: Saprobic Index, Acidification Index, Degradation Fauna Index
Macrophytes: Reference Index including percentage of acidic indicators (mosses)
Diatoms: Trophic Index, Reference Index including percentage of acidic indicators (mosses)
Detailed descriptions of these methods are published (Braukmann & Biss 2004, Schaumburg et al. 2004, 2005). For montoring of fish a method is under development. Some of the results are presented here, all of them will be published in the next German ICP Waters report.

Some Results
Fig. 1 shows the correlation between the WFD-ecological status class of the used bioelements and pH. The status class includes all the metrics of the WFD classification, not only the acidic indication. If a water body is acidified, no good WFD-classification can result.

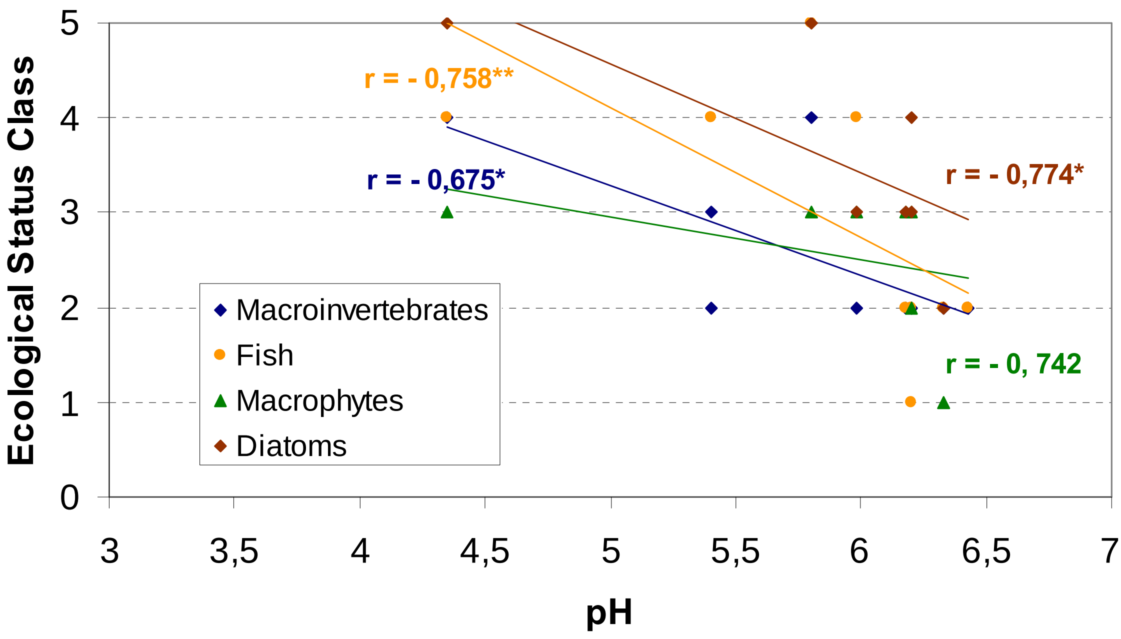

Figure 1: *Correlation between ecological status class (WFD) of bioelements and pH*

Good and significant correlation can be observed for the diatoms, fish and macroinvertebrates. Also good but no significant correlation is recognized for macrophytes.

In Table 1 are shown the resulting ecological status classes for the testet bioelements at German acidified streams

Table 1: *Ecological status classes for the testet bioelements at German acidified streams in order of increasing pH*

Name of stream	Fish	Makroinvertebrates				Macrophytes and Diatoms			pH (Avg. 2004)
		Sabrobic Index	Acidic Index	Degradation Fauna Index	Entire Calssification	Macro-phytes	Diatoms	Entire Calssification	
Zinnbach	4	2	4	2	4	3	5	5	4,35
Tirschenreuther Waldnaab	4	1	2	1	2				5,40
Tirschenreuther Waldnaab	4	1	3	2	3				5,40
Roeslau	5	1	4	2	4	3	5	5	5,80
Eger	4	1	2	2	2	3	3	3	5,98
Hinterer Schachtenbach	2	1	2	1	2	3	3	4	6,18
Grosse Ohe	1	1	2	1	2	2	4	4	6,20
Seebach	2	1	2	1	2	3	3	3	6,20
Vorderer Schachtenbach	2	1	2	1	2	1	2	1	6,33
Tirschenreuther Waldnaab, Gr.	2	1	2	1	2				6,43
Tirschenreuther Waldnaab, Gr.	2	1	2	1	2				6,43

The following results can be summarized:
The metrics Saprobic Index and Degradation Fauna Index show high or good conditions for the tested stream sites. They do not indicate any acidification. Fish classification and Acidic Index of macroinvertebrates do indicate acidification for the streams with extremely low pH. Acidic metrics for macrophytes and diatoms indicate acidification for all streams except one. The plant

components seem to be more sensitive to acidification and react earlier i.e. higher pH than the fauna components.

