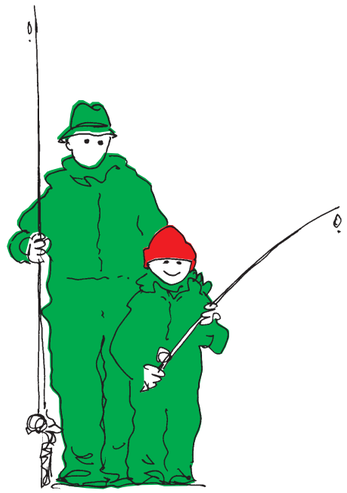
Convention on Long-range Transboundary Air Pollution

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

ICP-WATERS REPORT 80/2005

Proceedings of the 20th meeting of the ICP Waters Programme Task Force in Falun, Sweden

October 18-20, 2004



NIVA Norwegian Institute for Water Research

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Norwegian Institute for Water Research
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Abstract
Proceedings of presentations of national activities to the 20th meeting of the ICP Waters Programme Task Force in Falun, Sweden, October 18-20, 2004.

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 20th meeting of the ICP Waters Programme Task Force in Falun, Sweden, October 18-20, 2004

Prepared the ICP Waters Programme Centre
Norwegian Institute for Water Research
Oslo, month 2005

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 also 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, 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 and representative of low acid neutralising capacity (ANC) and low critical load levels of the distributions for all the 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 20th Task Force meeting of the ICP Waters programme, held in Falun, Sweden, October 18-20, 2004.

Oslo, May 2005

Brit Lisa Skjelkvåle
Programme centre

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10. HCB, PCB's and DDT's concentrations in fish muscle from 2 alpine lakes (Oncorhynchus mykiss) and 4 alpine rivers (Salmo trutta fario) in the Canton of Ticino, Switzerland **55**

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1. Overview of the contributions

The national contributions on ongoing activities presented to the ICP Waters Task Force meeting October 2004 are thematically grouped:

i. Water chemistry – trends and status of S and N
ii. Biological response
iii. Dynamic modelling
iv. Heavy metals and POPs
v. Alkalinity-workshop
vi. ICP Waters and the EU Water Framework Directive (WFD)

The presentations on humus concentrations in Nordic waters, N concentrations in the Csórrét Reservoir, long-term monitoring of the Bohemian Forest lakes, monitoring activities on Slovenian mountain lakes and on recovery from acidification in acidified lakes in Finland (Chaper 2 to 7) were presented under 'Water chemistry – trends and status of S and N'.

The theme 'Dynamic modelling' was addressed by the presentations on modelling of lake chemistry in Polish mountains using Magic (Chapter 8) and on dynamic biological response models (Chapter 9). This presentation adresses 'Bilogical response'.

'Heavy metals and POPs' was addressed in two presentations, i.e. on HCB, PCB’s and DDT’s concentrations in fish muscle in Swiss lakes (Chapter 10) and on trace metal measurements in Italy ICP-Waters sites (Chapter 11).

The presentations in the workshop on alkalinity measurements are summarized in Chapter 12, and one of the presentations in the workshop that addressed topics in addition to alkalinity is shown in Chapter 13.

The relation between ICP Waters and the EU Water Framework Directive were addressed in one presentation (Chapter 14 and 15).

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

2. Long-term variations in the humus concentrations in Nordic waters

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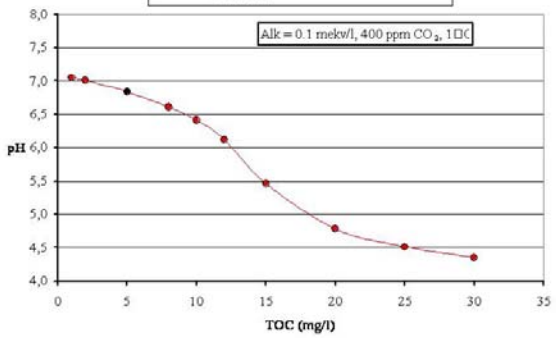
Swedish University of Agricultural Sciences,
Department of Environmental Assessment,
P.O. Box 7050, SE-750 05 Uppsala, Sweden

Content

- Relation between humus and acidity
- Spatial variation
- Temporal variation
- Process knowledge
- Land use effects
- Conclusions

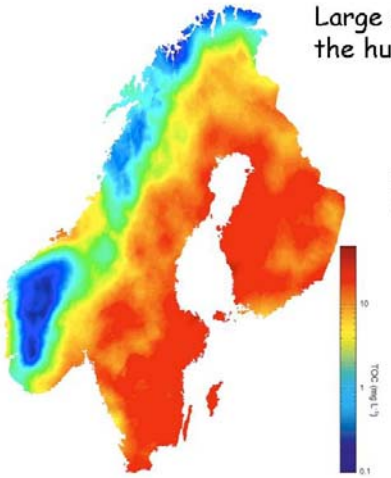
Humus increases ANC, but lower pH

ANC_{CBALK} = Alk + ß*TOC



Löfgren & Laudon, 2004

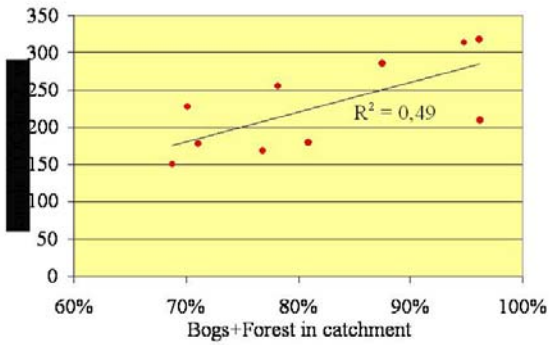
Large spatial variation in the humus concentration (TOC)



Increased TOC-concentrations during the 1990's

Löfgren et al. 2003

Large share of forest and peat land increases the humus leakage



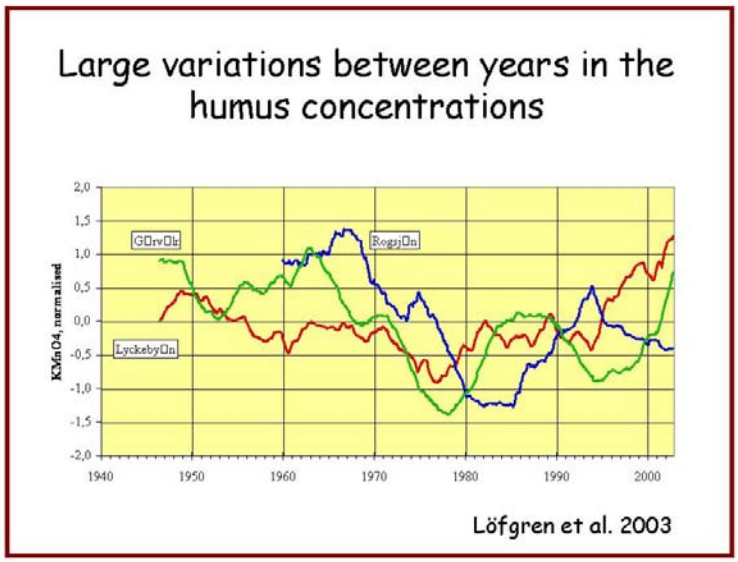
J.V. Eriksson, 1929

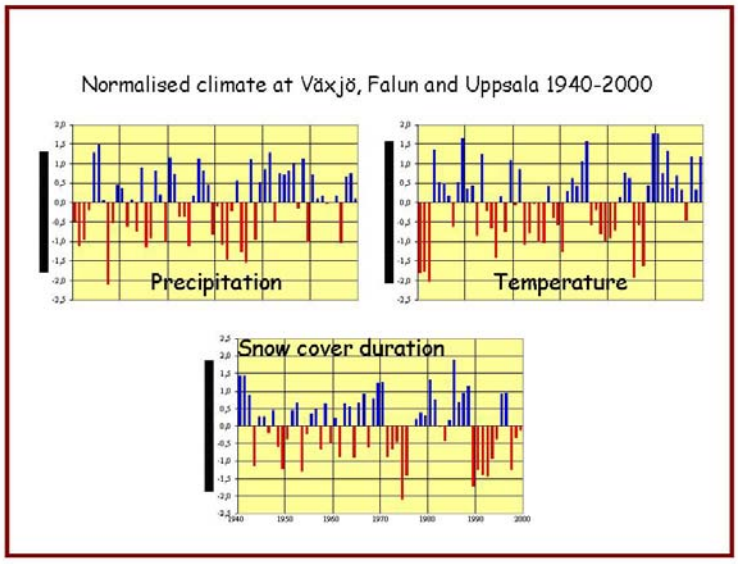
"Anyone who just briefly has given our streams in forested areas some attention, most certainly has observed the following facts. The smallest streams are often dark brown, especially if they are discharging from mires. When they enter into a larger stream, you observe that the water is lighter in color. Even though most inlet streams to a lake have dark brown water, the outlet exhibits a less colored water, at least not dark brown, if the lake has a volume of any significance".

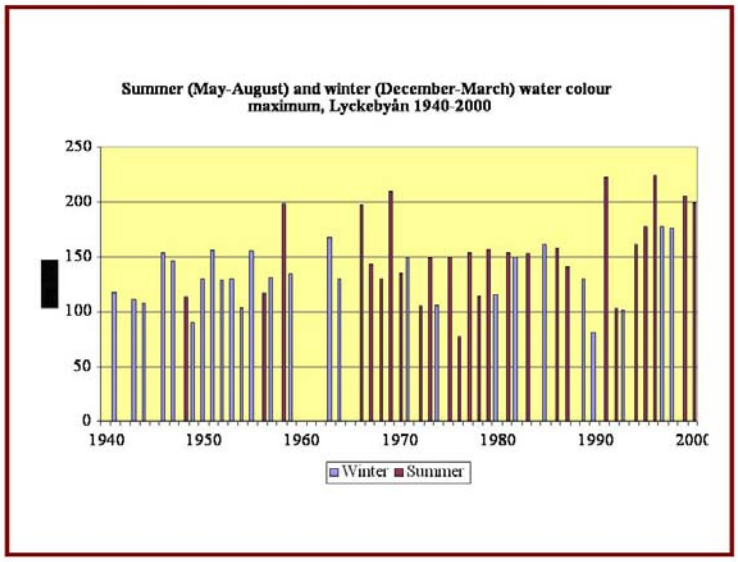
River	Time period	Mean $KMnO_4$ (mg/l)	Sdev $KMnO_4$ (mg/l)	No of obs
R. Domnsln	1916-1925	61.3	16.2	51
	1966-2001	71.4	31.2	375
R. Klarälven	1916-1923	23.4	7.7	37
	1965-2000	28.4	9.2	426
R. Ljusnan	1916-1923	30.3	7.5	37
	1969-2001	36.0	13.8	356
R. Ljungan	1916-1923	23.6	4.3	36
	1969-2001	25.6	5.1	389
R. Indalsälven	1916-1923	19.9	2.4	35
	1969-2001	18.1	4.5	364
R. Skellefteälven	1916-1923	16.2	10.5	31
	1969-2001	17.3	8.3	382
R. Piteälven	1916-1923	13.2	4.6	34
	1967-2001	14.6	7.9	412
R. Abiskojokk	1919-1923	6.2	2.9	19
	1982-2000	5.2	5.1	226

Three examples demonstrating the importance of the water system characters for the humus concentration levels

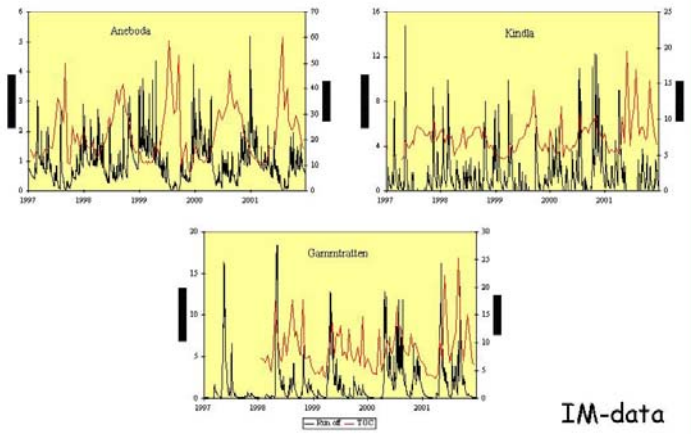
Water system	Specific run-off ($dm^3 km^{-2} s^{-1}$)	Hydraulic retention time (year)	Share of forest & peat land	Share of lake area	Water colour (mg $Pt l^{-1}$)	$KMnO_4$ (mg l^{-1})
R. Lyckebyån	7.6	<0.01	79%	4%	103	56
L. Görväln	7.2	0.6	70%	11%	23	24
L. Rogsjön	9.1	5.6	84%	14%	13	16


Large variations between years in the humus concentrations
KMnO4, normalised
2,0
1,5
1,0
0,5
0,0
-0,5
-1,0
-1,5
-2,0
1940
1950
1960
1970
1980
1990
2000
Löfgren et al. 2003

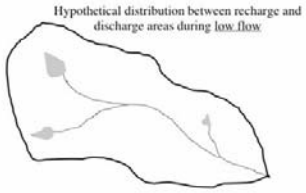

Normalised climate at Växjö, Falun and Uppsala 1940-2000
Precipitation
Temperature
Snow cover duration


Summer (May-August) and winter (December-March) water colour maximum, Lyckebyån 1940-2000
250
200
150
100
50
0
1940
1950
1960
1970
1980
1990
Winter
Summer

Large seasonal variations in the humus concentrations in small brooks

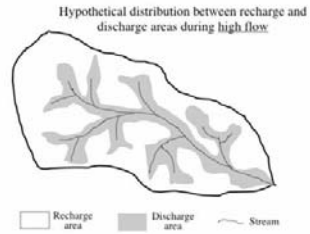


IM-data



Low run-off:

- Wetlands important humus sources
- Often peat

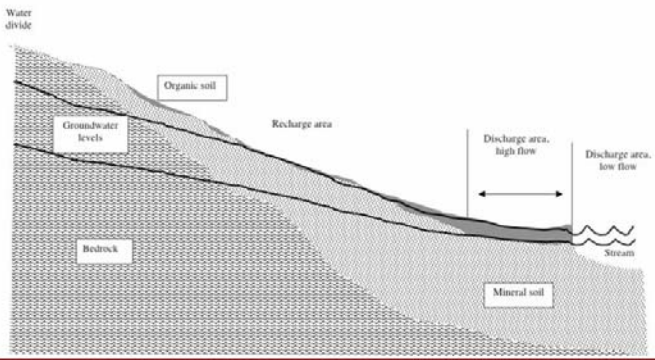


High run-off:

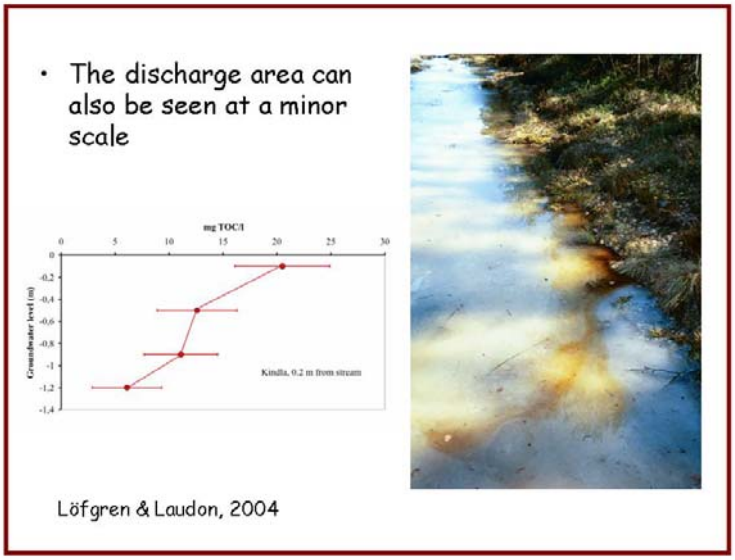
- Riparian zones important
- Peat or till?

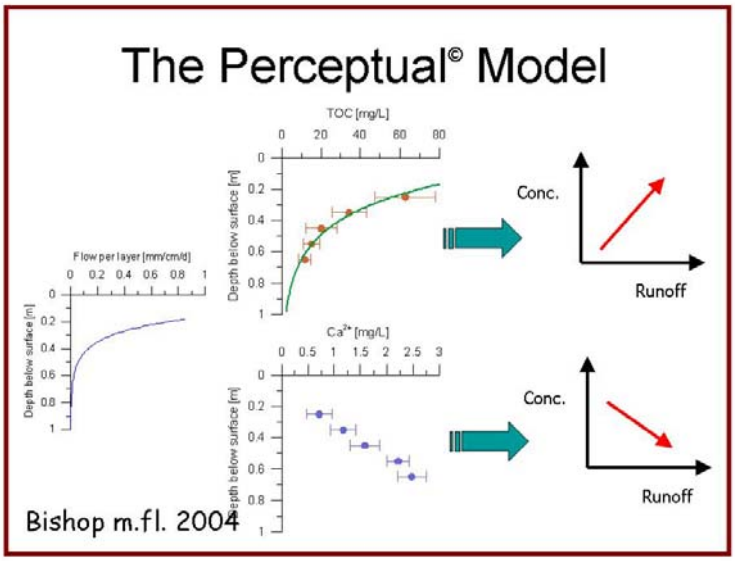
Discharge areas important for the humus leakage in forested areas

Hypothetical slope in a drainage basin

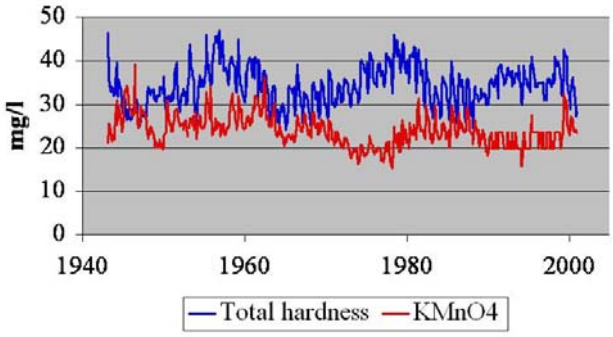


The discharge area can be visible in the nature

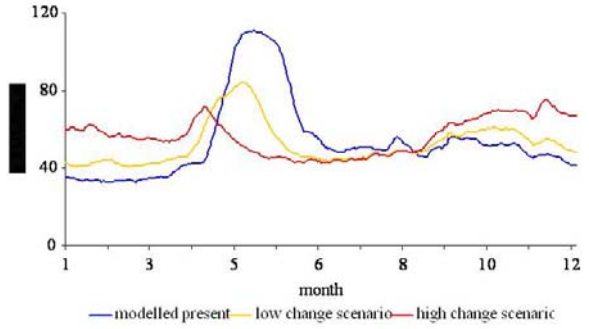

• The discharge area can also be seen at a minor scale
mg TOC/l
Kindla, 0.2 m from stream
Löfgren & Laudon, 2004


The Perceptual© Model
TOC [mg/L]
Depth below surface [m]
Conc.
Runoff
Flow per layer [mm/cm/d]
Ca2+ [mg/L]
Bishop m.fl. 2004

Humus & total hardness, L. Görväln



What will the effects be of a future climate change?

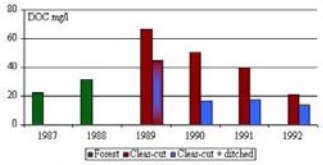


Forsius (2002)

Land use changes can theoretically increase the humus leakage from soils if there is:

1. an increased net production of water soluble organic matter in the terrestrial system and/or
2. the vertical and lateral water flux is changed, favoring the transport of humus in the soil and out to the surface water.

The scientific knowledge about forestry measure effects on humus leakage is low!



Löfgren & Lundin, 2003

Some land use factors that might have influenced the C-pools in soils:

+ Reduced natural fires and manmade burning
+ Reduced grazing and trampling by cattle
+ Extensive reforestation of arable land and heath land
+ Increased forest production
+ A shift towards more conifers especially Norway spruce
− Extensive dredging (into the mineral soil) of peat land and moist forest soils
+ Overgrowth of old ditches by mosses e.g. *Sphagnum* spp.
? .....

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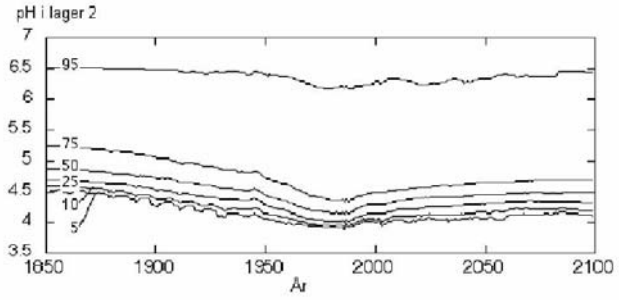
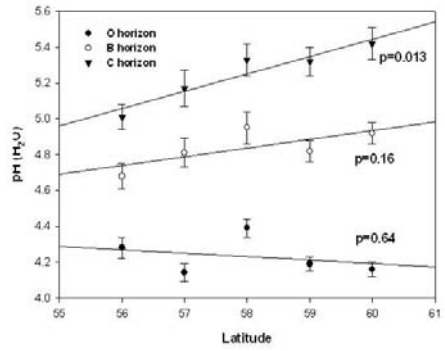
? .....