The biological methods for WFD-classification in Germany can be used also for indication of acidification. Germany will focus on macroinvertebtrates and diatoms for further monitoring of acidification. Monitoring of fish will not be used because of ist high expence.

In addition more metrics will be testet to show long term trends of biological recovery of aci dified streams. The following examples show possible candidates (Fig. 2, 3):

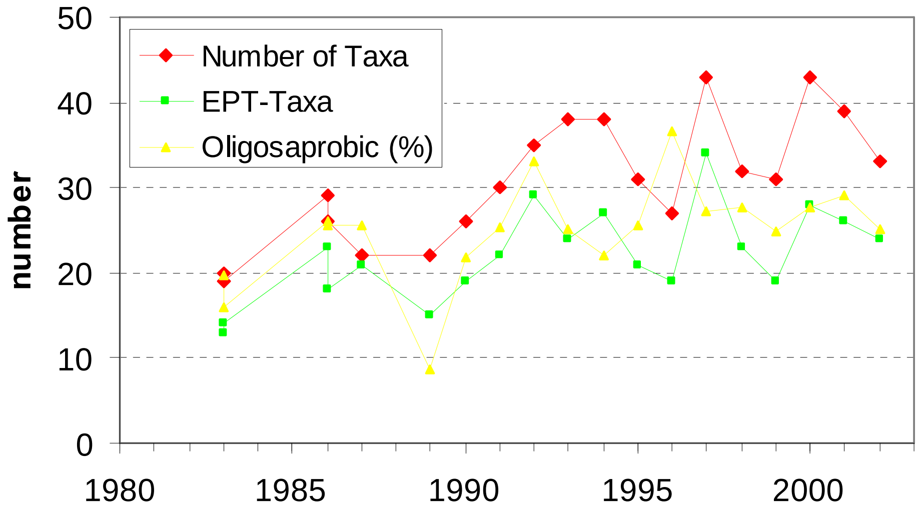

***Figure 2** Development of some metrics for macroinvertebrates in acidified German river „Große Ohe“*

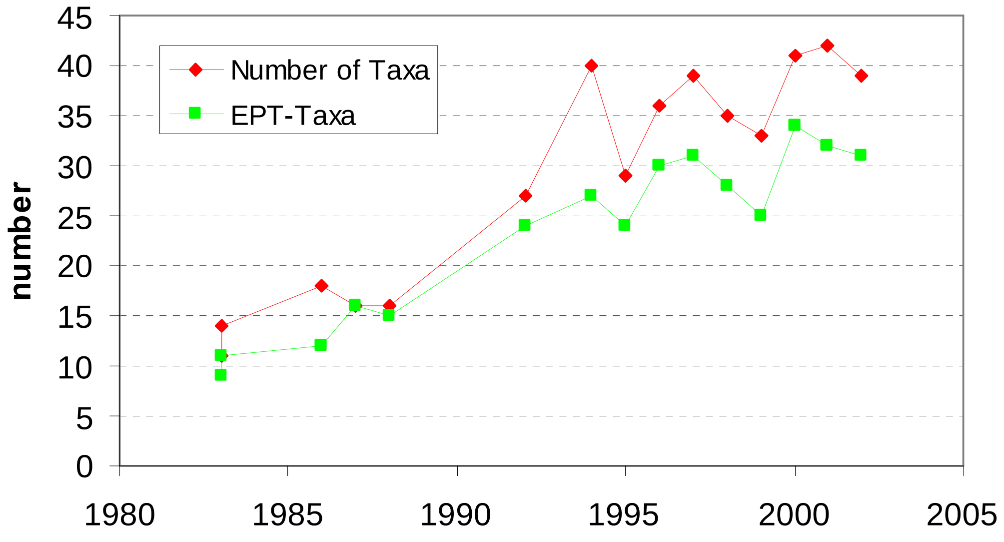

***Figure 3** Development of some metrics for macroinvertebrates in acidified German river „Seebach“*

Conclusions

- With the use of the WFD methods and additional biological metrics, slightly biological recovery at some German ICP-waters sites can be recognized
- All WFD bioelements are usefull to indicate acidification
- Germany will focus on macroinvertebrates and diatoms in Rivers (in lakes: phytoplankton, diatoms and zooplankton)
- For further bioindication numerous metrics will be tested
- In the ICP Waters monitoring program it could be helpfull to use more standardized biological methods to support knowledge of biological recovery
- It is suggested to use such methods also to compare biological data across participating countries of ICP Waters Program if data available

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14. Acidification and the WFD: Designing a macroinvertebrate-based tool to determine the pressure of lake acidification in the UK.

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Introduction
The Water Framework Directive (WFD) seeks to improve water quality throughout the European Union over the next two decades and beyond. Within a very broad remit the WFD includes a requirement to develop biological classification tools for the purpose of determining ecological status with respect to various environmental pressures. Freshwater acidification is one of the many “pressures” identified.