Potential effects by acidification and recovery on the humus leakage

- **The pH-buffering role of the organic acids of DOM**
  Changed pH leads to changed dissociation of organic acids and thereby changed solubility of the weakest acids.
- **The pH and ionic strength dependant solubility of essential complexing cations (e.g. Al^{n+}, Fe^{n+} and Ca^{2+}).**
  Changed pH leads to changed cation concentrations, changing the amount of metal-humates, leading to changed prerequisites for DOM-precipitation.



Percentiles on the pH-change between 1860-2100 in the upper part of the mineral soil (SAFE-simulations, n=664, Swedish forest soil survey, Munthe et al. 2002)



pH_{H2O} in the O, B och C horizons as a function of latitude. Karltun et al., 2002

Conclusions I

1. No dramatic changes have occurred during the last century in central and northern Sweden with regards to the humus levels in boreal and alpine rivers. In southern Sweden, the concentrations might have increased 5-10 mg $KMnO_4$/l.
2. The long-term (decade) humus dynamic in a single watercourse is mainly determined by weather variations. Precipitation seems to be a key factor, but temperature seems to influence the annual peak values.
3. Delayed humus concentration frequency between watercourses seems to be caused by different water retention times.

Conclusions II

- The extension and localization of organic soils cause differences in seasonal humus dynamics between catchments.
- The groundwater flow paths in the riparian zones are of great importance for the humus concentration variations in small watercourses.

Conclusions III

- Changed land use during the last century, increasing the soil carbon content and/or changing the groundwater flow paths, might have increased the humus leakage to surface waters.
- Climatic variation during the last 60 years overshadow the potential effects of the as yet relatively small soil and surface water acidity changes.
- The surface water acidity is to a large extent influenced by the humus dynamics. Wet years become more acidic compared to dry years.

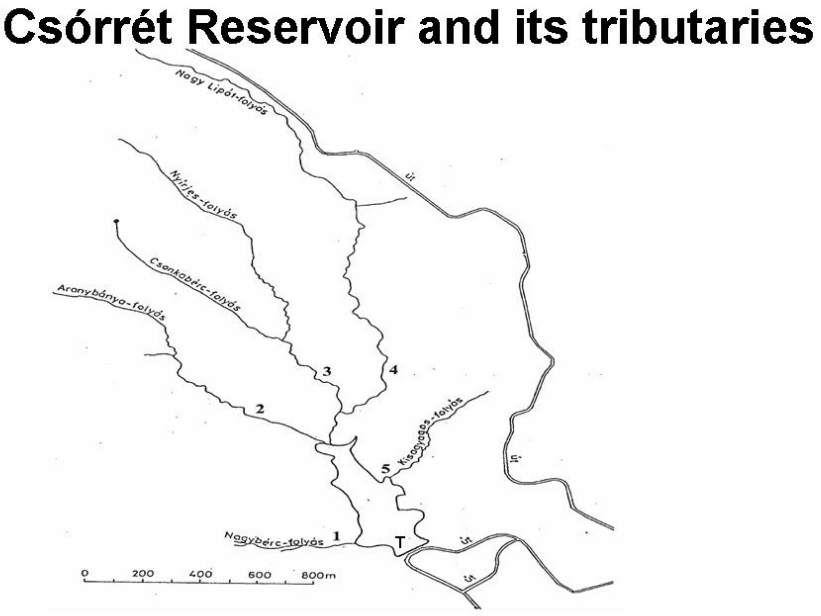
3. Changes in nitrogen compounds in the Csórrét Reservoir and its tributaries

BALÁZS LÁSZLÓ, ANDRÁS OSZTOICS** AND ISTVÁN LICSKÓ***

**Hungarian Academy of Sciences, Water Research Team*
***Budapest University of Technics and Economics, Department of Sanitary and Environmental Engineering*

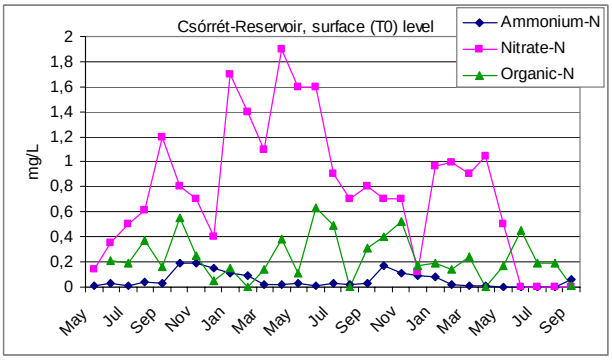
The Csórrét Reservoir

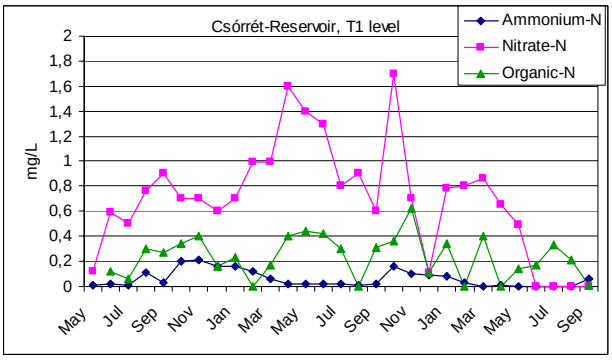
- Volume: appr. one million m3
- Continuous water intake: appr. 2000 m3/d
- Five tributaries (small creeks) in the water catchment area
- Forest with deciduous trees – high leaves loading for the reservoir
- The leaves transport organic nitrogen compounds into the reservoir

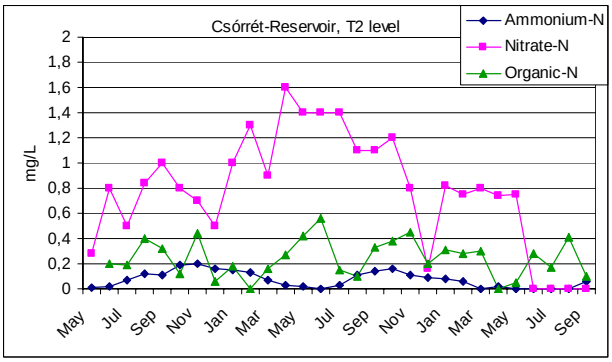


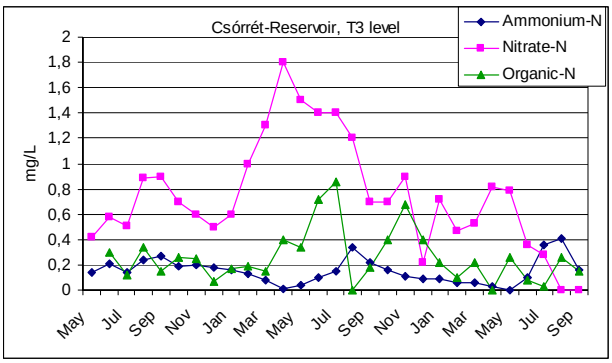
Production and decomposition of nitrogen compounds

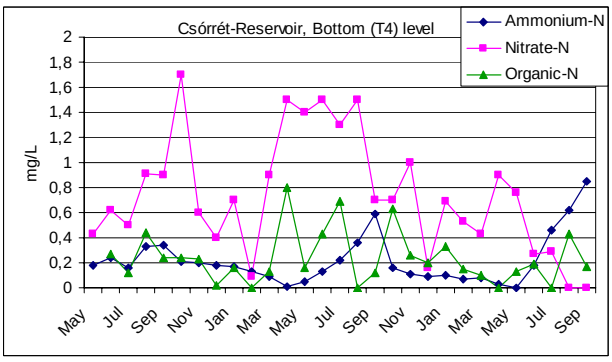
- Nitrogen fixing micro-organisms and alga production
- Result: organic nitrogen compounds appear in the reservoir
- Decomposition and hydrolyses of organic nitrogen compounds provides ammonium ions
- Microbiological oxidation of ammonium ions results in nitrate


Csórrét-Reservoir, surface (T0) level
Ammonium-N
Nitrate-N
Organic-N
mg/L
2
1,8
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
May Jul Sep Nov Jan Mar May Jul Sep Nov Jan Mar May Jul Sep


Csórrét-Reservoir, T1 level
Ammonium-N
Nitrate-N
Organic-N
mg/L
2
1,8
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
May Jul Sep Nov Jan Mar May Jul Sep Nov Jan Mar May Jul Sep


Csórrét-Reservoir, T2 level
Ammonium-N
Nitrate-N
Organic-N
mg/L
2
1,8
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
May Jul Sep Nov Jan Mar May Jul Sep Nov Jan Mar May Jul Sep


Csórrét-Reservoir, T3 level
Ammonium-N
Nitrate-N
Organic-N
mg/L
2
1,8
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
May Jul Sep Nov Jan Mar May Jul Sep Nov Jan Mar May Jul Sep


Csórrét-Reservoir, Bottom (T4) level
Ammonium-N
Nitrate-N
Organic-N
mg/L
2
1,8
1,6
1,4
1,2
1
0,8
0,6
0,4
0,2
0
May Jul Sep Nov Jan Mar May Jul Sep Nov Jan Mar May Jul Sep

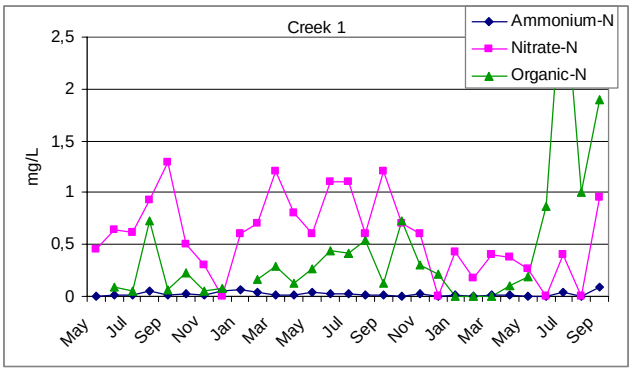
Observations so far

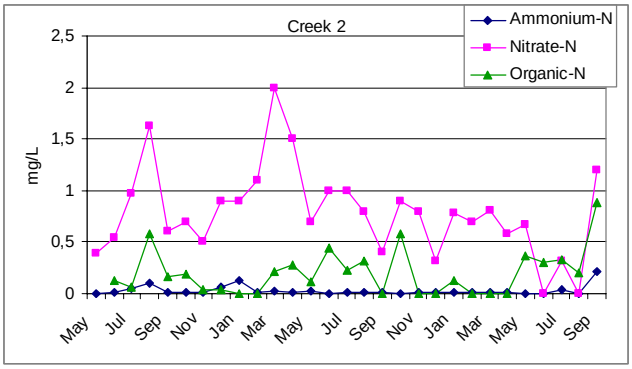
1. Well defined, periodical change in the ammonium ion concentration in all levels
2. The higher ammonium concentrations appears in the lower levels
3. The thermal turn-over plays significant role in the concentration change the different nitrogen compounds
4. The highest nitrate concentrations are probably connected to heavy rain and snow-melting in the upper levels
5. In the bottom level the highest nitrate concentrations appeared after the thermal turn-overs
6. This summer (rainy period) the nitrate concentration significantly decreased in all levels near to zero
7. The organic nitrogen compounds concentration increased when the nitrate started to decrease, except the bottom level
8. No significant connection between organic nitrogen compounds and ammonium ion concentration changes
9. Organic nitrogen compounds concentration is the lowest in cold period in all levels

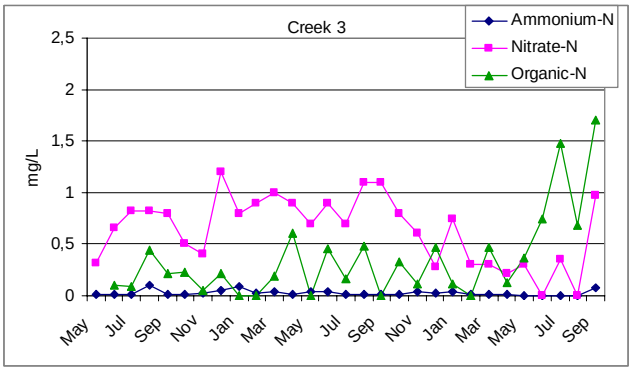
Direct nitrogen compound loading from the water catchment area:

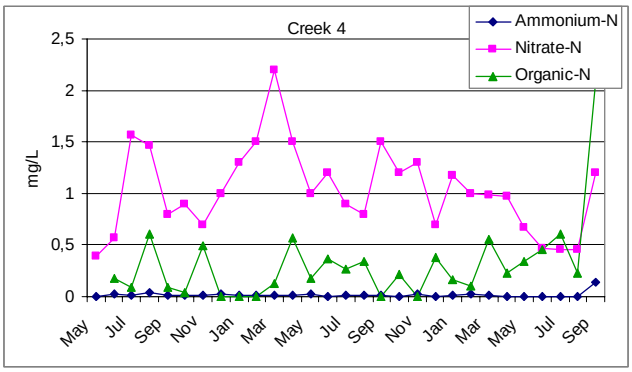
Organic nitrogen
Ammonium ions
Nitrate ions
Concentrations and loadings

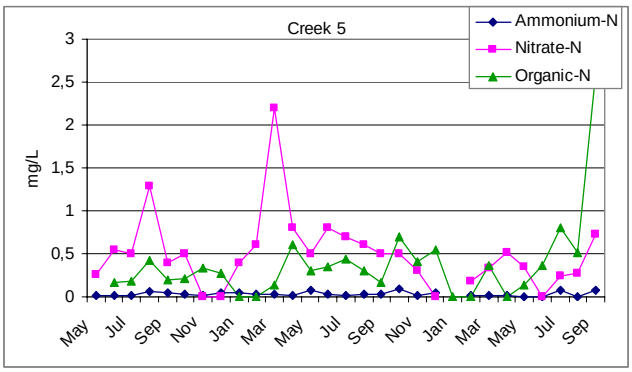
Creek No. 2. provides 40% and the creek No. 3. provides 30% of the total water supply of reservoir – except the direct precipitation











Conclusions

- Low ammonium concentration (near to zero) in all creeks
- The nitrate load of the reservoir, originated from creeks, is the most significant
- The internal nitrogen load is not so important as the external load
- The long rainy period of this year (late spring and summer) decreased the concentration of all nitrogen compounds in the reservoir
- By contrast, in the creeks at the end of summer time, the concentration of nitrogen compounds increased
- The relatively high nitrate content in the reservoir originated rather from the water catchment area and not from the fall-out or the internal loading

4. Long-term monitoring of the Bohemian Forest lakes

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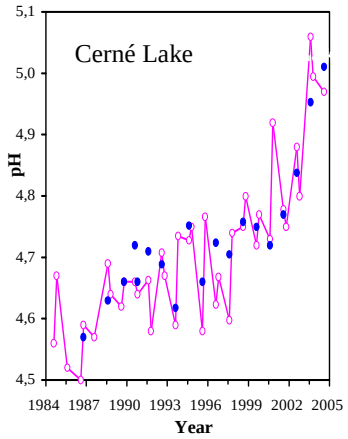
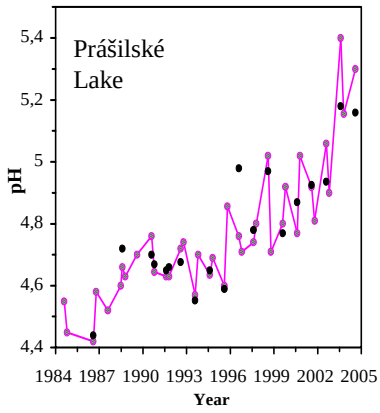
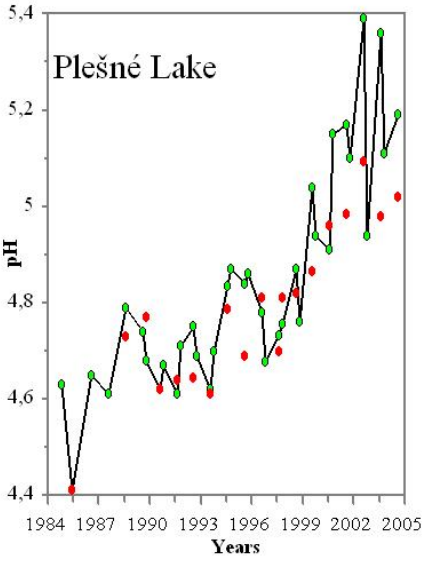
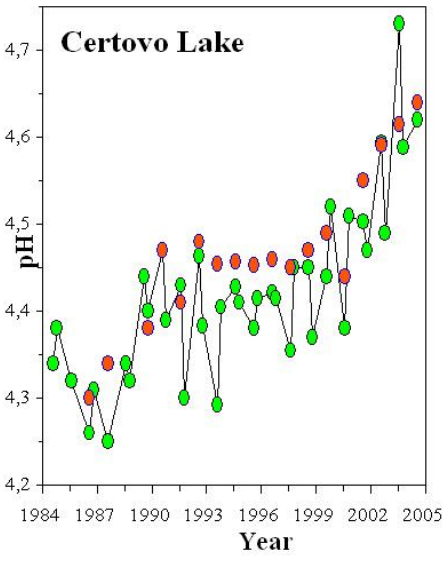
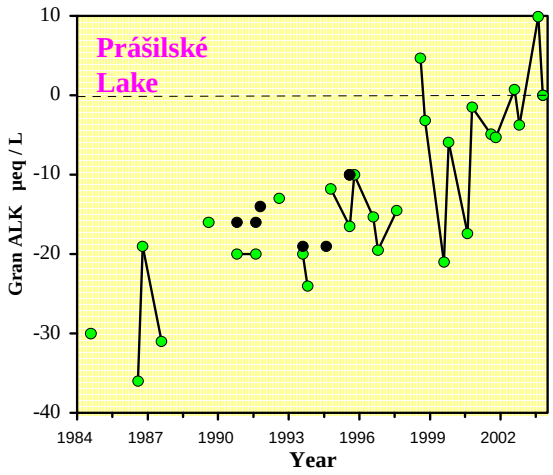
Acidification retreat

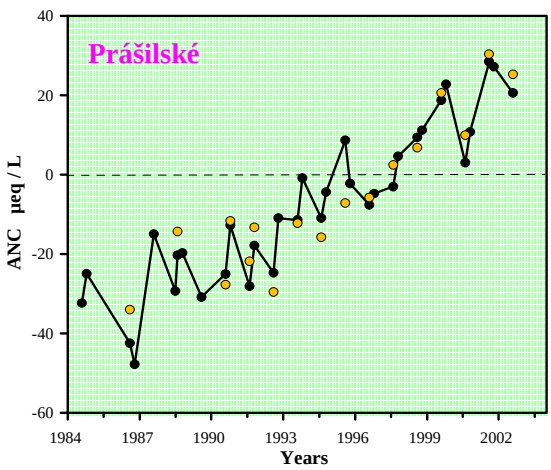


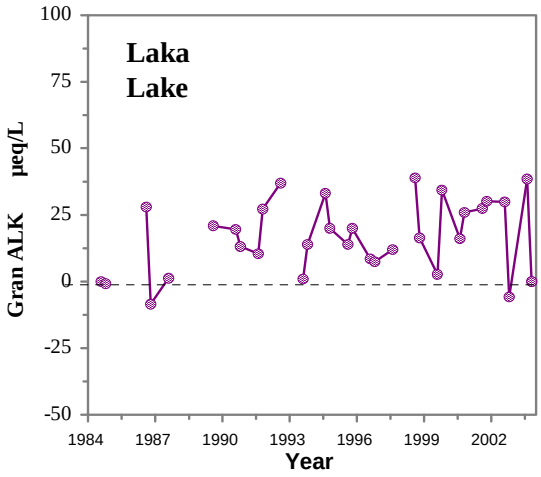


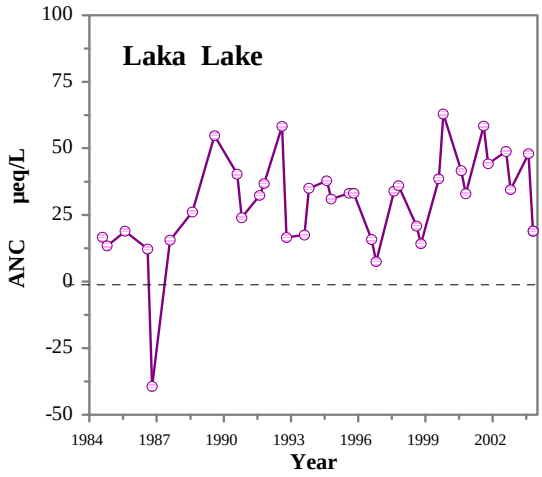




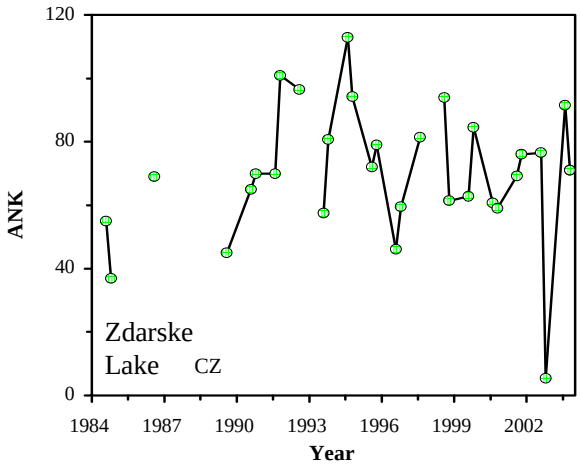


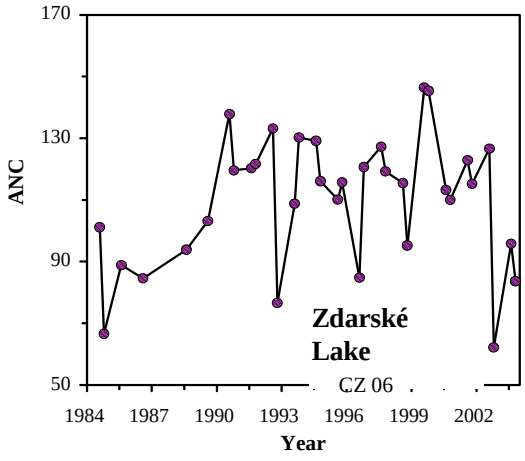




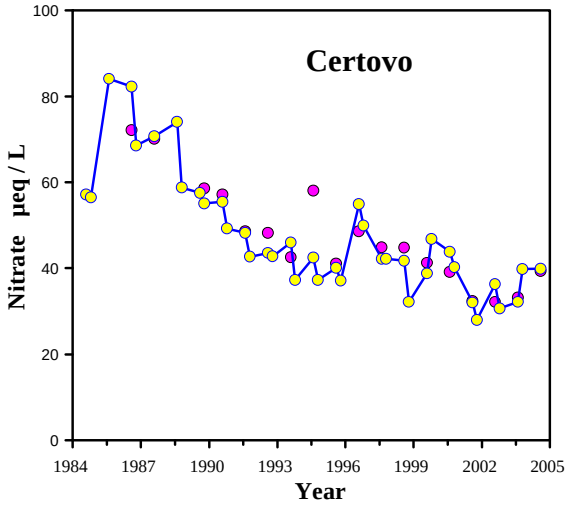


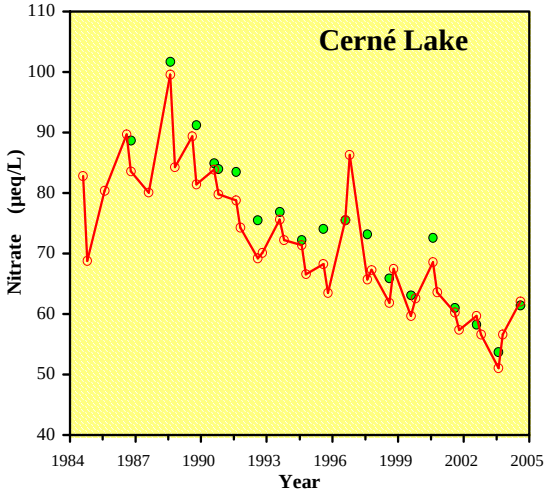
No change in circumneutral lakes



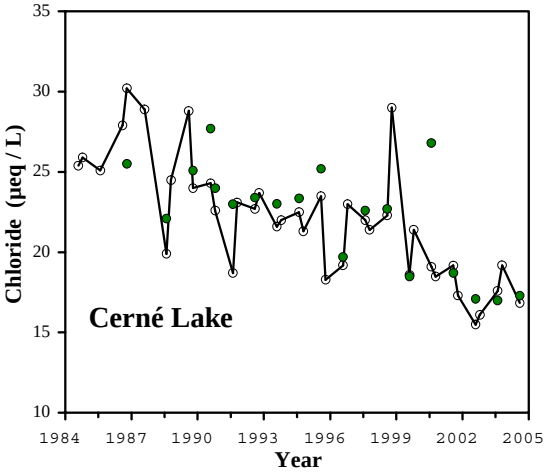


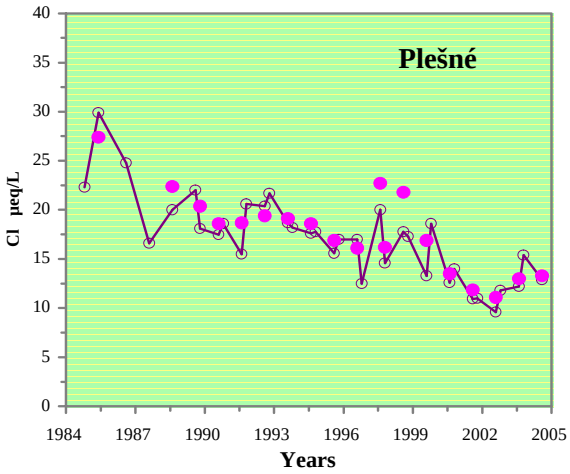
Decrease of nitrate

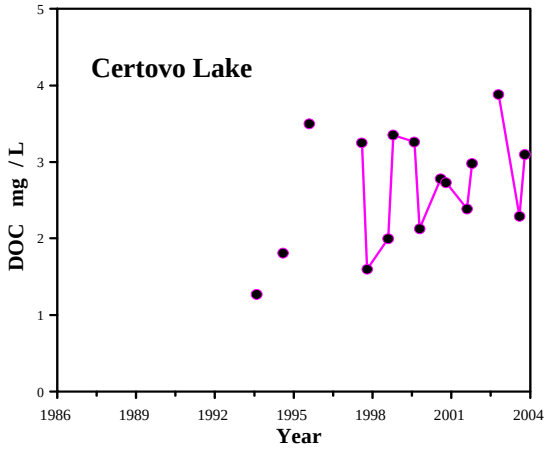


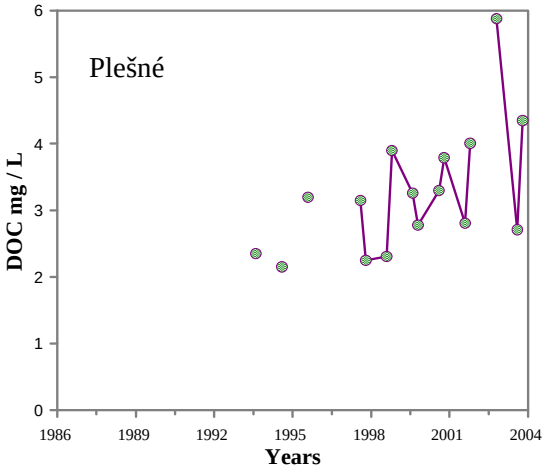


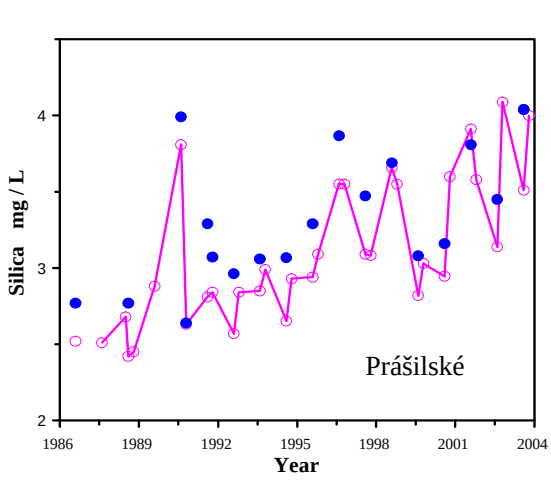
Decrease of chloride

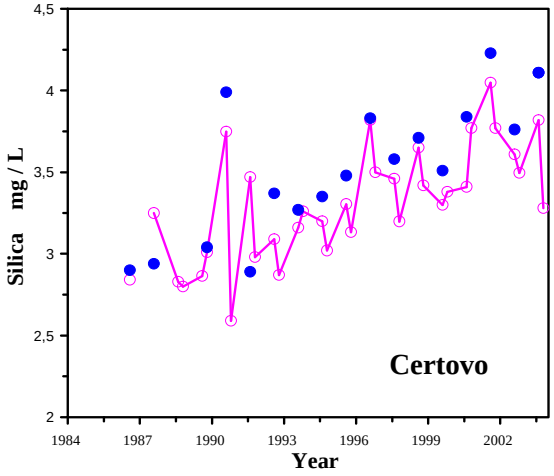


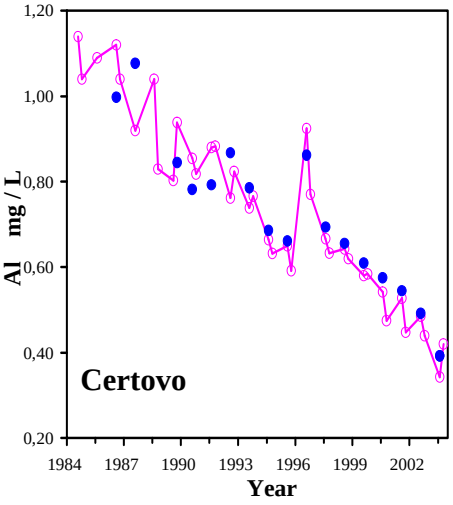


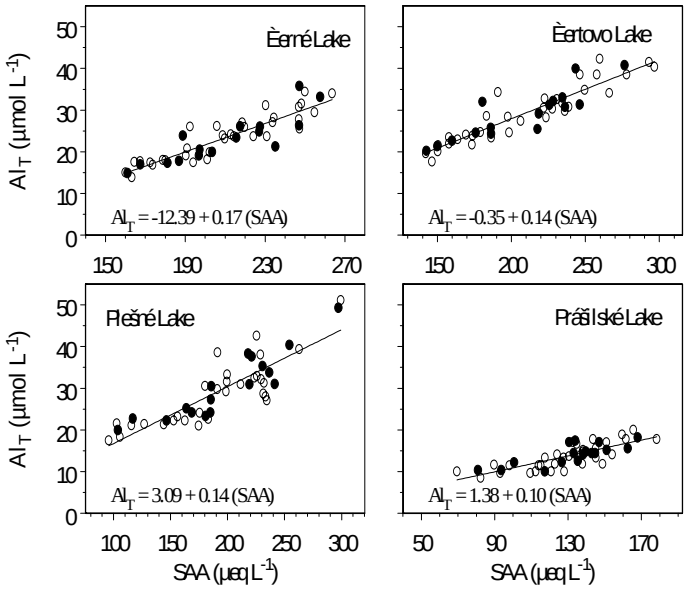


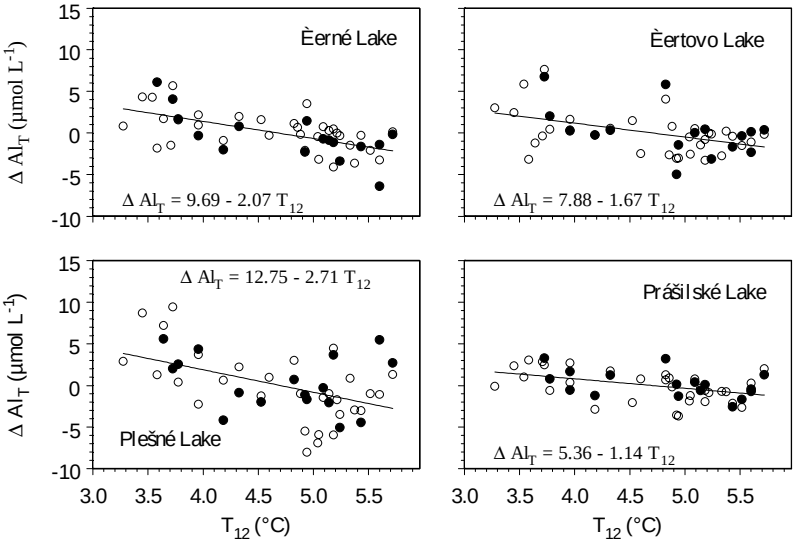


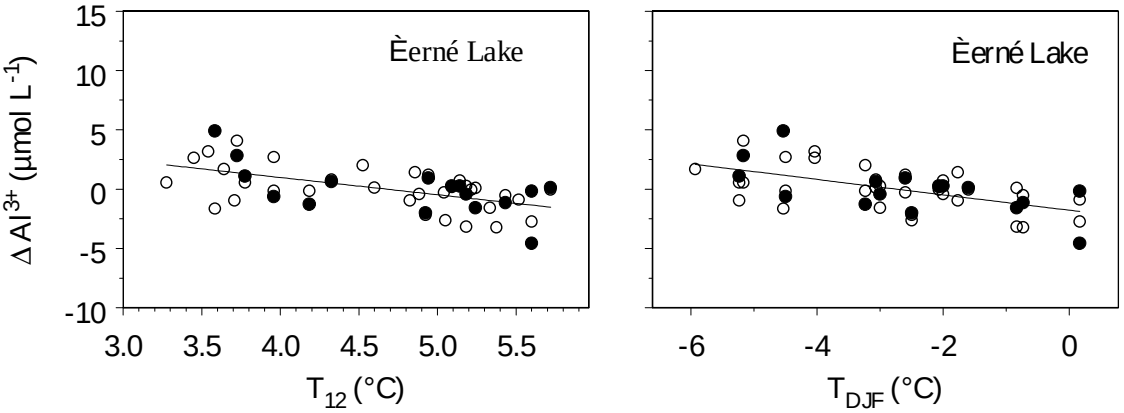

Silica mg / L
Prášilské
Year


Silica mg / L
Certovo
Year

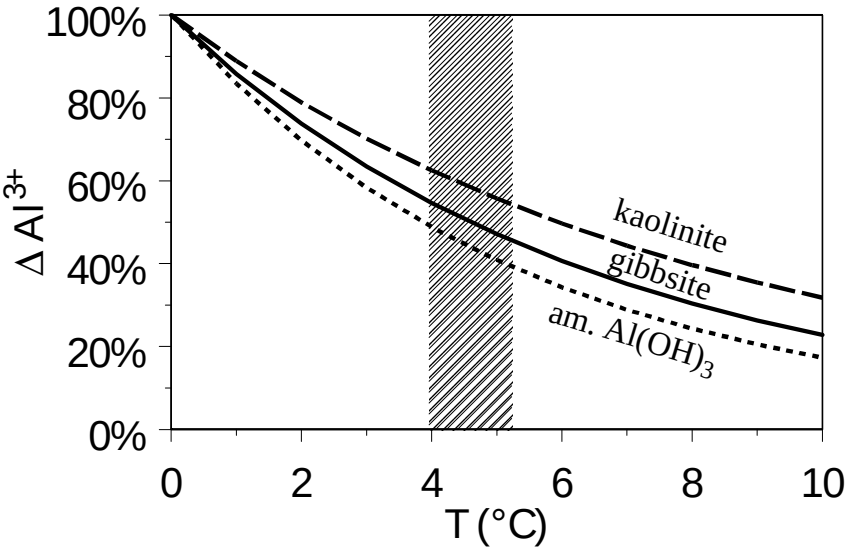

Al mg / L
Certovo
Year


Èerné Lake
Èertovo Lake
Plešné Lake
Prášilské Lake
Al_T (µmol L-1)
Al_T = -12.39 + 0.17 (SAA)
Al_T = -0.35 + 0.14 (SAA)
Al_T = 3.09 + 0.14 (SAA)
Al_T = 1.38 + 0.10 (SAA)
SAA (µeq L-1)


Δ Al_T (µmol L-1)
Èerné Lake
Èertovo Lake
Plešné Lake
Prášilské Lake
Δ Al_T = 9.69 - 2.07 T12
Δ Al_T = 7.88 - 1.67 T12
Δ Al_T = 12.75 - 2.71 T12
Δ Al_T = 5.36 - 1.14 T12
T12 (°C)



Veselý et al.,2003. Increasing temperature decreases aluminum concentrations in Central European lakes recovering from acidification. Limnol. Oceanogr. 48(6) 2346-2354.



Conclusions

- The pH of formely strongly acidified lakes Cerné, Plešné, and Prášilské in the Bohemian Forest is permanently > 5.0 at present.
- Beside sulfate concentrations also that of nitrate and chloride have decreased.
- Nitrate decreased relatively more than human emissions of N and relates to climate at present
- Silica and DOC concentrations are increasing
- The decrease in atmospheric deposition resulted in a sharp decrease of Al (up to 1.38 µmol L-1 yr-1).
- Climate warming over study is responsible for additional Al decrease by ~ 13 %.

5. Monitoring activities on Slovenian mountain lakes

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1 Introduction

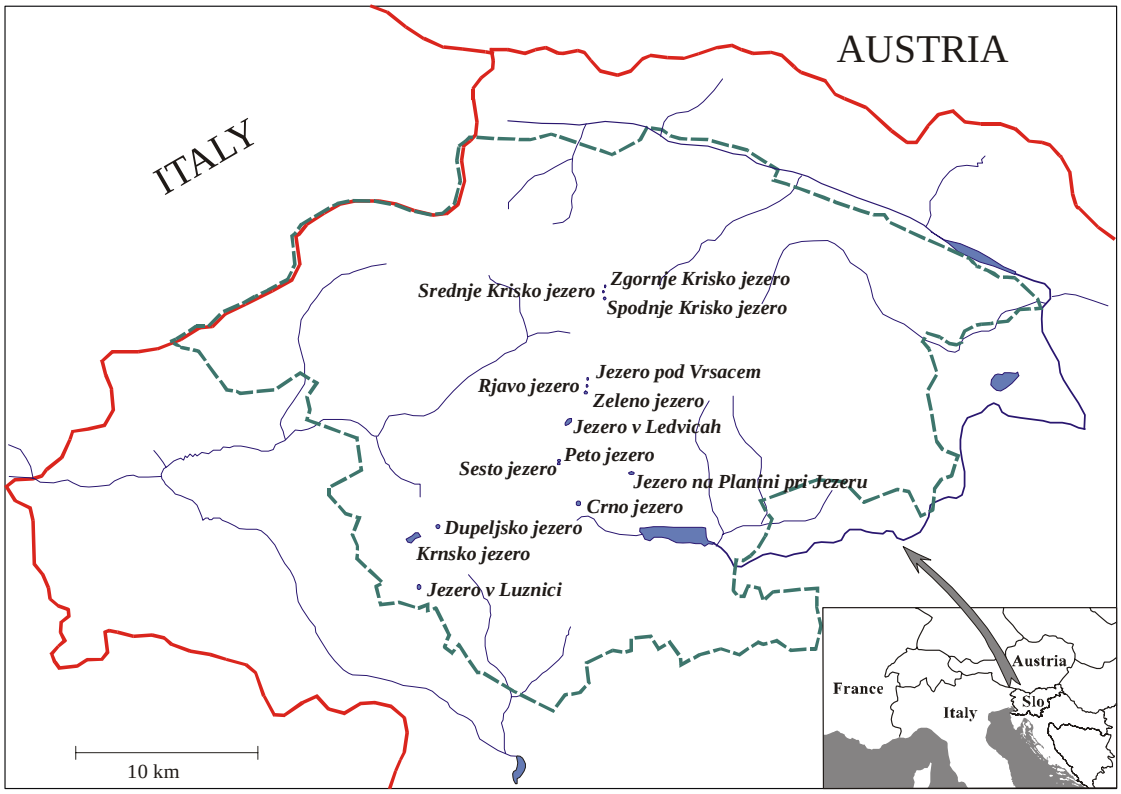

Figure 1. *Geographical position of Slovenian mountain lakes.*

First monitoring activities to analyze water quality of Slovenian mountain lakes started in 1991. Mountain lakes were initially sampled once per year, usually in late summer/early autumn. From 1995 onwards, a series of national as well as international research projects was initiated, in order to assess the condition of these lakes. As a consequence, the lakes were sampled more frequently. Water samples in all lakes were collected regularly twice per year, in late spring and early autumn. In addition, three lakes (i.e., Jezero v Ledvicah, Krnsko jezero and Jezero na Planini pri Jezeru) were sampled once per month in the ice-free period and some samples were also taken in winter when the lakes were covered by thick ice. Chemical and physical parameters were measured in the lake water and biological samples were also taken. Additionally, on-site meteorological data were collected using an automated weather station, situated near Jezero v Ledvicah to assess the overall condition of Slovenian mountain lakes.