The UK is affiliated to the WFD Northern GIG (Geographical Intercalibration Group) with regard to the issue of lake acidification, and benthic macroinvertebrates have been identified as the primary biological indicator group for this pressure. Under the guidance of UK environment agencies, and particularly the Scotland and Northern Ireland Forum for Environmental Research (SNIFFER), scientists at the Environmental Change Research Centre at UCL are involved in tool design. Depending on characteristics of the macroinvertebrate assemblage of each lake, and possibly with reference to additional physico-chemical data, the tool is required to assign one of five categories, (High, Good, Moderate, Poor, Bad), defined by WFD normative definitions, to indicate conditions relative to what is considered to be “high status”. Ultimately it is intended that the tool will be provided in the form of simple software that will allow the funding agencies to test further datasets. This work is still in development but progress to date is summarised below.

Physico-chemical indicators of acidification
In the UK water pH does not provide a reliable indication of acidification pressure, i.e. the extent to which sites have acidified. The water chemistry of acid sensitive lakes in the UK is influenced to a varying extent by organic acids, principally derived from peat soils which often dominate upland catchments in acid-sensitive regions. The contribution of organic acidity is indicated by dissolved organic carbon (DOC) concentration. High DOC lakes in the far northwest of Scotland, where levels of acid deposition are considered to be negligible, may exhibit pH values below 5.5.

Acid Neutralising Capacity (ANC), representing the balance between base cations and acid anions, can be linked to acidification pressure. In the absence of local anthropogenic activity or particularly anomalous geology, ANC of relatively “pristine” sites, such as those referred to above, will rarely be found to be negative, regardless of DOC concentration, but severely acidified sites will often exhibit a surfeit of acid anions over base cations. This is supported by assumptions implicit in the widely used Steady State Water Chemistry Model (SSWC) (Henriksen et al., 1986), which also suggests that the degree to which a site has acidified can be inferred from the contemporary ANC in the context of either current base-cation or acid anion concentration. Hence, for example, sites which currently have only slightly positive ANC are also unlikely to have acidified providing contemporary base cation concentration is very low.

Concerns remain, however, regarding how best ANC should be determined. Evans et al. (2000) demonstrated that calculation of “charge-balance” ANC (ANC_{CB}), according to the conventional approach (i.e. ANC_{CB} = ($[Ca^{2+}]+[Mg^{2+}]+[Na^{+}]+[K^{+}]$) - $[SO_4^{2-}]+[NO_3^{-}]+[Cl^{-}]$), was subject to the compound errors associated with the determination of the seven constituent ions. One alternative approach, often referred to as the Cantrell method is to use the equivalent sum of Gran alkalinity and an estimate of the contribution of organic anions to the ion balance (i.e. $ANC_{Cantrell}$ = Alkalinity + F*DOC). The UK Acid Waters Monitoring Network (AWMN) uses a variant of the above for trend assessments. This takes into account the protonation of soluble monomeric aluminium (i.e. ANC = Alkalinity + F*DOC – $x*Al_{sol\ mon}$). This shows a clearer linear relationship with ANC_{CB} in more acid sites: in contrast Cantrell ANC shows a systematic positive bias for ANC_{CB} <0. The main limitation in application of the AWMN approach is data availability; routine chemical measurements by UK agencies have rarely included estimates of all three of these determinands. For this reason ANC_{CB} is the favoured parameter in this project. The effect of compound random errors should be smaller where annual means are used, rather than raw data.

Relationship between macroinvertebrate communities and acidity parameters
A recent trend assessment of AWMN biological data showed that temporal change in ANC provides the strongest chemical predictor of change in macroinvertebrate communities, both within and between sites (Monteith et al., 2005). This finding would suggest that macroinvertebrates have the potential to infer ANC and hence, when used in conjunction with base cation or acid anion data, acidification pressure.

A relatively small amount of data has been available for tool development until recently. To date we have concentrated on the assessment of data from approximately 40 acid-sensitive lakes, comprising macroinvertebrate kick samples (spring only) and mean water chemistry data (minimum of four seasonal samples encompassing the spring of the year in which biological samples were taken). Further data has become available over the course of 2005.

Canonical Correspondence Analysis (CCA) revealed that the macroinvertebrate assemblages in these lakes show a strong relationship with ANC which was strongly related to the second axis of variation in the species data (Table 1). The first ordination axis is dominated by DOC. The total amount of variance in the macroinvertebrate assemblage which could be explained by ANC was very similar to that which could be explained by pH or other measures of acidity when these determinands are applied as single explanatory variables in CCA. Initial analysis identified certain species which were associated with low pH but not low ANC, reflecting a preference for naturally acid (i.e. high DOC), but not acidified, waters.