Table 1. *Topographical characteristics of Slovenian mountain lakes.*

	Altitude [m]	Surf. Area [ha]	Max. Depth [m]	Catchment [ha]
Jezero pod Vrsacem (1J)	1993	0.56	7	54
Rjavo jezero (2J)	2002	1.34	10	36
Zeleno jezero (3J)	1983	0.61	3	24
Jezero v Ledvicah (4J)	1830	2.19	15	175
Peto jezero (5J)	1669	1.00	11	90
Sesto jezero (6J)	1669	0.66	9	90
Crno jezero (7J)	1325	0.86	9	140
J. na Planini pri Jezeru (JPJ)	1430	1.56	11	95
Zgornje Krisko jezero (ZgKJ)	2150	0.66	9	16
Srednje Krisko jezero (SrKJ)	1950	0.29	9	26
Spodnje Krisko jezero (SpKJ)	1880	0.87	9	13
Krnsko jezer (KJ)	1383	4.53	18	550
Dupeljsko jezero (DJ)	1340	0.25	3	46
Jezero v Luznici (JL)	1800	0.47	10	66

There are 14 mountain lakes in Slovenia. Their geographical position is shown in Figure 1, while topographical characteristics are summarized in Table 1. All the lakes are situated in the Julian Alps (NW Slovenia) and located at elevations from 1325 m to 2150 m. Most of them lie above the tree level, but 6 lakes, Peto jezero, Sesto jezero, Crno jezero, Jezero na Planini pri Jezeru, Krnsko jezero and Dupeljsko jezero, are located below the tree level. The main bedrock consists primarily of Triassic limestones and dolomites. Nevertheless, more diverse geology can be found in some areas, with inclusions of manganese-pyrite crusts, Jurassic and Cretaceous limestones and also marl-limestones. All the lakes are of glacial origin, small (surface area of 0.3 to 4.6 ha), shallow (2 to 15 m) and surrounded by steep slopes (Brancelj, 2002). The annual precipitation rate is high, exceeding 3000 mm per year in the western part of the Julian Alps and decreasing in the easterly direction. Most lakes have no permanent surface inflows. From early November until late April/May, the lakes are normally ice covered. All the lakes are situated in the Triglav National Park where human activities are limited by law. The only exception is Jezero na Planini pri Jezeru, where there is a mountain hut situated just above the lake.

2 Methods

Water samples were taken in 2.5 (Jezero v Ledvicah, Krnsko jezero and Jezero na Planini pri Jezeru) or 5 m intervals (other lakes) from the deepest part of the lakes using a Van Dorn sampling device. They were filtered through a 0.2 µm filter to eliminate solid particles and reduce biological activity. Conductivity, oxygen concentration/saturation and temperature were measured in the field. Other parameters were measured in the laboratory in the shortest possible time.

Standard laboratory procedures were followed for analyses of water samples, according to APHA et al. (1998). The pH was measured with a digital pH instrument. Alkalinity was determined by the Gran titration method. Major anions (chloride, nitrite, nitrate, phosphate and

sulfate) and cations (sodium, ammonium, potassium, calcium and magnesium) were determined with an ion chromatograph equipped with conductivity detection cell. Total nitrogen and total phosphorus were analyzed after oxidation of water samples with persulfate and subsequent spectrophotometric determination of the nitrate and ortho-phosphate concentration in the digestates, respectively using a UV-VIS spectrophotometer. Standard solutions and blank samples were used to calibrate the instruments and check the calibration curves.

3 Results and discussion

In most lakes, the pH was slightly basic throughout the year, ranging from 7.5 to 8.5 in the surface waters (Figure 2), thus showing the absence of acidification at all sites. Nevertheless, pH values as low as 7.1 (eutrophic lake) and as high as 9.4 (shallow lake, overgrown by vegetation over the entire lake bottom) were observed.

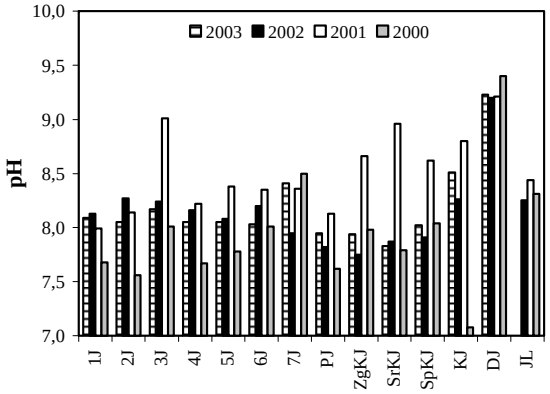

Figure 2. *The pH in the surface waters of the lakes in the period from 2000 to 2003 (lake abbreviations as in Table 1).*

Hydrogen carbonate/carbonate was the most abundant anion in the lakes, contributing over 90 % of the total anion concentration. It also accounted for the high alkalinity. On average, the alkalinity ranged from 1.0 to 2.0 mmol/L in the surface waters (Figure 3). On the other hand, calcium was the most abundant cation. It constituted over 90 % of the total cation concentration, but varied considerably in the lakes, ranging from 10 to 45 mg/L (Figure 3). In most lakes, however, it averaged 25 mg/L. In carbonate watersheds,

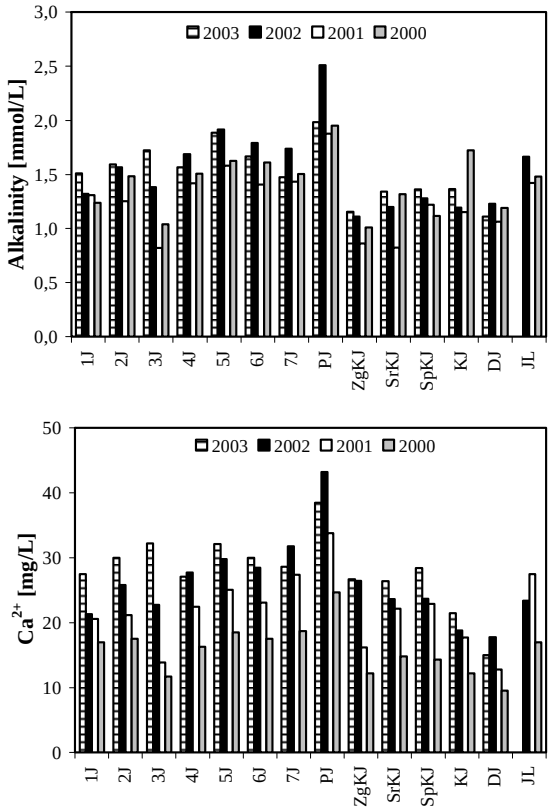

Figure 3. *The alkalinity and calcium concentration in the surface waters of the lakes in the period from 2000 to 2003 (lake abbreviations as in Table 1).*

weathering is the main source of carbonate (related to the alkalinity) and calcium in the water column. The lowest alkalinity and calcium concentrations were therefore observed in the lakes, having the smallest catchment areas. In addition, low alkalinity was also observed in several shallow productive lakes (i.e., Zeleno and Dupeljsko jezero), where lake waters were oversaturated with oxygen. The pH values were consequently high, while the alkalinity was lower due to a shift in the carbonate equilibrium. In contrast, the highest alkalinity was observed in eutrophic Jezero na Planini pri Jezeru. Transparency of the water column in this lake is low, resulting in low photosynthesis. Consequently, carbon dioxide concentration is high, and the pH dropped, while the alkalinity increased, according to a shift of the carbonate equilibrium. Similar trends were also observed for calcium, since calcium concentration in the water column is also determined by weathering and the carbonate equilibrium.

Nitrate concentrations mostly ranged from 1 to 2 mg/L in the surface waters (Figure 4). However, lower concentrations were observed in the lakes with small catchment areas (e.g., Krisko lakes) and in the productive lakes. In the latter lakes, nitrate concentration dropped as low as 0.05 mg/L, due to the high concentration of primary producers in these lakes, which caused an uptake of nitrates by aquatic organisms. Total phosphorus in the surface waters varied from 10 to 20 µg P/L in most lakes (Figure 4). However, this range was regularly exceeded in the more productive lakes, where concentrations as high as 64 µg P/L were observed.

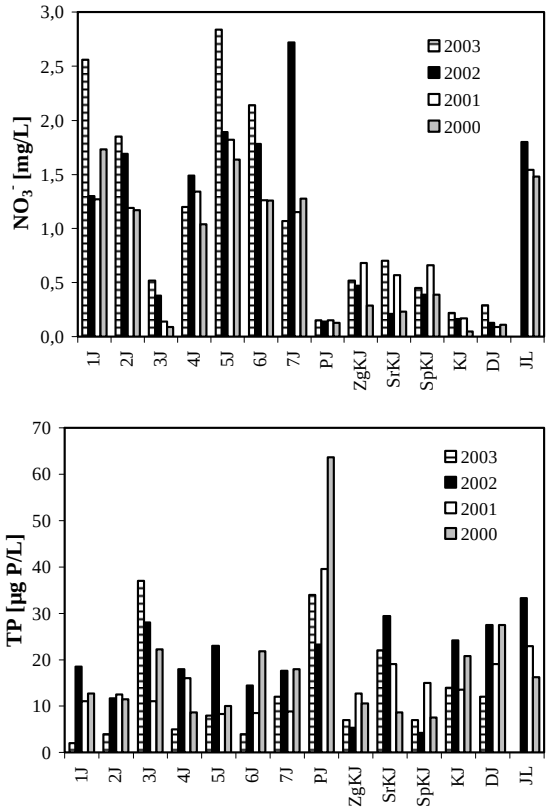

Figure 4. *Nitrate and total phosphorus concentration in the surface waters of the lakes in the period from 2000 to 2003 (lake abbreviations as in Table 1).*

Sulfate concentrations in the surface waters of most lakes, ranged from 1 to 2 mg/L, while chloride concentrations were quite low and uniform, ranging from 0.2 to 0.8 mg/L. Sodium and potassium concentrations in the surface waters were also fairly low. The former normally ranged from 0.5 to 1 mg/L, while the latter were quite uniform in the lakes, averaging 0.5 mg/L. In contrast, magnesium concentrations in the surface waters varied considerably, from 1.0 to 7.2 mg/L.

Nitrite and phosphate concentrations in the surface waters were below the limits of detection (0.05 mg/L) in all the lakes. Ammonium concentrations were also mostly below the detection limit of 0.05 mg/L, except in some productive lakes where low concentrations of up to 0.1 mg/L were observed.

The surface water conductivity was fairly uniform. It averaged 150 µS/cm in most lakes (Figure 5). Lower values were observed in the lakes with small catchment areas and in the shallow productive lakes, averaging 100 µS/cm. In the latter lakes, the low total concentration of dissolved ions (and consequently low conductivity) resulted from precipitation of calcium carbonate in the surface waters, due to a shift in the carbonate equilibrium. The highest conductivity was in contrast observed in the highly productive Jezero na Planini pri Jezeru, exceeding 180 µS/cm, and resulted, most probably, from dissolution of calcium carbonate in the surface water.

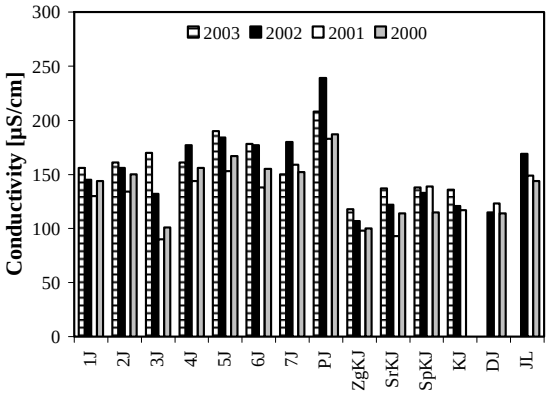

Figure 5. *Conductivity in the surface waters of the lakes in the period from 2000 to 2003 (lake abbreviations as in Table 1).*

All parameters were fairly uniform with depth in the oligo/mesotrophic lakes. In contrast, marked variations of some parameters were observed in the eutrophic lakes. The pH and oxygen concentration decreased, while the alkalinity, calcium, ammonium and total phosphorus concentrations as well as conductivity increased with depth (Muri and Brancelj, 2003).
Annual variations of parameters were also observed. Among the parameters presented, nutrients (Figure 4) showed the highest variability. It was found out that in the years with long duration of snow and ice cover, and consequently cold lake water, nutrient concentrations were lower, since primary producers were less abundant. As a consequence, the overall condition of the lakes temporarily improved.

4 Conclusions

All Slovenian mountain lakes are situated on limestone bedrock. The pH is thus slightly basic at all times and acidification of lake waters is not observed.
Most Slovenian mountain lakes are still in a good condition. The lakes are rated as oligotrophic to oligotrophic/mesotrophic, since their concentrations of nutrients (total phosphorus) and chlorophyll are low, while transparency in the water column is high. In contrast, intensive primary production was observed in several lakes, i.e. Zeleno, Dupeljsko, Krnsko jezero and Jezero na Planini pri Jezeru. These lakes are mesotrophic to eutrophic. Jezero na Planini pri Jezeru is somehow in the worst condition, since it has high nutrient and low dissolved oxygen concentrations and low transparency. As a consequence, the water quality has deteriorated.

References

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Brancelj, A. (ed.) 2002. High-mountain lakes in the eastern part of the Julian Alps. ZRC, Ljubljana.
Muri, G. and Brancelj, A. 2003. Seasonal water chemistry variations in three Slovenian mountain lakes. Acta Chimica Slovenica 50, 137-147.

6. Recovery from acidification – biological responses to chemical recovery in acidified lakes in Finland

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Introduction

Chemical recovery

In concordance with overwhelming decrease of acidic deposition, recovery from acidification with decreasing concentrations of sulphate and a subsequent increase in alkalinity has been observed in Finnish RMLA lakes (Regional Monitoring of Lake Acidification, n=164) during the 1990s and continuing to date. Significant decreasing trend in SO_4* concentrations was detected in about 80% of the monitoring lakes in northern and up to 95 % of the lakes in southern Finland during the period 1990-2002 (Mannio & Vuorenmaa, 2004). Consequently, alkalinity is significantly increasing in some 50% of the RMLA lakes, with a regional range from 40% of the lakes in central and northern Finland to 85% of the lakes in southern Finland. There is also a signal of increasing pH in lakes particularly in the southern Finland, where one third of lakes exhibited significant increase of pH (Fig. 1).

The RMLA approach is based on both variable environmental conditions and gradients in initial ionic concentrations and deposition levels, decreasing from the south towards northern Finland (e.g. Forsius et al., 2003). Southern Finland has been exposed to higher air pollution loads compared to other regions, showing correspondingly stronger S emission reduction responses over the past 10-15 years (Vuorenmaa, 2004).

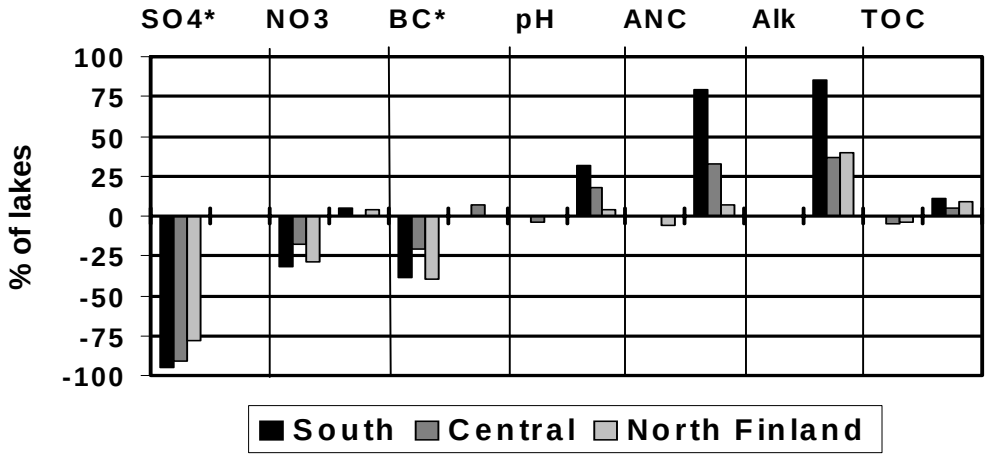

Figure 1. Trends in RMLA lakes (n=164) in 1990-2002 for three regions in Finland. The percent of lakes with significant increasing or decreasing trend (p<0.05) for key water quality variables is shown.

The Finnish ICP Waters lakes (n=8) are included in the RMLA network, and temporal trends for key acidification variables for some ICP waters sites are shown in figure 2

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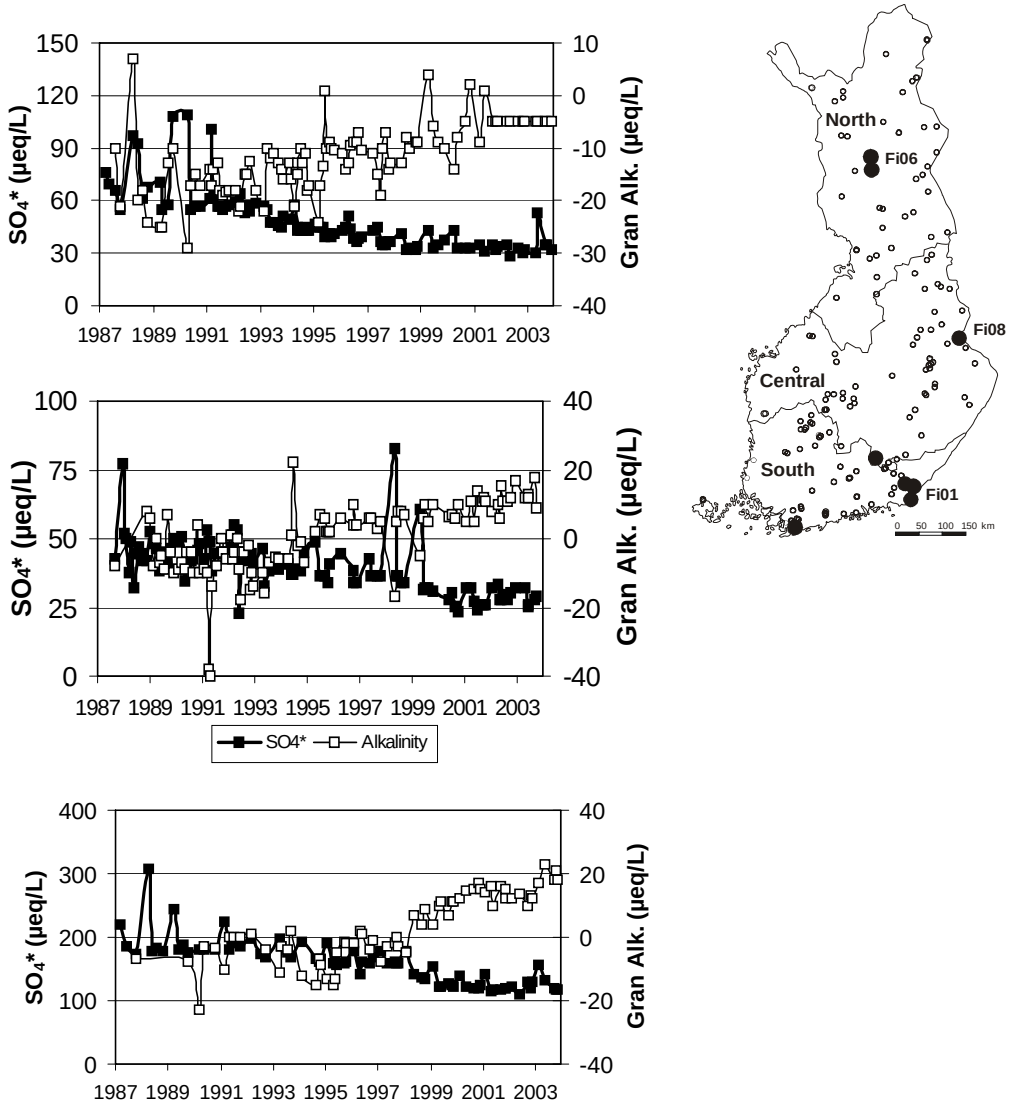

Figure 2. Time series for selected water chemistry parameters at three Finnish ICP Waters sites Vasikkajärvi (Fi06) (upper), Kakkisenlampi (Fi08) (middle) and Hirvilampi (Fi01) (lower), years 1987-2003. Location of the RMLA lakes, ICP Waters sites (black dots) and the three lake regions (South, Central, North) are also shown.

Biological recovery ?