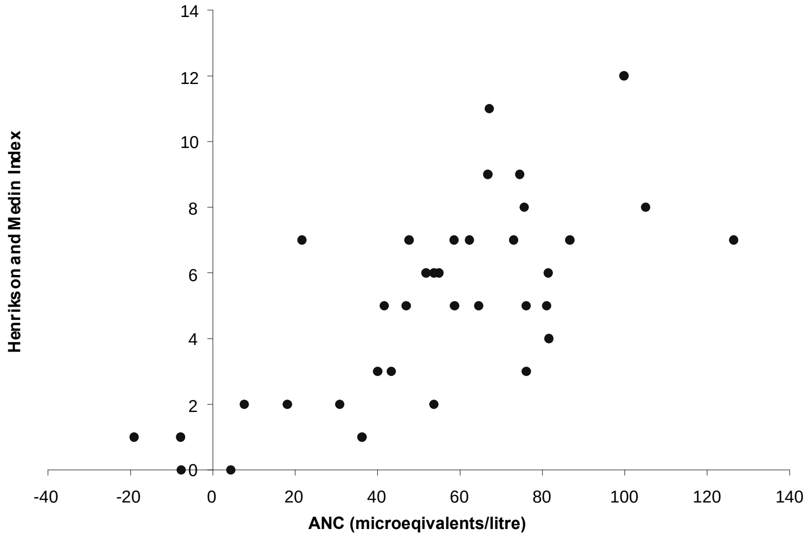
Table 1 *CCA biplot scores for chemical variables and ordination axes for macroinvertebrate assemblages for 35 acid-sensitive UK lakes*

	CCA1	CCA2	CCA3	CCA4
H^+	0.43	-0.68	-0.05	-0.37
alkalinity	-0.09	0.67	0.17	0.25
conductivity	0.19	0.31	0.05	-0.19
calcium	0.27	0.71	-0.05	0.01
magnesium	0.03	0.46	0.07	-0.22
potassium	-0.03	0.45	0.14	-0.19
nitrate	0.02	-0.66	-0.46	0.36
sulphate	0.19	-0.03	-0.33	-0.13
labile aluminium	0.48	-0.76	0.00	-0.18
dissolved organic carbon	0.70	0.38	-0.02	-0.23
ANC_{CB}	-0.05	0.86	0.13	-0.19

We also investigated the relationship between existing macroinvertebrate classifications and chemical parameters. The most robust of these was found to be the Swedish Henrikson and Medin Index (Henrikson and Medin, 1986), a multi-metric index which, with its emphasis on the presence/absence of sensitive and non-sensitive groups, is clearly compatible with WFD

"Normative Definitions". This Index appeared to be well suited for application to the UK's peat influenced waters and showed a particularly strong correlation with ANC (Figure 1).

Figure 1 *Relationship between the Henrikson and Medin Index and Acid Neutralising Capacity for 35 acid-sensitive UK lakes*



Conclusions

Our initial results suggest that the macroinvertebrate assemblage of lakes may have the potential to be used to infer ANC, and hence in the context of the base cation or acid anion concentration, be used to determine the likely extent of acidification at a site. It is also possible that existing acidification metrics may be suitable for this task. However, analyses to date are limited by the amount of data of sufficiently high quality. Considerably more data is now available and analyses are to be repeated shortly. In addition to the analysis applied to date we intend to investigate the use Regression Trees and Bayesian Belief Networks to determine the most powerful technique with which we can link the macroinvertebrate communities to ANC and possibly other physico-chemical metrics of acidification pressure. The outcome will determine the eventual approach to tool development.

Acknowledgements

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15. Implementation of Water Framework Directive: Surveillance monitoring of acidified waters

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Abstract

During the implementation of Water Framework Directive (WFD) of the European Union an important and urgent task is to develop a three-level monitoring system (surveillance, investigative and operational). The monitoring system should meet at least two conditions: determination of the characteristic status of the water body and statistical evaluation of the confidence of appropriate classification. Moreover, the operation of the monitoring system should not be very expensive. The aim of this study is to examine how the surveillance monitoring can be developed in small creek and related drinking water reservoir exposed to acidification. Physico-chemical and chemical water quality components (among others: pH, conductivity, alkalinity, total hardness, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, NO_3^-), were monitored during one year period on the Hungarian ICP area (Nagy Creek including its tributaries and Csórrét reservoir). Detailed survey of spatial and temporal changes in the concentrations of these components was carried out. The results showed significant changes, even in such a small water course like Nagy Creek. The horizontal changes in the reservoir were not significant, but the vertical ones were large in the stratified period. It clearly turned out that the minimum frequency of sampling suggested by the WFD (three months/year) is certainly too rare to meet the conditions of characterization and classification requirements of WFD due to the spatial and temporal changes. The necessary number of samples significantly depends on measured components. If 10 % relative error of estimation is allowed, one sample/water body is enough in case of some components, but in other cases 6-8 samples should be taken spatially in a water body for getting the characteristic status. Horizontally the reservoir should be monitored once in space, but vertically at five depths because of the stratification. To follow the temporal changes, the minimum acceptable sampling frequency is biweekly for the components having higher variations. The findings mean significant increases in monitoring costs comparing the present status due to the implementation of WFD. These costs can be decreased somewhat by sophisticated monitoring procedures (for example, only the highly variable components are measured frequently, or combined water samples are taken).