There are clear signs of chemical recovery in Finnish lakes but essential knowledge regarding biological recovery is sparse or non-existent. Therefore Finnish Environment Institute, Finnish Game and Fisheries Research Institute, and the Universities of Helsinki and Jyväskylä established a joint project 'Recovery processes in acidified Finnish headwater lakes (REPRO)'. Key aims of the project were to: (i) examine the relationships between changes in deposition chemistry vs. lake chemistry and biological change, and identify how the biological recovery is

connected to chemical recovery, and (ii) quantify the changes in selected biological indicators. A resurvey of a selected subset (30 lakes from South and Central Finland, Fig. 3) of 140 headwater lakes collected during the HAPRO-project (Finnish Acidification Research Project, 1985-90) was conducted during summer/autumn 2001-2002. The field studies comprised water chemistry, fish sampling (Tammi et al., 2004), diatoms in both littoral periphyton and sediments (Eloranta & Kwandras, 2004), and macrozoobenthos in both littoral zone and sediments (Hynynen & Meriläinen, 2004). The Finnish ICP Waters sites FI01, FI02, FI03, FI07 and FI08 were included in the project.

Other approaches of the project were: (iii) biogeochemical studies and proton budget calculations at intensively studied forested catchments (Forsius et al., 2004); (iiii) up-scaling of results using statistically based lake survey data (Forsius et al., 2003), and (iiiii) development and application of dynamic acidification models for the analysis of the response of the lakes to future emission reduction scenarios (Jenkins et al., 2003; Posch et al., 2003).

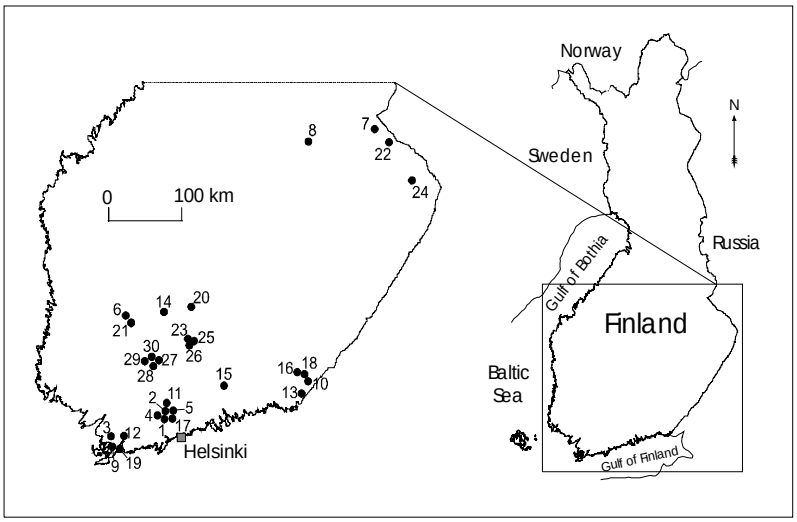

Figure 3. Location of biological study lakes in Finland. The numbers refers to those in Fig. 4.

2. Some results from biological studies

Fish

The response of perch populations to the increased alkalinity and decreased labile aluminium concentrations (Fig .4) was seen in improved reproduction success, indicated by a higher CPUE in numbers and a lower mean weight (Fig.5). The growth rate of perch was declined as the population density was increased.

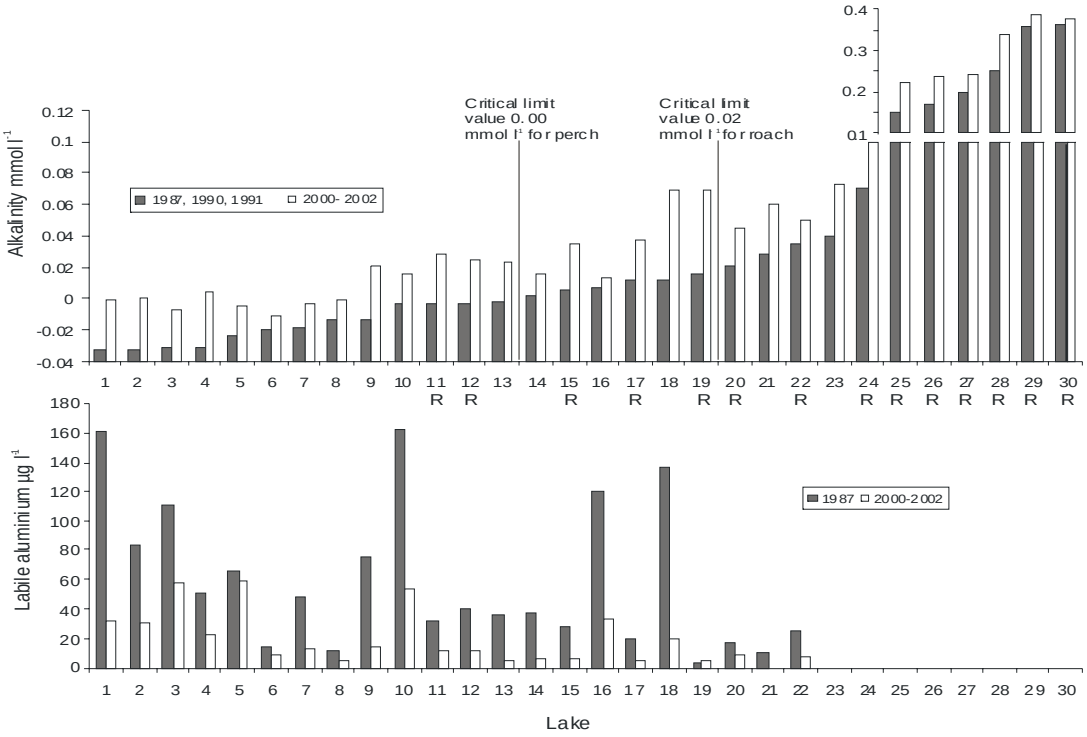

Figure 4. Mean alkalinity (upper) and mean concentration of labile aluminium (lower) in the study lakes during two sampling periods. The lakes are sorted in numerical order according to the alkalinity level in the late 1980s. Perch exist in all lakes, and lakes with existing or lost roach populations are marked with R. The vertical dotted lines indicate the lakes under critical limit values as deduced from the values of the late 1980s. Note that the scale of maximum values of alkalinity for lakes 25-30 is compressed.

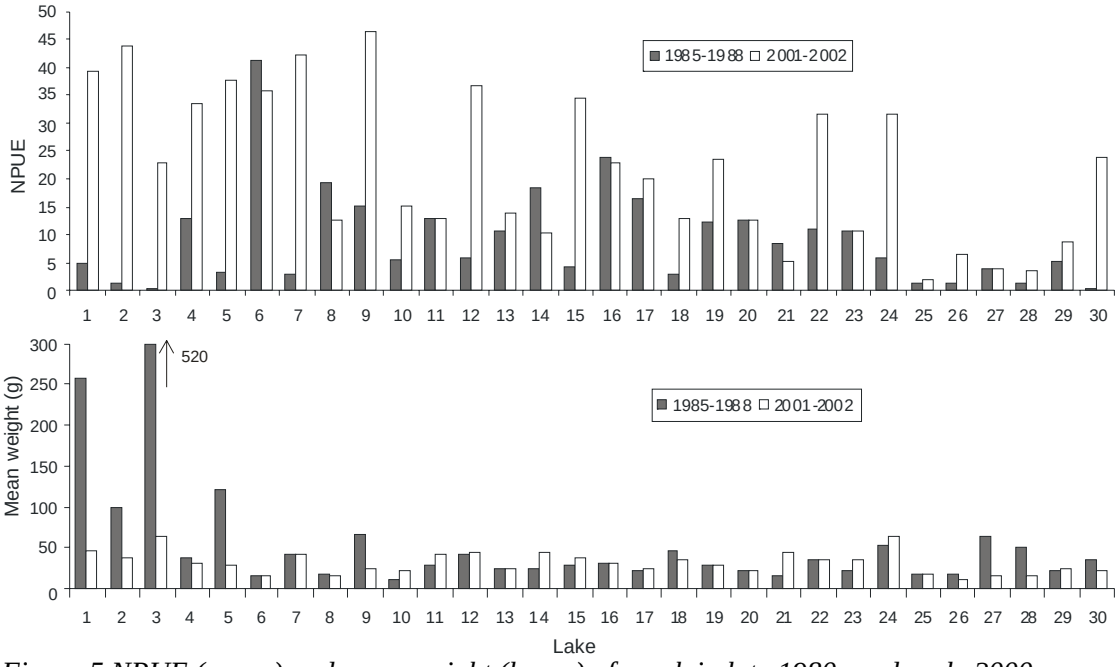

Figure 5.NPUE (upper) and mean weight (lower) of perch in late 1980s and early 2000s.

Roach populations were not recovered in the same way as perch, there being no major changes in NPUE or mean weight. In two most acidified roach-bearing study lakes which were in a critical state at the end of the 1980s, populations of roach were most probably extinct. Lower growth rates were observed in the roach populations of all study lakes. The critical water conditions and increased density of the perch populations had probably affected the recovery patterns of the roach populations in the sampled lakes (Tammi et al., 2004).

Macrozoobenthos

Acid sensitive and moderately acid sensitive benthic species revealed slight recovery in the formerly most acidic (pH ≤5.5) but recently recovered lakes. The most significant factors affecting the response of benthic communities were increased mean lake pH and decreased labile aluminium concentration. The results revealed that a good ecological status may also be reached in acid impacted lakes, but the time-lag needed for the distinct recovery of acid sensitive species remained unanswered in this study. Since the damage occurred over many decades, it is realistic to assume that distinct biological recovery in these lakes will not take place rapidly, but may occur slowly over the course of time. Paleolimnological chironomid analysis revealed structural similarity between the present and pristine chironomid assemblages. This implies that no major changes in chironomid communities of these acidic lakes have occurred during the past centuries (Hynynen & Meriläinen 2004).

Littoral diatoms

Littoral diatoms indicated the most clear positive pH-change in the lakes at the southern Finland, where acid stress was the strongest and where in the last two decades the decrease of the acid load is the greatest. In the central parts of Finland the change was not as clear, with the variation in the individual lake level (Fig. 6).

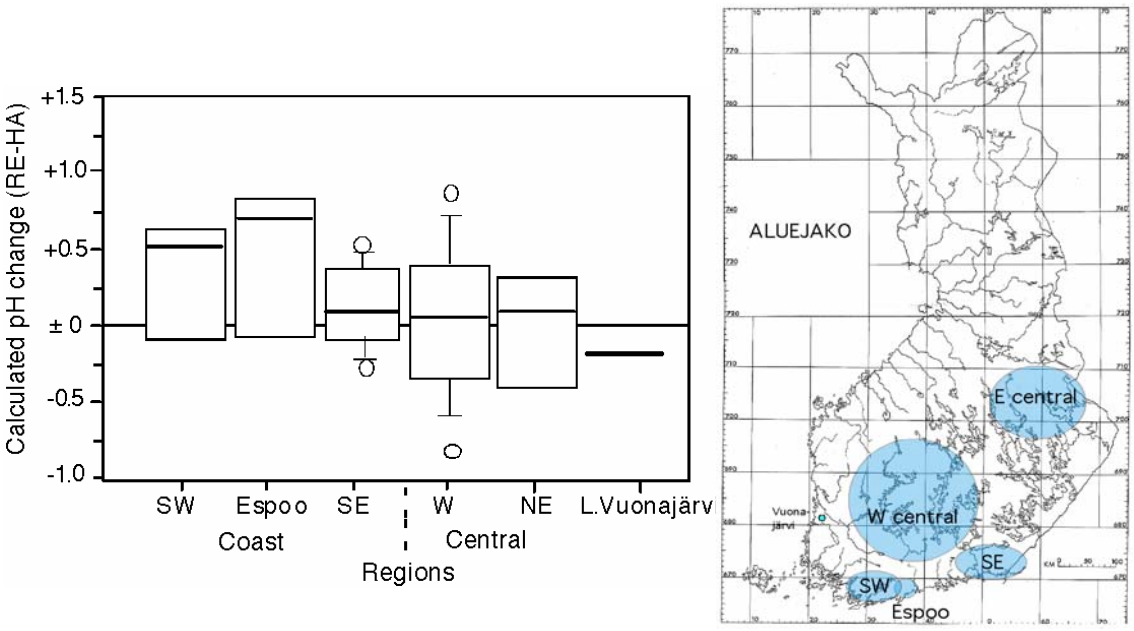

Figure 6. Box plot of changes of diatom inferred pH (calculated pH) values since HAPRO project in 1980s to REPRO project in 2001 in different regions of Finland. Vertical bar in the box indicates median and the lower and upper lines of the box 25 % and 75 % percentiles, respectively.

3. Future work

The regional coherence of the chemical recovery allows a reduction in the number of annually visited lakes. On the other hand, anticipated climatic changes and variability would suggest more seasonally visited lakes (Vuorenmaa et al.). This kind of re-organisation of the monitoring structure is planned for the next period 2006-2008. Additionally, biological and contaminant monitoring is easier to integrate to fewer sites. In all, this will serve also better the objectives of EU Water Framework Directive.

Scientific publications of the project

Forsius, M., Vuorenmaa, J., Mannio, J. & Syri, S.: 2003. Recovery from acidification of Finnish lakes: regional patterns and relations to emission reduction policy. *Science of The Total Environment* 310: 121-132.

Forsius, M., Kleemola, S. & Starr, M.: 2004. Proton budgets for a network of European forested catchments and the impact of nitrogen deposition. *Ecological indicators* (accepted in 2004)

Hynynen, J. & Meriläinen, J.J.: Recovery from acidification in boreal lakes inferred from macroinvertebrates and subfossil chironomids. *Hydrobiologia* (accepted in 2004)

Jenkins, A., Camarero, L., Cosby, B.J., Ferrier, R., Forsius, M., Helliwell, R., Kopacek, J., Majer, V., Moldan, F., Posch, M., Rogora, M., Schöpp, W. & Wright, R.F.: 2003. A modelling assessment of acidification and recovery of European surface waters. *Hydrology and Earth System Science* 7(4): 447-455.

Kwandrans, J. & Eloranta, P.: 2004. Sediment diatoms as indicators of acidified lake recovery. – In: C. Holdynski & I. Lasniewska (ed.): Algae and biological state of water. – *Acta Botanica Warmiae et Masuriae* 3: 123–133.

Mannio, J. and Vuorenmaa, J.: 2004. Acidification and trace metals in lakes. In: Eloranta, P. (ed.) *Inland and coastal waters of Finland*. Helsinki, University of Helsinki, Palmenia Centre for Continuing Education, Palmenia Publishing. pp. 73-83.

Posch, M., Forsius, M., Johansson, M., Vuorenmaa, J. & Kämäri, J.: 2003. Modelling the recovery of acid-sensitive Finnish headwater lakes under present emission reduction agreements. *Hydrology and Earth System Sciences* 7(4): 484-493.

Tammi, J., Rask, M., Vuorenmaa, J., Lappalainen, A. & Vesala, S.: 2004. Population responses of perch (Perca fluviatilis) and roach (Rutilus rutilus) to recovery from acidification in small Finnish lakes. *Hydrobiologia* 528: 107-122

Vuorenmaa, J.: 2004. Long-term changes of acidifying deposition in Finland (1973-2000). *Environmental Pollution* 128: 351-362.

Vuorenmaa, J., Forsius. M. & Mannio, J.: Increasing trend of total organic carbon concentrations in small forest lakes (in Finland) 1987-2003. (*manuscript*)

An executive summary –manuscript from the REPRO project is in progress and will be published in 2005.

7. Report of national ICP-Waters activities in Latvia, 2003/2004

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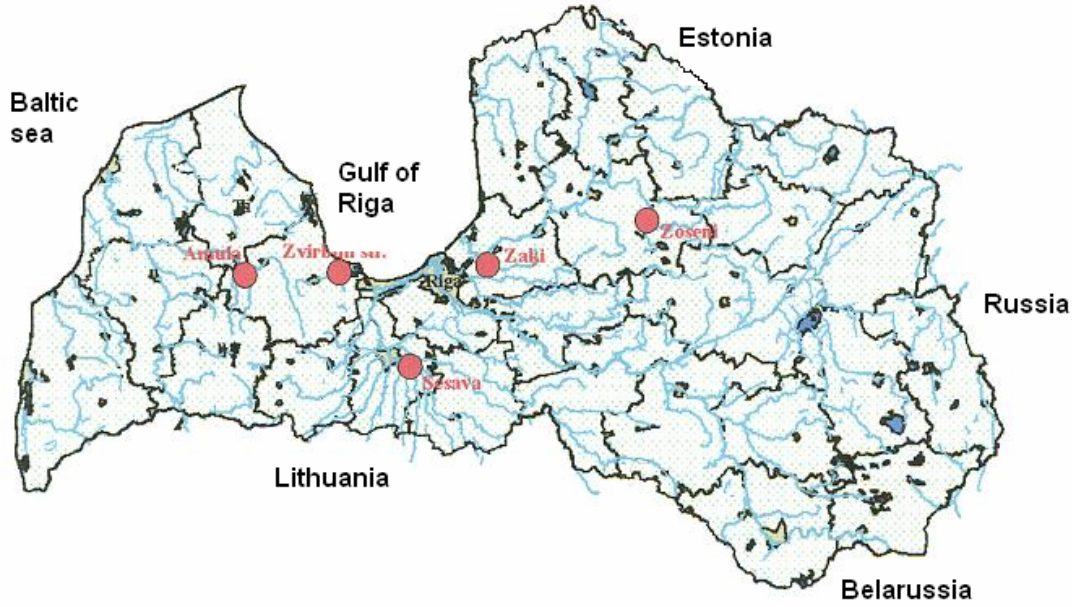
The ICP-waters programme activities continued in 2003/2004 at five sites: L.Jugla-Zaki, Amula – mouth, Sesava – mouth, Zvirbuli and Tulija – Zoseni.



The 2003/2004 activities focussed on:

- QA/QC of sampling and analysis;
- Working out and implemetation of national legislation under the Water Framework Directive relating to monitoring and characterization of surface water body types and normative definitions of ecological status classifications.
- Preperation for the implementation of the forthcoming Directive of European Parlament and of the Council relating to arsenic, cadmium, mercury, nickel and polycyclic aromating hydrocarbons in ambient air and tasks, which are in focus of measurments and assessment in ICP programms under the Convention on Long-range Transboundary Air Pollution.
- Assessment of the results of measurements of new heavy metals (Ni, Mn, As) and dissolved organic carbon **(DOC)** in 2003.

Summary of the results

1 QA/QC of measurements

1.1. The laboratory participated in two intercomparisions (hydrochemical and hydrobiological) held by NIVA. The intercomparision 0317 results were fairly good, except for iron and lead (accuracy 26-34%), the reason for the "omitted values" for sulfate was mistakes in the measurment units, reported by the Latvian laboratory. The preliminary results of the hydrobiological intercomparison are good.

1.2. For the assessment of the quality of sampling and transportation procedures in 2003 "field blank" samples were made. The results show that the concentrations of nutrients in the "field blank" samples were on the detection limit level and constituted 0.2-20% of the concentrations in real samples.

1.3. To assess the quality of sampling and chemical analysis, a "flag" system was used for the outliers, ion balance (including DOC data), conductivity and the concentrations of substances below the detection limits.

1.4. Quality of works was in focus. The Latvian Hydrometeorological Agency has received an ISO:9001:2000 certificate.

2. Some measurement results

The annual mean concentration at the ICP-W sites in 2002/2003 was for Ni 0.98 – 4.20 µg/l, for Mn – 16.4 – 86.1 µg/l and for As – 0.33 – 1.92 µg/l. The highest concentrations in 2003 showed Mn in Sesava, As in Sesava and L.Jugla-Zaki; Ni concentrations were of the same level (Fig.1).

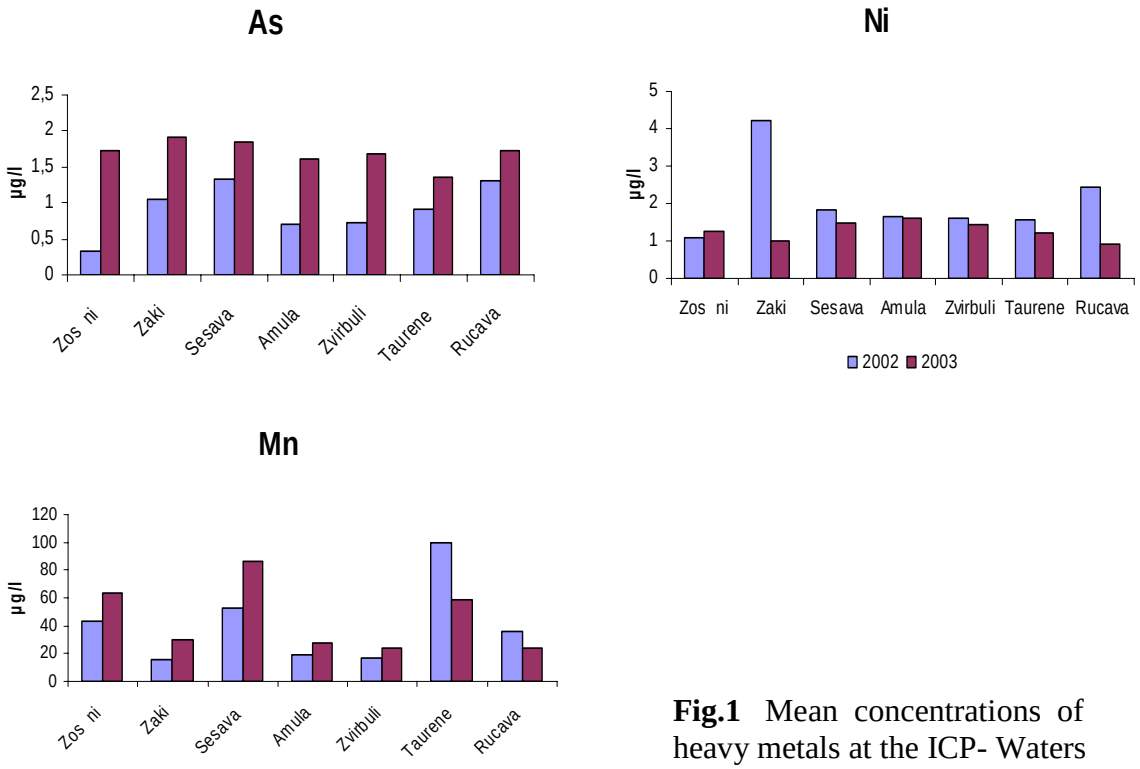


Fig.1 Mean concentrations of heavy metals at the ICP- Waters and ICP-IM sites 2002-2003

It should be noted that Mn in surface water objects of Latvia is of the natural origin.

Ni, Mn and As measurements are incorporated in the ICP-IM and regional GAW/EMEP programs.
The concentrations of the above metals in the forest streams at the ICP-IM sites are practically of the same level as at the ICP-W sites.
Wet depositions over the Latvian territory in 2002 were 0.1-0.5 mg/m^2 for As, 2.4-5.8 mg/m^2 for Mn and 0.4-0.9 mg/m^2 for Ni.
Seasonally, no marked changes were observed in 2003 in the concentrations of the heavy metals at the ICP-W sites, with somewhat higer concentrations in the autumn and winter compared to the summer values (Fig.2.).

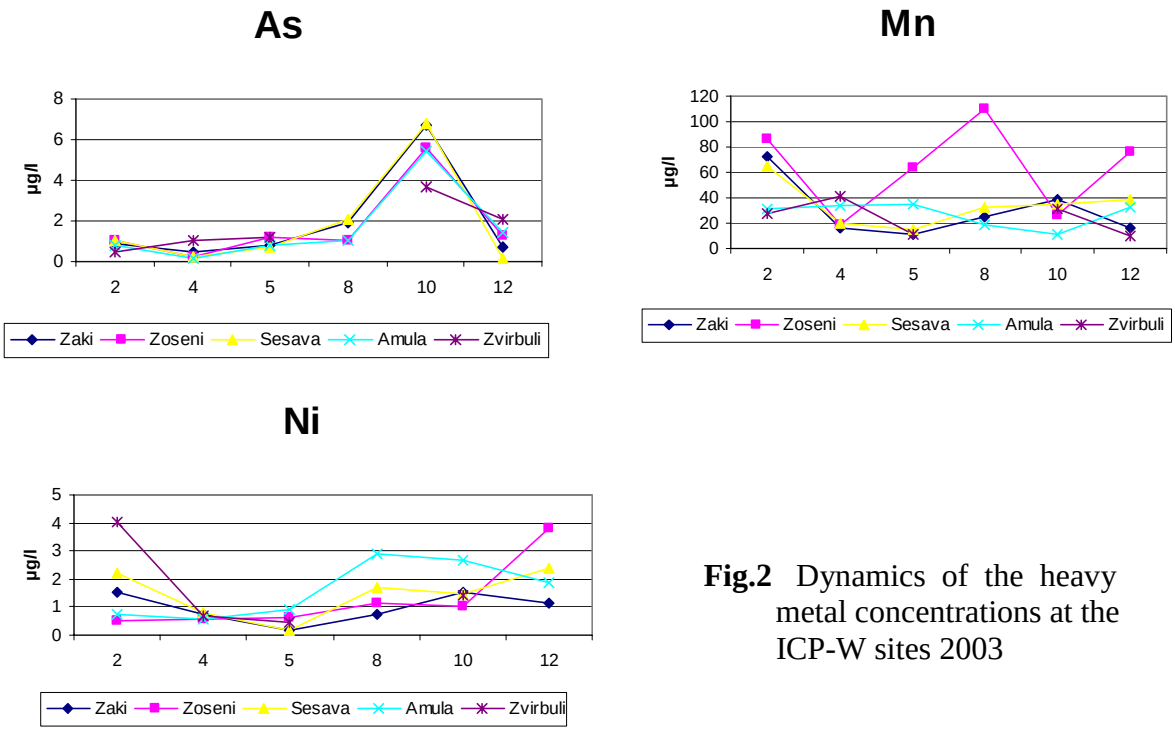


Fig.2 Dynamics of the heavy metal concentrations at the ICP-W sites 2003

2.2. The annual mean concentration of **DOC** at the ICP-W sites varied within a wide range from 12.3 mgC/l (Amula) to 69.7 mgC/l (Zvirbuli).

The reason for high DOC values in Zvirbuli is that the stream flows directly trough a swamp rich in organic matter. Of all ICP-W sites maximum values of BOD and COD were obtained for the Zvirbuli stream. That testifies to the presence of both easy decaying and more stable organic substances (Fig.3). It is worth mentioning that the high DOC amount in the forest strem at Rucava is due to a swamp.

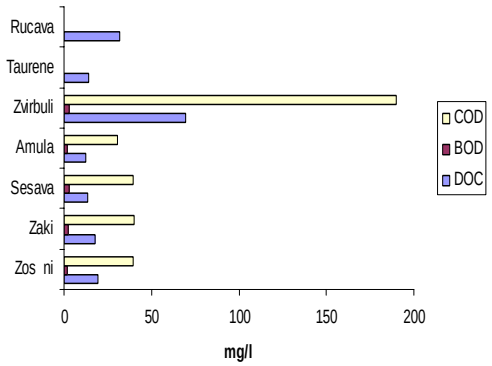


Fig.3 Annual mean concentrations of organic matter, 2003

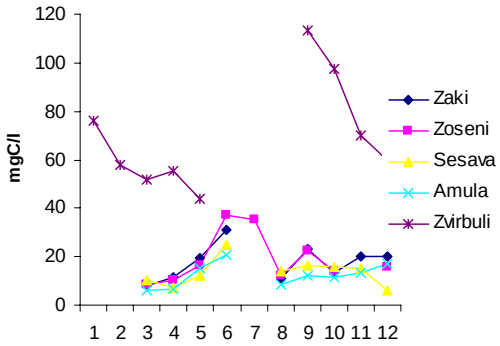


Fig.4 Dynamics of the DOC concentrations at the ICP-W sites, 2003

The seasonal DOC concentrations show generally higher concentrations in the low-water period in summer and lower –in autumn and winter. The increase of the DOC concentration (up to 113 mgC/l) in base flow storage after summer drying up is peculiar to the Zvirbuli stream (Fig.4).

2.3. The measurement results are used for national and international reports and research papers:

- Lyulko. I. (Ed.) 2003. Air quality and its impact on the environment, 2002. Observation Network department Latvian Hydrometeorological agency, Riga, 2002 (in Latvian).
- Overview of the 2003 studies in Rucava and Taurene, Latvia. IU “Pededze”, Latvian University, Riga, 2004 (in Latvian).
- I.Indriksone, I.Lyulko, M.Frolova. Assessment of transboundary transmission of air pollution. International Conference EcoBalt’2003, Riga, 2003.
- The Nordic-Baltic Regional Assessment for Long-range Transboundary Air Pollution, 1980-2000. Ajoint contribution by Denmark, Estonia, Finland, Latvia. Lithuania, Norway and Sweden to the EMEP Assessment Report, http://www.emep.int

3. Future activities

- To report the 2003 ICP-W data to the ICP-W database.
- To go on participating in the hydrochemical intercomparison events.
- To implement Hg measurement under the ICP-W program.
- To carry out feasibility studies on rivers to incorporate new stations in the ICP-W network.

To cooperate with other ICPs within EMEP and on the WFD relevant issues

8. Modelling the effects of acidic deposition on lake chemistry at Polish Tatra Mountains using the MAGIC model

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Introduction

As acid deposition in Europe decreases as a result of reduction in sulphur and nitrogen emissions, there is an increased interest in getting answers to the two questions: (1) whether these reductions are sufficient to promote ecosystem recovery, and (2) when this recovery will occur.

In order to address these issues, dynamic models of surface water acidification are required. In this study, the MAGIC software was used for reconstructing and forecasting acidification of two lakes located in the Polish Tatra Mountains.

Site description

Ones of the most sensitive aquatic ecosystems in Poland are the Tatra mountains catchments, which is a direct consequence of the specific bedrock lithology, soil type, land use and rainfall characteristics. The Tatra Mountains, the highest part of the Carpathian arc, are situated on the border between Poland and Slovakia. The post-glacial lakes of the Tatra Mts are situated above the upper forest zone, on the level of mountain-pine and alps. The study concentrated on two acidification sensitive lakes, Dlugi Staw and Zielony Staw, located in the granitic area of the mountains, selected after an earlier extensive investigation (Henriksen el al., 1992). The lakes lie close to each other and receive similar loads of acidity in precipitation. They differ in morphological and hydrological characteristics (table 1) as well as in intensity of biological processes occurring in their catchments and waters. There is no forest in either catchments, only 4% of the catchment of Zielony Staw is covered with dwarf mountain-pine. The waters of lakes are ultraoligotrophic, inhabited with the phytoplankton dominated by smaller nanoplanctonic forms.

Table 1 Morphological and hydrological parameters of studied Tatra Lakes (Szafer i in., 1962; Rzycho , 1998)

Lake	Unit	Zielony Staw	Dlugi Staw
Altitude	m a.s.l.	1672	1784
Surface lake area	ha	3.84	1.59
Depth max.	m	15.1	10.6
Volume	10^3 m^3	290	81
Catchment surface area	ha	37.2	62.6
Retention time	yr	0.54	0.09
Precipitation	m yr^{-1}	1.79	1.89
Runoff	m yr^{-1}	1.54	1.62

Methods

Sources of data

Water and soil chemistry data was provided by monitoring of lake water carried out in the years 1992-2004. Assessment of atmospheric deposition was based on literature data, own results obtained from research carried out in 1992-2002 as well as on data provided by the National Deposition Monitoring.

Modelling

MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidification on surface water chemistry. The aggregated nature of the model requires that it be calibrated to observed data from a watershed before it can be used to examine potential system response. Calibration is achieved by setting the values of certain parameters within the model which can be directly measured or observed in the system of interest. Detailed description of the MAGIC model is given by Cosby et al., 2001.

Calculations of chemical composition of water and soil were carried out for the period of 1880-2030. Emission forecast was based on Gothenburg Protocol (for 2002) and EMEP estimations.

Results

Results of dynamic modelling allow determining time frames of water chemical composition in the context of increasing or decreasing acidic atmospheric deposition.

Reaction of both lakes to a similar pollutant deposition, obtained as a result of model calculations, is different. The main difference is observed in concentrations of nitrate ions and reaction time of selected parameters to changes in the deposition. There are very slight differences in concentrations of sulphate ion in both lakes and they are similar to concentrations observed in precipitation. Sulphur retention in both catchments is of no significance. According to literature (Kopaczek et al., 2004) nitrogen retention capacity in the mountain catchment is positively correlated with soil volume and plant coverage degree. Dlugi Staw catchment contains less soil per surface unit than the Zielony Staw catchment and the plant coverage there is smaller. This is reflected in significantly higher concentrations of nitrate ion in Dlugi Staw water. Higher concentration of nitrate ions and lower supply of alkaline cations result in significantly lower alkalinity of Dlugi Staw water in comparison to Zielony Staw (Figure 1).

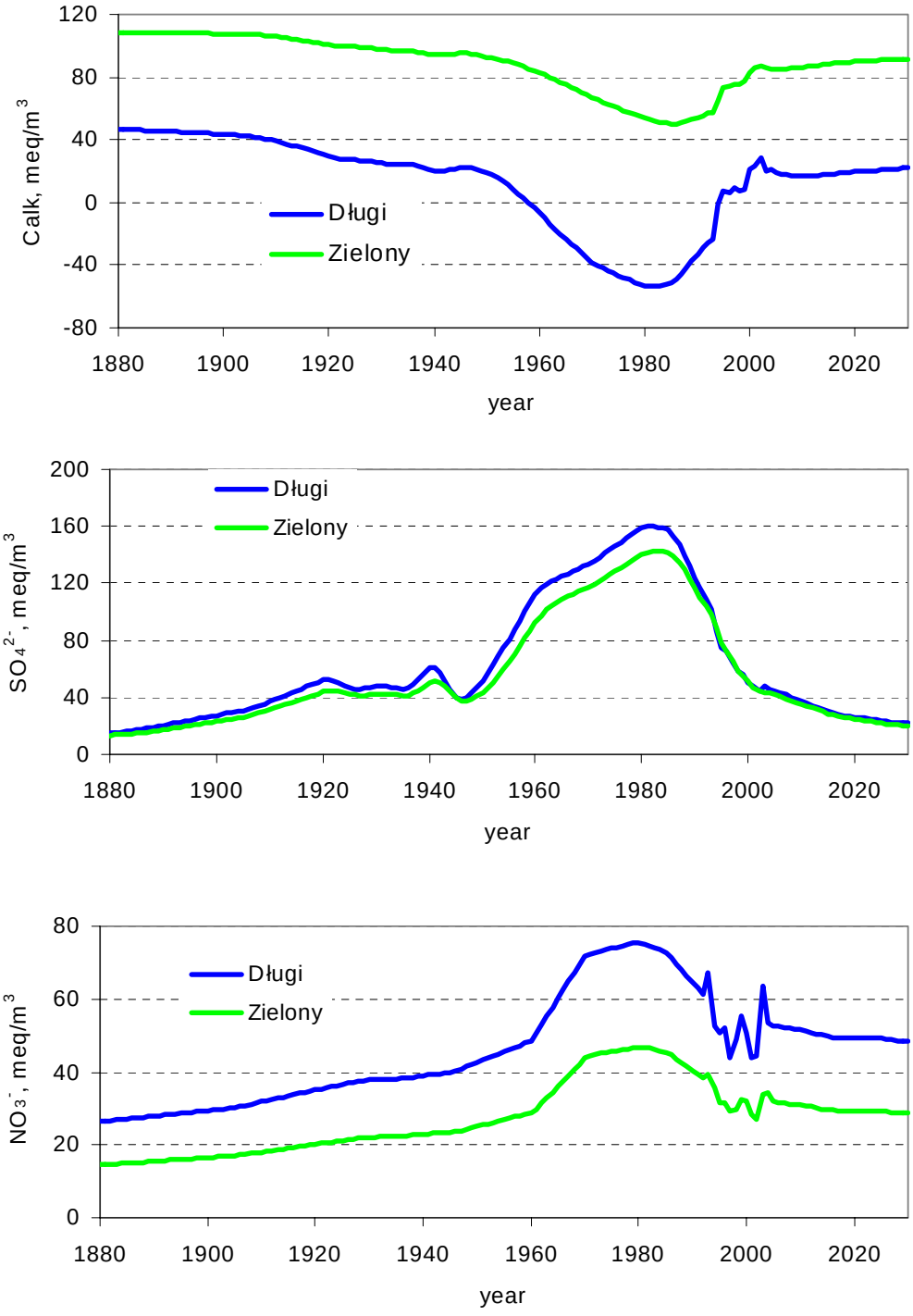

Figure 1 Values of C-alk (ANC), SO_4^{2-}, NO_3^- in Zielony and Dlugi Staw as simulated by MAGIC

Much higher dynamics of changes was noted in the case of Długi Staw. Although its acidification was more rapid, it shows more rapid recovery of its chemical composition. As for Zielony Staw, it was more resistant to acidification but its recovery is slower. The above-mentioned differences result from different water retention time in both lakes, which is calculated as a proportion of the lake volume to the total annual precipitation volume within the catchment. The relevant values are 0,09 years for Długi Staw and 0,54 years for Zielony Staw.

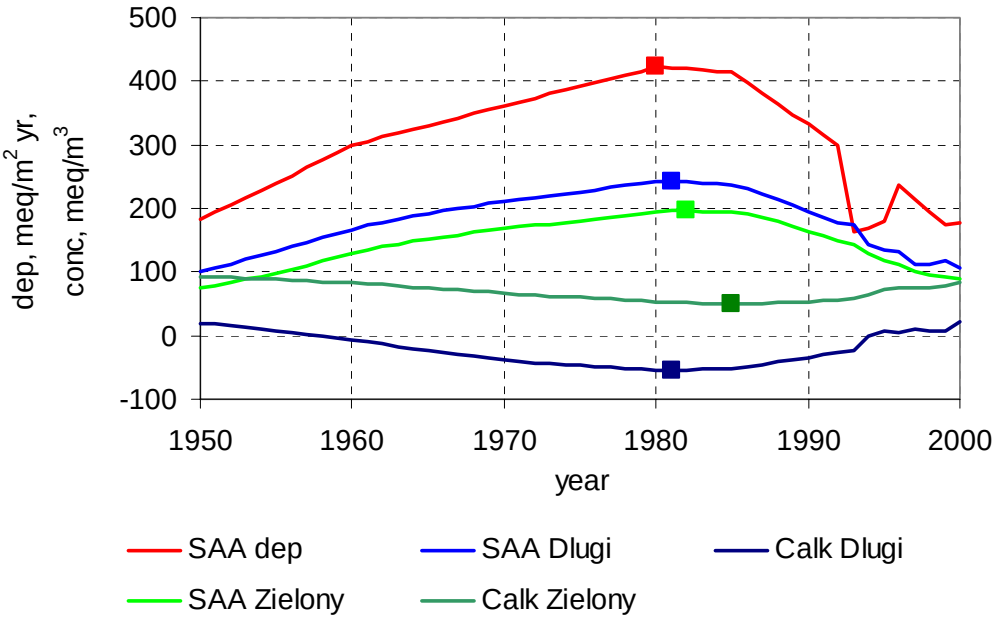

Figure 2 Delay in lakes answer to changes in acid anions deposition. SAA – sum of strong acid anions ($SO_4^{2-}+NO_3^-$), Calk – alkalinity (ANC)

Calculations made using MAGIC system confirmed different sensitivity of both lakes to acid deposition as well as different reaction time to changes in its volume and composition, as it had already been noted in monitoring research. Forecast of changes in chemical composition of water indicates that the recovery process is rather slow and depends mainly on future deposition reduction; e.g. it is very likely that realisation of Gothenburg Protocol will not result in total reversal of changes within the nearest 30 years.

References

Cosby, B.J., Ferrier, R.C., Jenkins, A., Wright, R.F., 2001; Modelling the effects of acid deposition: refinements, adjustments and inclusion of nitrogen dynamics in the MAGIC model. Hydrology and Earth System Sciences, 5(3), 499-517

Henriksen, A., Mill, w., Kot, M., Rzychon, D., Wathne, B.M., 1992; Critical loads of acidity to surface waters: a case study from the Polish Tatra Mountains. 34 pp. Acid Rain Research Report 29/1992.

Kopacek, J., Cosby, B.J., Majer, V., Stuchlik, E., Vesely, J., 2003; Modelling reversibility of Central European mountain lakes from acidification: Part II – the Tatra Mountains. Hydrology and Earth System Sciences, 7 (4), 510-524.

9. Dynamic biological response models – an overview

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Monitoring programmes have over the last ten years shown increasing recovery in water chemistry following reduction in sulphur emission (Stoddard et al. 1999, Skjelkvåle et al. 2003). Improvement in water quality has also to some extent resulted in recovery of acid sensitive fauna (Raddum et al. 2001, 2004). It has for long existed response models for ground water, evaluating water quality following different sulphur reduction scenarios over time. Such models can also give information about the water quality before the start of acidification. One common model for such estimates is the MAGIC model (Cosby et al. 1985). At present a few biological models for recovery of aquatic fauna has been developed, but testing and verifications of such models is difficult since response data are in an early face. Below we will give information about two models for recovery of invertebrates and one model for recovery of fish populations.

Recovery of biological communities will follow different ways depending on the reason for the damage and for how long time the damage has existed. It is important to discriminate between two main reasons for biological damages:

1) Those where no toxicity is involved (eutrofication, habitat disturbances, harvesting etc.)
2) Those where toxicity is the main reason for the damage

Acidification belongs to type 2 and recovery following removal of the toxic water implies reappearance of sensitive species, which have to be adopted in the ecosystem. The response models of biology should therefore include critical load and tolerance of sensitive fauna followed by biotic response models.