INTRODUCTION

The implementation of Water Framework Directive of the European Union (WFD) is one of the largest challenges in water management of the European Union. It is an ongoing and long term task and the closest deadline is the end of 2006 when the three-level monitoring system (surveillance, investigative and operational) should be put into operation in every member states. The surveillance monitoring serves the control of ecological status of the waters and contains biological, hydro-morphological, physico-chemical and chemical groups of components (reference indicators). This monitoring should be repeated in every water bodies by six-year intervals (WFD 2000).

Acidification is one of the largest environmental problems in many countries, where the buffer capacity of waters is low. WFD prescribes the monitoring and control of acidification, but leaves the selection of appropriate reference indicators open for the member states. WFD also describe a minimum frequency of sampling for different groups of reference indicators (seasonally for physico-chemical components). Some aspects of monitoring of acidified waters were discussed in SCHAMBURG (2005) and WORTELBOER (2005).

There are two important conditions of monitoring in WFD: description of characteristic status in water body and determination of the confidence of the classification. Characteristic status means that the representative ecological status of the water bodies should be determined by the monitoring in time and space. Confidence of the classification means that the exact statistical analysis should be made in order to determine the probability of the misclassification of the ecological status. This is an important issue, because the misclassification may cause measures which are not necessary, or, in other hand may cause lack of measures. The costs related to this error can be high. The classification of ecological status is based on Environmental Quality Ratios (EQR values), which can be calculated according to Fig. 1. This value can change between 0 and 1, and five-class classification system should be used within this range (WFD 2000). It means that the maximum acceptable relative error of estimation necessary to minimize and it should not be higher than 10 % in case of each reference indicators.

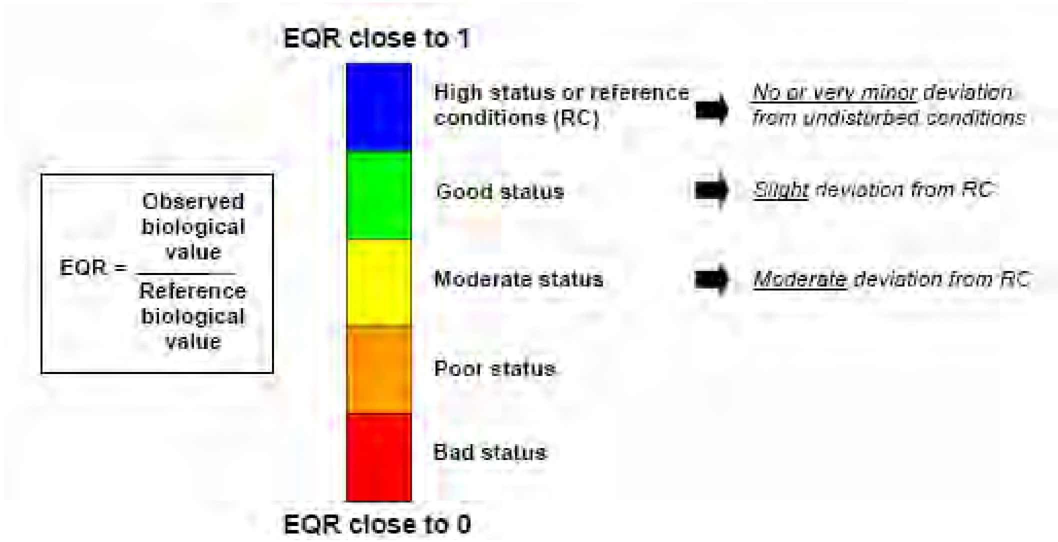

Figure 1 *Classification scheme according to WFD (WFD 2000)*

The aim of this study is to examine how it is possible to meet the monitoring requirements of WFD concerning the physico-chemical components of acidification in Csórrét reservoir and its inflowing waters, with special emphasis on the necessary sampling frequency in time and space.

MATERIALS AND METHODS

Site

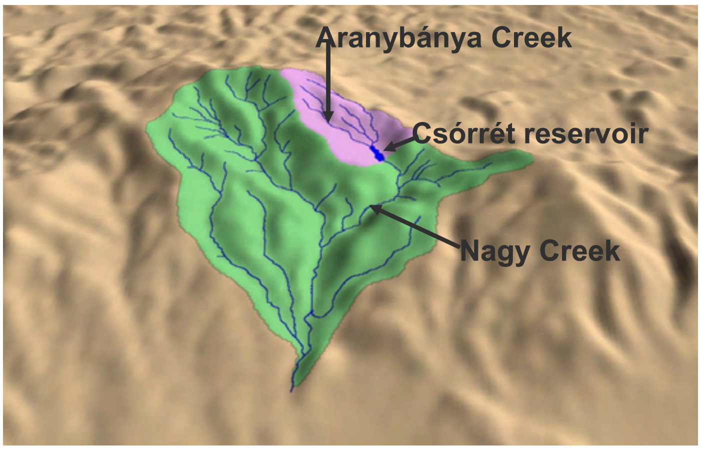

Fig. 2 *Watershed of Nagy Creek including Csórrét reservoir*

The Csórrét reservoir is the only ICP site in Hungary, concerning the International Cooperative Program on assessment and Monitoring of Acidification of Rivers and Lakes. The Csórrét reservoir was built in 1973 to supply drinking water to the nearby settlements. The volume of the reservoir is 1 million m^3, its deepest point is 20 m. There is continuous water withdrawal from the reservoir at an average rate of 1200 m^3/day LÁSZLÓ ET AL. (2004). Five creeks flow into the reservoir, but only three of them contribute 80% of the total flow (Fig. 2). Total discharge to the reservoir is 1.8-2.0 million m^3, thus the theoretical retention time is half a year. Its total catchment area is 8.4 km^2. The only human activity in the area is forest management. 95-98% of the area is covered with deciduous and coniferous forest in 1:1 ratio (LÁSZLÓ ET AL. 2005, LICSKÓ ET AL 2003).

Sampling and measuring

Our one-year detailed monitoring program was launched in May, 2004. Water samples were collected from the reservoir and the 5 creeks monthly. A detailed survey of spatial changes was made in Aranybánya Creek (the largest tributary of the reservoir) and in the reservoir. Hydrolab Surveyor 4 equipment was used to monitor 8 water quality components including pH and conductivity at each point. The creek and the reservoir were sampled at many points (Aranybánya Creek: 13 points, reservoir: 15 points, Nagy Creek: 4 points, see Fig. 3). Water samples were taken for further investigations. Beside the above mentioned two important components of acidification, alkalinity, total hardness, concentrations of certain ions (nitrate, sulfate, calcium, magnesium) were determined among other components. This spatial survey was made under average flow conditions.

Statistical analysis of the data was made using Excel programs (average, geometric mean, standard error, relative error, confidence interval, etc.). The average value represented the characteristic status of the water.

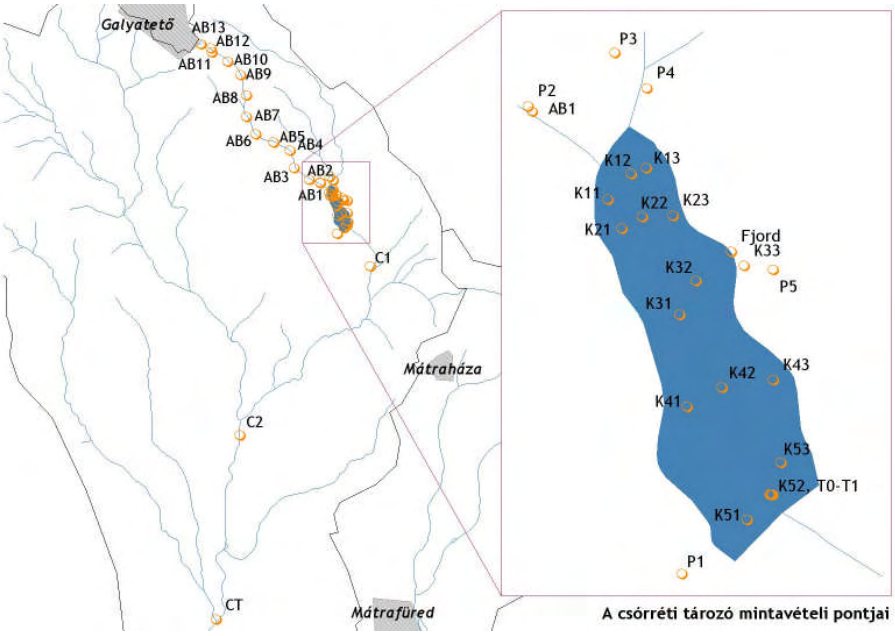

***Figure 3** Sampling points at Nagy Creek and Csórrét reservoir*

RESULTS AND DISCUSSION

Spatial changes

The spatial changes were significant in case most of the measured quality components in Aranybánya Creek. Fig. 4 shows the longitudinal changes in pH values. It is shown that the lowest pH occurred at the origin of the Creek and it increased toward the outlet of the reservoir. This increase is probably due to algal activity. Because of the stratification, the pH in the bottom layer was significantly lower than in the upper layer, and it was similar to that of the spring of the creek.

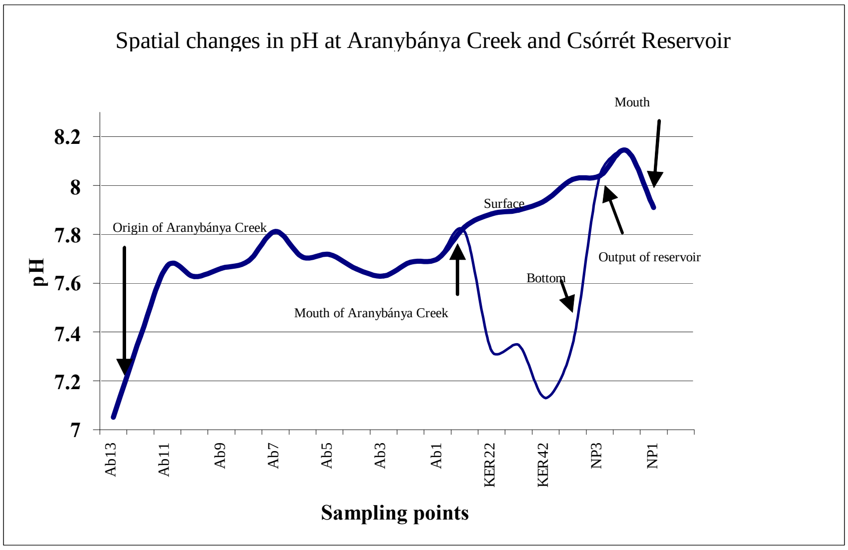

Figure 4 *Changes in pH in Aranybánya Creek and Csórrét reservoir*

In the present monitoring system it is assumed that one sample represents a larger section of surface waters. This assumption was tested in our system.