A comprehensive dynamic biological response model is described by Yan et al. (2003). This model involves dispersal and population growth models, with feedbacks between model modules etc, see Framework 1 and 2 (Figure 1 and 2, from Yan et al op. cit.). Framework 1 shows the main processes in the ecological recovery of species and actions of management. When a manager has selected a species, he has to choose a recovery target, which implies identification of lethal water quality. This requires monitoring of the water quality to see if the quality is good enough. If the answer is yes the next question is if colonist are available and that the population size is viable. Dispersal models can now be run. The presence or absence of confounding factors for the development of the species communities will determine the need for running modified population growth models or not. The output from the growth models has to be compared with recovery targets.

Framework 2 highlights the biological interactions and necessary research and management actions (Figure 2). The arrows indicate principal flow of effects and feedbacks as well as flow of information. One starts with choosing species and their lethal water quality thresholds and can then select recovery targets. This can imply that S emissions must be reduced or that lakes

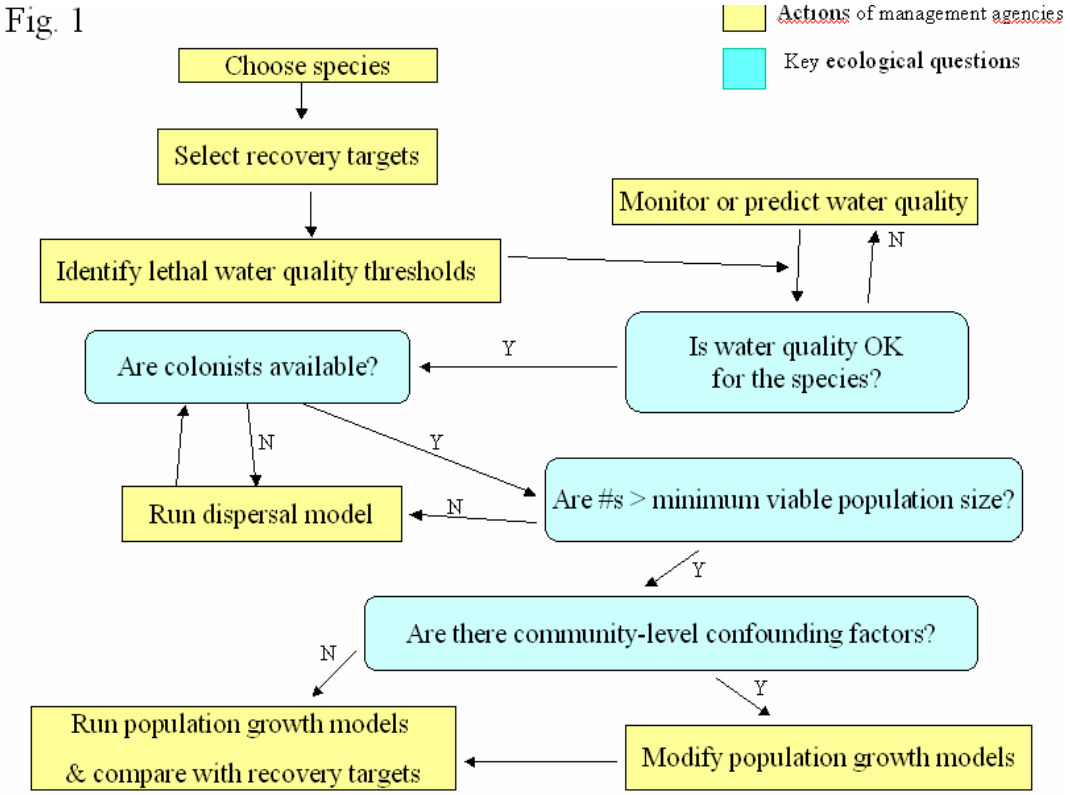

Figure 1. Framework 1. A flow diagram of processes in the ecological recovery of species from acidified localities. Yellow boxes indicate actions of management agencies, blue boxes indicate questions about key ecological processes (Yan et al. 2003).

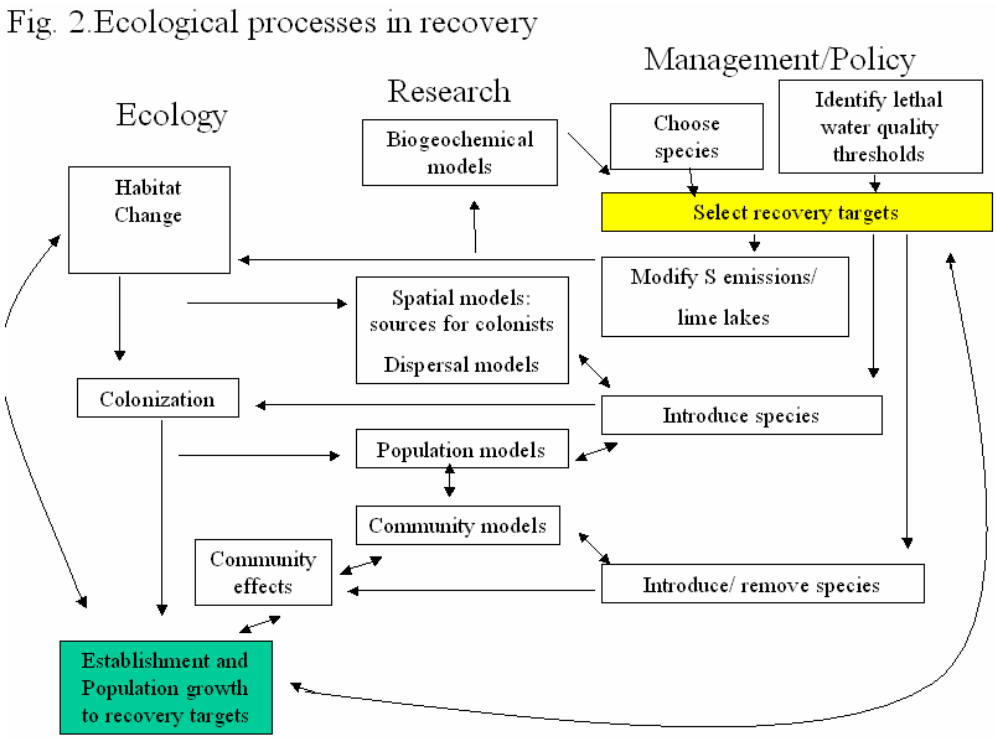

Figure 2. Framework 2. The schema highlights the ecological processes in recovery (from Yan et al. 2003). Arrows indicate the principal flow of effects.

have to be limed. Liming can change the habitat. Species can be introduced or they can reappear naturally. This implies run of spatial and dispersal models where feedbacks to the introduction of species will be in focus. The colonization will depend on this. The run of population models and community models interact both with introduction and removal of species, which in the end will give the community effect. Establishment and population growth to recovery target can in turn give feedbacks on the habitat and biotic effects on other parts in the ecosystem.

The purpose of Yan et al. (2003) is not to build a recovery model, but to produce a conceptual framework of the recovery process after acidification. For making dynamic recovery models for biology it is stressed that the focus must be on the identifications of key underlying ecological processes.

MIRACLE

The MIRACLE model (Modelling Invertebrate Recovery of ACidified Lotic/Lentic Ecosystems) by Raddum and Fjellheim (2002) assumes selected critical stages in recovery of sensitive invertebrates. It is coupled to the groundwater model MAGIC (Cosby et al. 1985, Cosby et al. 2001).

The recovery of sensitive species in lakes and rivers will be different. More uncertainty in the process is connected with the development in lakes, while recovery in streams is more predictable. In the following we will go through needed information for modelling recovery of invertebrates in running water.

For the modelling, we need information about the improvement in water chemistry (starting and endpoint), distance to source localities (refugia) of sensitive species, inter - and intra watershed dispersal, information about the life cycle/fecundity and water chemistry variation in relation to critical limits (responds curves) of the species. Species composition of key invertebrates is available from a large number of sites in different watersheds in western and southern Norway. From this database we have a trainingset of invertebrates which can be used for calculating the probability of recording a species/community in relation to water chemistry. It is planed to do such estimates during 2005.

The recovery of sensitive invertebrates, in a logical development, will consist of the following main stages:

1) Time needed to achieve the target water chemistry after reduction of S deposition, MAGIC estimations. (The endpoint of water chemistry can be either above, vary around or be below the critical limits, of species).

2) Time needed for dispersal of the species to the watershed (inter watershed dispersal)
This will depend on the organism, distance to source localities, pathways for the species etc.

3) Time needed for occupation of suitable sites (internal dispersal). When a species is established at a site, pioneer community, it need time to disperse to all suitable habitats inside a lake or a river system.

4) Time needed for reaching a stage of natural fluctuations. When the species has occupied their potential habitat it will be feedbacks on other species, the habitat etc. as pointed out by Yan et al. (2003) and the recovery is now subjected to the biotic interactions, species/communities growth models and the ecological balance in general.

The initiating parameters are the improvements in water quality, which can be predicted through a groundwater model like MAGIC. The chemical starting point is very important, as this will determine the fauna before the recovery starts. Serious damaged ecosystems, which contain very tolerant species, will recover more slowly than systems still holding some sensitive species. The chemical endpoint and expected yearly variation will give information about the time needed to achieve the target chemistry and consequently an estimate of the starting time for sensitive fauna to recover. At this point chemistry and seasonal variation in water quality should be compared with the critical limits of different species. The water quality can be:

i) below the critical limits of the species and excluding them,
ii) vary around the critical limit, giving an on/off situation of species,
iii) or above the critical limit, allowing sensitive species to recover.

The different situations are illustrated in Figure 3.

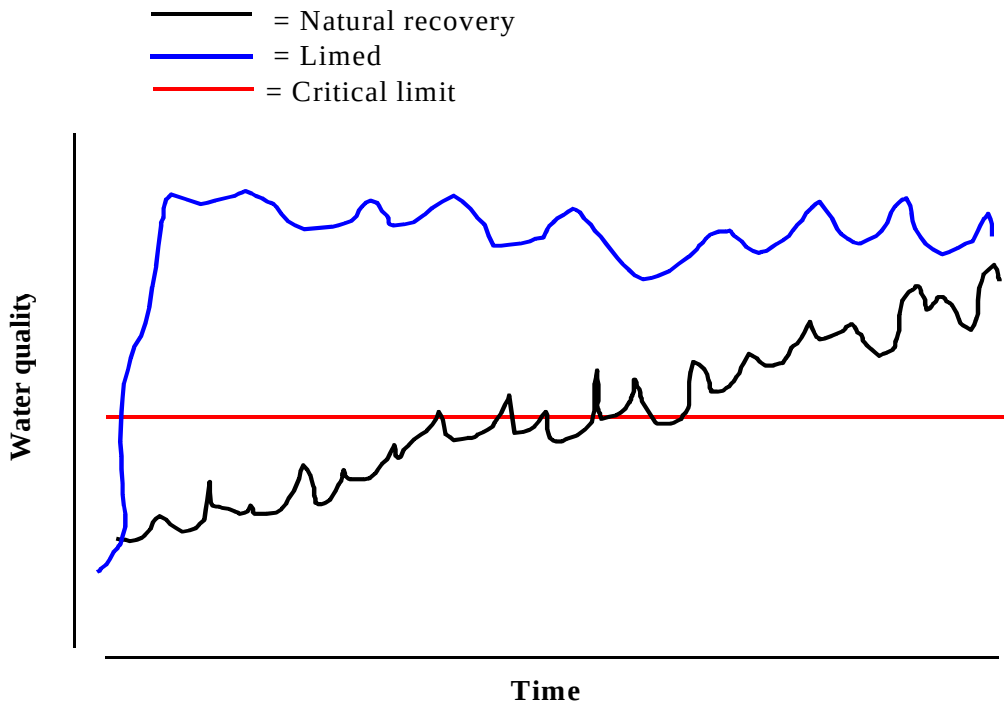

Figure 3. The difference in water quality improvements between liming and natural recovery. Liming gives an immediate water chemistry endpoint with variations. Sensitive species with critical limits below the target water chemistry can recolonize. The natural improvement in water chemistry goes slowly and the improvements will pass through a series of critical limits.

Reappearance of sensitive species, stage 2, depends on the species dispersal ability, distance to source populations and inter watershed dispersal. Fast dispersal occurs among winged insects. Slow dispersal is among invertebrates with the whole life cycle in water like molluscs, oligochaeta etc. The lowest dispersal rate is probably among organisms fulfilling their life cycle in deep waters. However, for the different types there are variations. In lotic systems recovery from refugia can occur immediately through drift of organisms. Up stream dispersal is established for winged insects through the recolonization cycle.

When the pioneer individuals have been established, the intra watershed dispersal starts. Again winged insects can spread out rapidly both down – and up stream, while molluscs etc. have to move or be transported in water or sometimes by birds through air. The drift of invertebrates in

running water secures a rapid dispersal downstream. When all or most of the suitable habitats have been occupied by the species, we define stage 3 as finished.

Time needed for reaching the stage of natural fluctuations, stage 4, is difficult to predict or measure. However, this is of interest in the recovery process, but will mostly depend on biological interactions, se Framework 2 of Yan et al. (2003). However, for the most common and wide spread species in running water the time needed to achieve this stage seem to be close to that of stage 3. This is based on empirical data from a large number of liming projects. For other species this will be difficult to define and measure, especially among species with many generations per year and species vulnerable to predation. A restoration of a fish community can thus interact at least on the abundance of species of invertebrates.

A summary of the stages is illustrated in Figure 4.

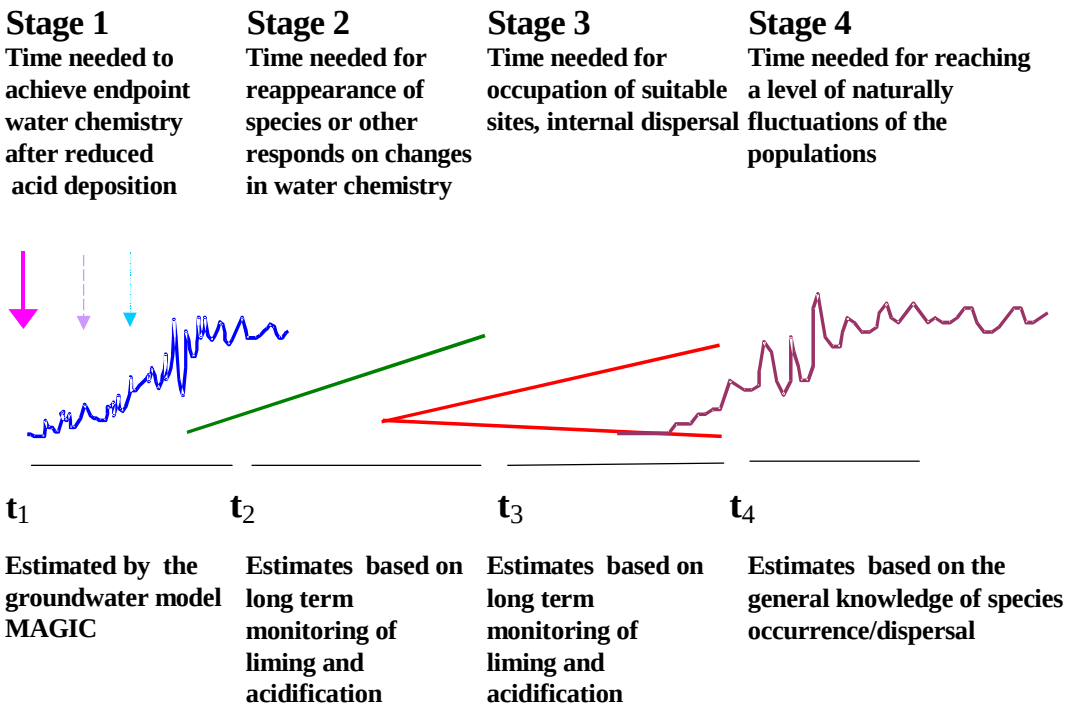

Figure 4. Main logical steps (stage 1-4) in recovery of invertebrates in running water.

For continuously limed watersheds the time lag in recovery follow the steps in Figure 4. The time needed for each step can be measured and the necessary time for reaching stage 4 can and have been measured for many watersheds.

Figure 5 show a MAGIC estimation of ANC for Lake L. Hovvatn, Southern Norway (after Hindar 2004). The lowest ANC was both estimated and measured in the 1970 ties. The chemical recovery will almost stop around 2020, about 50 year after the start. ANC will, however, not reach previous levels. In this case the water quality will be far below the critical limit of most sensitive species and recovery of sensitive biology will probably not take place.

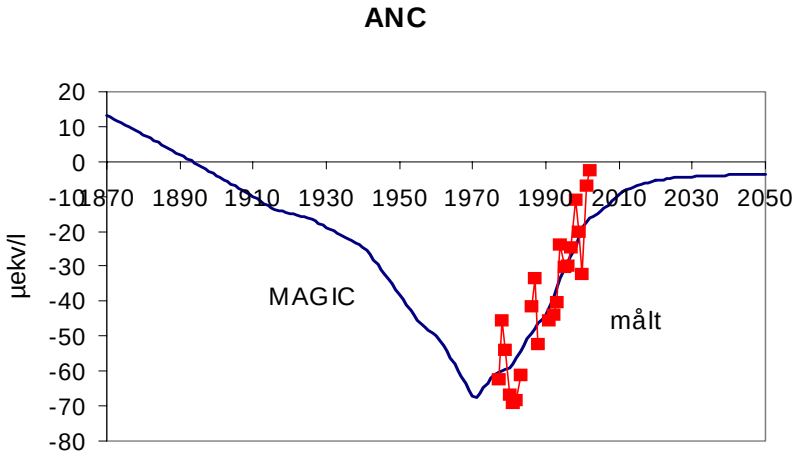

Figure 5. MAGIC estimate (blue) and measured values (red) of ANC in Lake L. Hovvatn, Southern Norway (Hindar 2004).

Figure 6 shows time needed for reappearance of different sensitive species, stage 2, and occupation of suitable habitats, stage 3, in the limed part of River Audna (from Raddum and Fjellheim 2003).

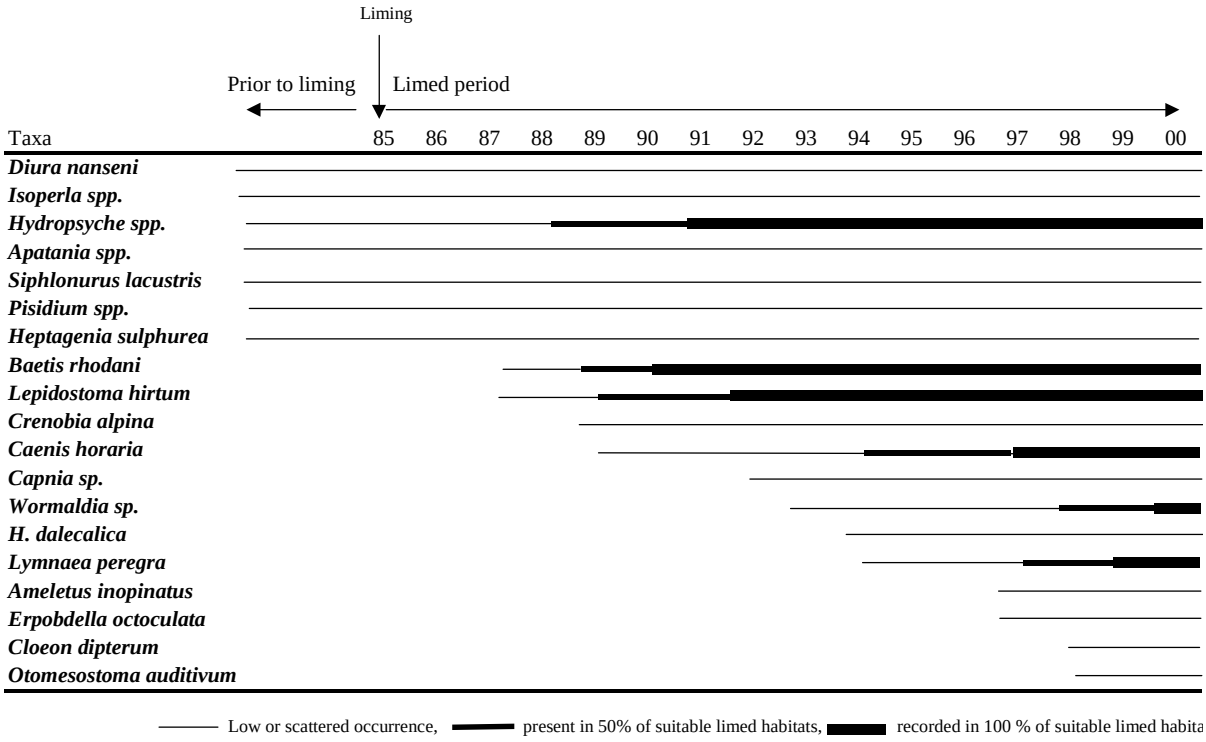

Figure 6. Recovery of sensitive species after liming of River Audna.