It was found that the variation of the values was large for many components along the longitudinal section. Due to high spatial variation in water quality, the "one water body – one sample" approach may be not true. It was analyzed that – accepting the 10 % relative error – which components could be measured once in a water body in order to get the average status with a 90 % of confidence (Fig. 5). It was found that the pH and concentration of calcium and sulfate can be characterized by one sample per water body. The other components should be measured more frequently in space. (It should be mentioned that the pH has a log scale!) The next question is: How many samples should we take in a water body for the investigated components? Fig. 6 shows the required number of sample at each component.

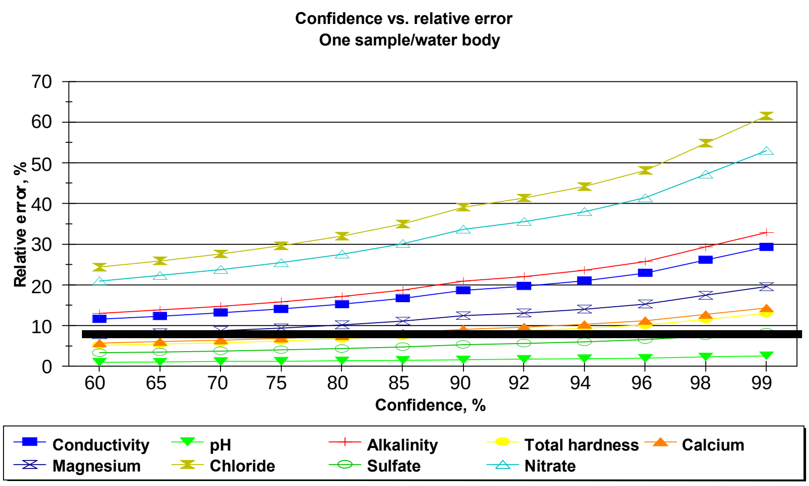

Figure 5 *Values of relative errors if one sample is taken in water body (Aranybánya Creek)*

In order to get a good average picture of the Aranybánya Creek, only one sample should be collected at the mouth section of the creek for pH, calcium and sulfate. For alkalinity and conductivity we have to sample at 5 points. For chloride even more samples we should take (at least 9). It should be mentioned that due to the much less horizontal spatial changes, one sample per occasion is appropriate to describe the status of the water of the Csórrét reservoir with an error less that 10 % at each measured components. But the vertical changes are high when the reservoir is stratified. The statistical analysis of the results showed that the reservoir should be sampled at 5 depths at the water intake tower.

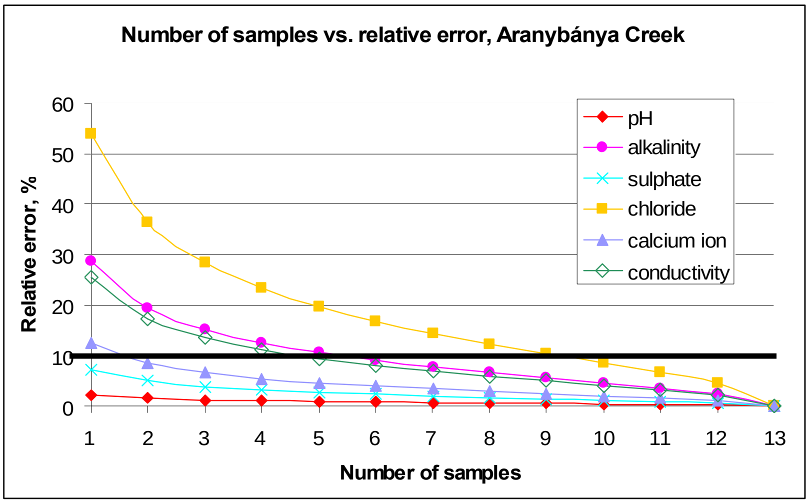

Figure 6 *Minimum number of samples representing water body (Aranybánya Creek)*

Temporal changes

The minimum frequency in time was monthly at Nagy Creek – Csórrét reservoir system. It was too rare to analyze the required number of samples statistically in time. That is why we were looking for another data base and the data of River Zala were selected for such analysis. This river situating in western part of Hungary and it is the largest tributary of Lake Balaton (average flow: 9 m^3/s, at the mouth of the river). This river has a detailed data base from the past.

Weakly data were used for the analysis (2004). The results are shown in Fig 7. It can be concluded that the seasonal sampling frequency for the components is not enough in order to characterize the yearly average status for some of the components. Only the pH and the conductivity remained within the 10 % range of error. Monthly sampling is necessary for nitrite ion and biweekly for nitrate ion. If we take into account the other components not related to acidification (and not indicated in Fig. 7) we ca conclude that the biweekly sampling is the only acceptable frequency to meet the requirement of WFD. The usual sampling frequency in Hungarian rivers varies between 6-52/year. The monthly sampling is representative. It can be expected that monitoring needs following the temporal changes will increase in the future due to implementation of WFD.

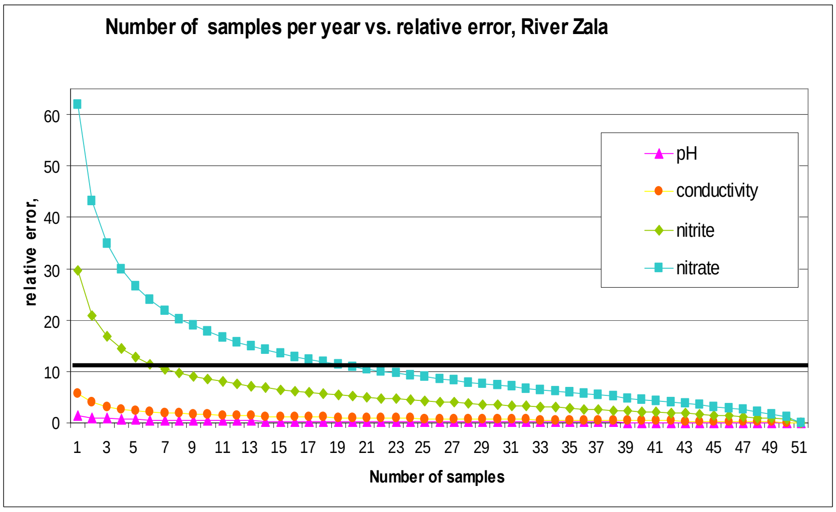

Figure 7 *Required number of samples in time (data from River Zala)*

Cost implications

The designation of the Hungarian rivers and lakes is done (KVVM, 2005). The number of Hungarian river water bodies is around 1100 while we have approximately 100 lake water bodies.

The present national water quality monitoring system consists of 150 points where mostly physical and chemical measurements are made. Neither of the biological characteristics suggested by WFD is measured yet. If we analyze the future changes in this system we can conclude that:

- The number of sampling points will increase significantly. We will have to investigate 200 water bodies yearly (1200 water bodies in six-year intervals).
- It turned out from our analysis that one sampling point per water body is not appropriate for most of the components to characterize the average status of the water body. Consequently there will be dramatic increase in monitoring needs and their costs too.
- It is necessary to extend our monitoring to groups of living organisms mentioned in WFD (phytoplankton, epiphytes, macrophytes, macro invertebrates and fish). This will further increase the operational costs of monitoring.
- Monitoring of dangerous organic micro pollutants will be a challenge in the future due to the lack of methods and practice for many materials.

All in all, the monitoring needs and costs will increase dramatically due to the implementation of WFD from the beginning of 2007. The question is: How these costs could be decreased? If we go back to our components, the following ways are seen:

- We do not analyze all components in all samples. The components with slight variation are measured rarely, but the components having large variation are measured more frequently. In this case we can save approximately 30-40 % of the monitoring costs.
- We collect composite sample from a water body and this sample is analyzed. This means that only one sample per water body is analyzed. Significant savings can be realized in this way in laboratory costs, however, the costs of sampling increase somewhat.
- We apply the possibility for grouping the water bodies indicated in WFD (WFD 2000, Guidance on Monitoring 2002). That means that the water bodies having the same type and similar human impacts are grouped and only one of them is monitored.

CONCLUSIONS

The following conclusions can be drawn from the results of this study:

- The results showed significant spatial and temporal changes in physico-chemical status of a water body, even in such a small water course. This statement is true for the components representing acidification also.
- The horizontal water quality changes in the Csórrét reservoir were not significant, but the vertical ones were large in the stratified period.
- It clearly turned out that due to spatial and temporal changes, the minimum frequency of sampling suggested by the WFD (three months/year) is certainly too rare to meet the conditions of characterization and classification requirements of WFD in case of many components.
- The necessary number of samples in time and space significantly depends on measured components. If 10 % relative error of estimation is accepted, in case of some components one sample/water body is enough, but in other cases 6-8 samples should be taken spatially in order to get the characteristic status. The reservoir should be monitored once in horizontal way, but at five depths because of the vertical stratification.
- In order to follow the temporal changes, the minimum acceptable sampling frequency is biweekly for the components having higher variations.
- The results show significant increases in costs of surveillance monitoring comparing to the present monitoring practice. These costs can be decreased somewhat by sophisticated monitoring procedure (for example, only the highly variable components are measured frequently, or composite water samples are taken).

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