Some species were not completely extinct prior to liming. Of these the three species Hydropsyche spp. occupied all habitats 6 year after liming. The species not recorded in River Audna before liming, recolonized over a period of two – thirteen years, stage 2. Stage 3 was for the most common species finished after 5 years. If this knowledge is transferred to natural recovery a possible outcome could be:

- Chemical recovery = 30 – 50 years

- Reappearance of sensitive organisms = 2 – 10 years after chemical recovery above the critical limit of species
- Occupation of suitable habitat = 5 years

This indicates that several decades are necessary for recovery of sensitive species. The recovery will depend on how fast and to which extent water chemistry will recover.

FIB-model

The FIB-model (”Fisk I Bedring” or ”Fish in Recovery”) is a new model for fish population recovery (Rosseland 2004, Rosseland et al. 2004). The FIB-model tries to visualise the expected time for a defined recovery, where the goal is to have a “healthy fish population”.

“What is a healthy and recovered fish population?”

ICP-WATERS as well as national monitoring and action plan for liming depends on a definition of what we mean with a re-established and healthy fish population. For some people, just to observe that fish reappear in a lake can be enough to declare recovery. Monitoring of fish population in a management program normally uses catches by standard fishing gear, which can be quantified to a certain number- or weight of fish based on “Catch per Unit Effort”, CUE. The FIB-model, however, defines a “healthy fish population” as being sustainable, and with all expected year classes represented, typical for its geographical and climatic zone. The FIB model therefor use a more qualitative method based on ageing, where the occurrence of all expected year classes is the final goal.

Up to now, the existence of fish as well as the size of the catch, have dominated in the debate of successful recovery. As such observations now are common in lakes close to areas that have been limed for many years, this has led to the discussion of reducing the mitigation projects. However, how can we separate an effect of successive and natural reproduction from the migration and invasion of fish from upstream or downstream-cultivated areas? Has natural reproduction really started? Only a few well-documented cases of natural reproduction exist so far.

In the FIB-model, female fish has the key role. Each lake will be defined to have a typical spawning age, as well as a maximum age for females only. The mathematical principle behind the model is the ”Fibonacci-numbers”. The model give value to the existing year-classes in a lake or stream, starting with the value 1 for the oldest year class and ending with the highest value for the youngest year class which can be monitored in the lake, either by electro fishing or gillnets/trap-nets. For each lake, one will have to determine the oldest possible year class that exist or can have existed there, and then back-calculate to the youngest. In the present visualisation, we have assumed repeated spawning every year until maximum age, despite the fact that in extreme environments like in alpine and Arctic areas, several resting years between spawning do occurr.

At the start of a simulation, we define a set of year classes to be represented. This can be all or a few, representing from “a healthy” to slightly or strongly affected population. The model can simulate stocking, liming, episodic mortality (due to acid episodes, freezing of spawning areas, drought etc.), and then demonstrate the time until all year classes will be represented.

In Table 1, the lake simulation starts with the year classes 7 and 8. The female age at first spawning is 4 years, with a maximum age of 8 years. From start, successful reproduction occurs when spawners are represented. Table 1 and Figure 7 illustrate that it will take 14 years to reach a stage where all year classes are represented.

Table 1. A FIB-model run for a lake with maximum fish age 8 years, and a female spawning age of 4 years. The starting point is a strongly affected population consisting of the two oldest year classes, which spawn successfully from start.

Age classes	8	7	6	5	4	3	2	1	0	Sum
Fibonacci numbers	1	1	2	3	5	8	13	21	34	88
Year										
0	1	1								2
1	1								34	35
2								21	34	55
3							13	21		34
4						8	13			21
5					5	8				13
6				3	5				34	42
7			2	3				21	34	60
8		1	2				13	21	34	71
9	1	1				8	13	21	34	78
10	1				5	8	13	21	34	82
11				3	5	8	13	21	34	84
12			2	3	5	8	13	21	34	86
13		1	2	3	5	8	13	21	34	87
14	1	1	2	3	5	8	13	21	34	88

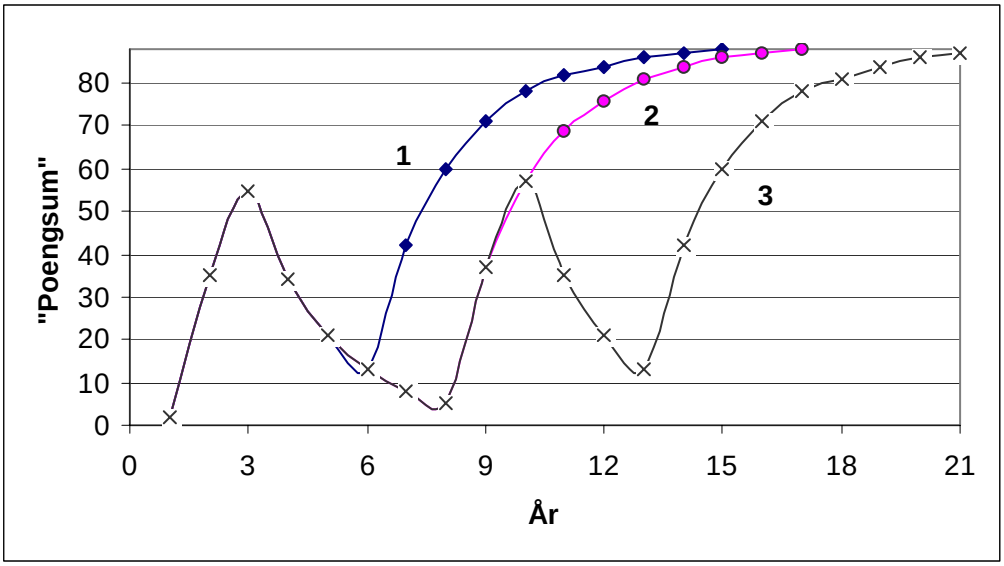

Figure 7. A FIB-simulation of a lake with the two oldest year classes represented (7 and 8 years) with successful reproduction from start. Age at first spawning is 4 years. After 14 years, all year classes are represented (1, Table 1). Unsuccessful reproduction in year 6 and 7 results in a 16 years recovery (2), while another reproduction failure in year 10 increases the recovery period to 21 years. (After: Rosseland et al. 2004)

A lake undergoing natural recovery, or being limed, can experience single years or repeated years with reproduction failure due to episodic marginal and toxic water quality. In case of the lake in Table 1 and Figure 7, a reproduction failure in year 6 and 7, will result in 16 years of recovery (2), whereas another failure in year 10 results in a recovery period of 21 years (3).

Another lake, with maximum age of 10 years, is shown in Figure 8. Spawning age for females is 6 years, and the two oldest year classes remaining have successful spawning from start. Even with no episodes of toxic water quality, the population will need 26 years to reach the stage where all year classes are represented, Figure 8.

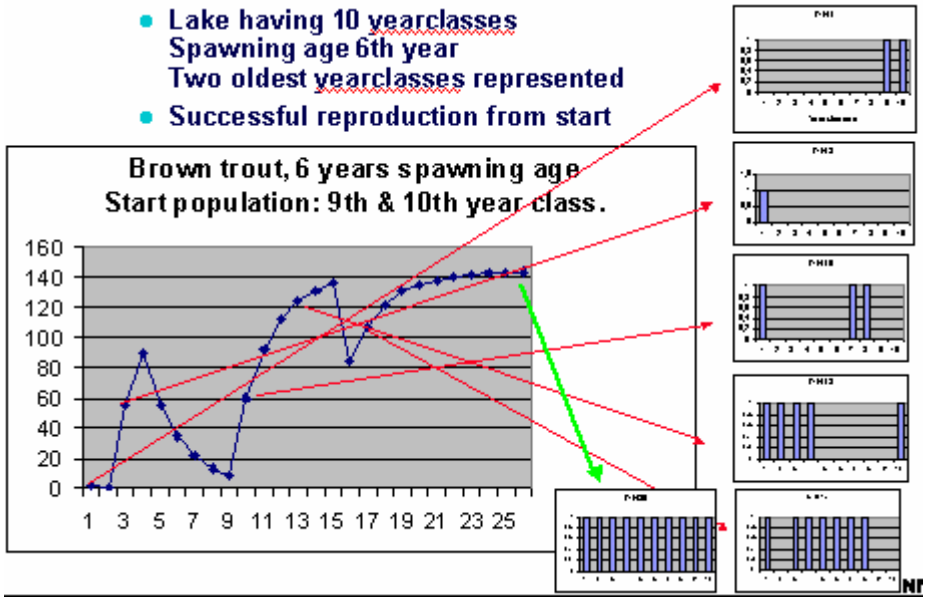

Figure 8. A FIB-simulation of a lake starting with the two oldest year classes, 9 and 10 years. First spawning occurred at age 6, and where successful from start. The time to reach a full year class representation was 26 years. The year-class representation at different stages in the recovery process is illustrated. (After. Rosseland 2004).

In alpine and Arctic areas, fish can reach ages of more than 30 years. In such cases, as well as during recovery from acidification after a lake has reach an ANC_{limit} for reproduction, the time lag of biological recovery will be decades.

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10. HCB, PCB's and DDT's concentrations in fish muscle from 2 alpine lakes (Oncorhynchus mykiss) and 4 alpine rivers (Salmo trutta fario) in the Canton of Ticino, Switzerland

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Introduction

Persistent organic pollutants (POP's) are chemical substances that persist in the environment, bioaccumulate through the food web and pause a risk of causing effects to human health and the environment (UNEP definition). Nowadays, the production and the release of POP's into the environment has been restricted or banned in many developed countries (Aahrus protocol), but in some developing countries their usage is still allowed or unregulated. The discovery of the occurrence of relatively high concentrations of POP 's in polar regions, considered as pristine areas, a few decades ago, was at first surprising. The transport mechanism was explained by Wania and Mackay (1993) in the 90ties: as a result of the positive correlation between vapour pressure and temperature and dependent on their volatility, POP's can be transported for long distances through the atmosphere from warm (low latitude) to cold regions (high latitude). This latitudinal fractionation of organic compound is known as global fractionation process. Since temperature decreases not only with latitude but also with altitude it was expected that accumulation of POP's occurs also in mountain regions. This hypothesis has been confirmed by numerous publications: POP's in remote mountain regions could be detected in atmospheric deposition (Carrera et al. 2002, Fernanández and Grimalt 2003), in snow (Blais et al. 1998, Carrera et al. 2001, Fernanández and Grimalt 2003), in surface waters (Fernanández and Grimalt 2003, Galassi et al. 1997, Vilanova et al. 2001), in sediments (Fernanández and Grimalt 2003, Galassi et al. 1997, Grimalt et al. 2001, Grimalt et al. 2004), in soils (Grimalt et al. 2004), in fish (Catalan et al. 2004, Grimalt et al. 2001, Hofer et al. 2001, Rognerud et al. 2001, Schmid et al. 2005, Vives et al. 2004) and in zooplankton (Galassi et al. 1997).
In order to quantify the contamination of DDT's , PCB's and HCB's in the Swiss Alps, we determined its concentrations in fish muscle from two alpine lakes and four alpine rivers. We compared our results with literature data and discussed their possible origin.

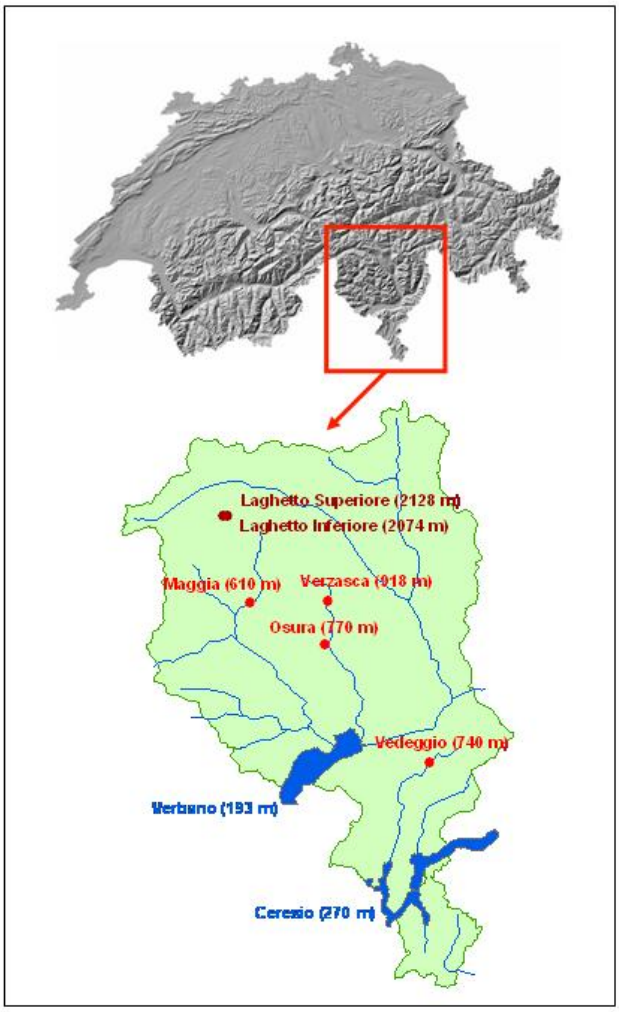
Study site

The two lakes (Laghetto Superiore and Laghetto Inferiore) and the four rivers (Verzasca, Osura, Maggia and Vedeggio) investigated in this study are situated in the Central Alps in the Canton of Ticino in Switzerland. Their coordinates, altitudes and catchment areas are presented in table 1, while their location is shown in Figure 1. Laghetto Superiore and Laghetto Inferiore are connected by the outflow of Laghetto Superiore. Laghetto Superiore does not have any surface water inflow and Laghetto Inferiore has an outflow that belongs to the catchments area of the river Maggia. All sampling sites are situated in remote areas far from local pollution sources. The lakes are oligotrophic and low in total organic carbon and acid neutralizing capacity.

Table 1: General features related to the sampling sites.

Sampling sites	Coordinates		Altitude	Catchments area	Lake Area	Lake maximum depth
	North	East				m
			m asl	ha	ha	
Verzasca	46°21’27’’	8°47’35’’	918			
Osura	46°17’48’’	8°47’07’’	770			
Maggia	46°21’20’’	8°38’11’’	610			
Vedeggio	46°07’53’’	8°59’40’’	740			
Laghetto Superiore	46°28’36’’	8°35’08’’	2128	178	5.2	29
Laghetto Inferiore	46°28’37’’	8°35’38’’	2074	122	8.3	33

Figure 1: Sampling sites in the Swiss Canton of Ticino.



Sampling procedure

In lakes fish were caught by angling, while in rivers they were captured by electrofishing. Rainbow trout (*Oncorhynchus mykiss)* is the dominant fish species in lakes, while in streams brown trout (*Salmo trutta fario*) prevails. Sampling occurred twice a year (summer and autumn) in 2000 and 2001 and only once a year (autumn) in 2002 and 2003. All fish were measured for length and weight and aged by scale analysis.

Chemical analyses

For every sampling site and sampling date a homogenized sample of fish muscle was prepared. Organochlorine compounds were extracted and isolated as described in Steinwandter (1985). The so obtained extracts were first purified by gel chromatography and then purified further and fractionated on a silicagel column. The extraction efficiency was determined by addition of a known amount of PCB-167. Organochlorine compounds were then determined by gas chromatography with electron capture detection and in case verified by MS. A DB-5 column was used with hydrogen as the carrier gas and PCB-198 was used as an internal standard. The lipid content was determined gravimetrically after extraction with cyclohexane: ethylacetate.

Results

Fish population characteristics

The sampled fish number and the their average weight, length, conditioning index (C.I), age and lipid content are shown in Table 2. Between 2000 and 2003 the average number of fish sampled in rivers was 14 (max. 19 and min. 10) and 15 (max 22 and min 4) in lakes. The average fish weight was slightly higher in rivers (97 g, max. 175 g and min. 38 g) than in lakes (75 g, max. 172 g and min. 33 g). Fish length, conditioning index, age and lipid content were similar in rivers and in lakes. Mean length, conditioning index, age and lipid content were 21 cm (max. 27 cm, min. 16 cm) and 20 cm (max. 26 cm, min. 15 cm), 1.00 (max. 1.27, min. 0.76) and 0.96 (max. 1.26, min. 0.62), 39 month (max. 69, min. 21) and 36 month (max. 54, min. 19), 1.5% (max. 2.3%, min. 1.1%) and 1.2% (max. 2.3%, min. 0.7%) for rivers and lakes, respectively. The percentage of fish having a conditioning index lower than 1 was 54% in rivers and 73% in lakes, indicating a not ideal physical state especially in lakes.

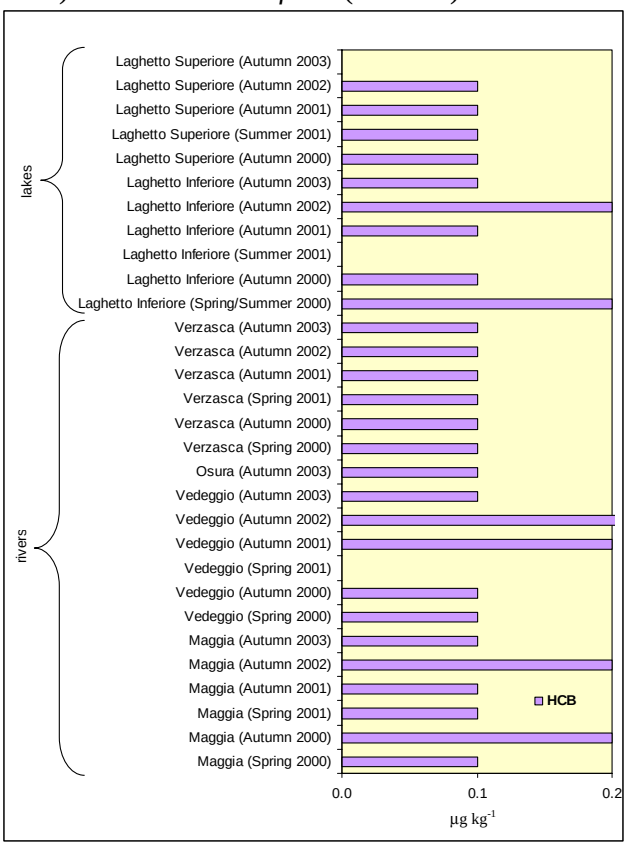
Table 2: Number of fish and average and standard deviation of weight, length, conditioning index (C.I) and age of the fish sampled in the two lakes and the rivers between 2000 and 2003.

		Laghetto Inferiore	Laghetto Superiore	Verzasca	Osura	Lavizzara	Vedeggio
Spring/ Summer2000 2004we 2000	Fish number	4		13		13	10
	Weight (g)	81.7±29.1		82.4±16.3		110.8±15.0	86.6±13.1
	Length (g)	19.7±1.5		20.8±1.2		22.4±0.7	20.8±1.2
	C.I.	1.03±0.15		0.91±0.06		0.98±0.07	0.96±0.08
	Age (month)	43±1		39±6		38±3	39±7
	lipid (%)	2.3		1.4		1.3	2.0
Autumn 2000	Fish number	12	15	14		19	12
	Weight (g)	96.2±22.4	103.3±26.0	90.3±16.8		110.8±23.9	103.7±25.2
	Length (g)	21.3±1.6	21.5±2.0	20.8±1.2		22.0±1.5	21.3±1.6
	C.I.	0.98±0.04	1.03±0.08	1.00±0.10		1.03±0.07	1.06±0.06
	age	40±6	40±6	39±6		37±7	36±6
	lipid (%)	1.1	1.8	1.2		1.5	1.4
Spring/ Summer 2001	Fish number	10	15	17		18	13
	Weight (g)	63.0±30.0	86.6±20.1	64.9±11.5		95.2±16.8	124.3±28.8
	Length (g)	18.9±3.1	21.3±1.7	19.0±1.3		21.3±1.3	23.3±1.7
	C.I.	0.88±0.09	0.88±0.09	0.95±0.06		0.98±0.09	0.96±0.09
	age	39±8	37±8	40±7		35±8	39±7
	lipid (%)	0.8	1.1	1.3		1.5	1.7
Autumn 2001	Fish number	12	14	17		13	11
	Weight (g)	43.8±11.5	86.6±39.5	77.2±12.2		108.1±21.9	105.9±20.8
	Length (g)	16.3±1.3	20.3±2.8	19.9±1.1		22.2±1.5	19.2±1.3
	C.I.	0.99±0.05	0.97±0.05	0.97±0.07		0.98±0.08	1.01±0.04
	age	33±0	33±9	40±9		42±8	43±8
	lipid (%)	0.9	0.9	1.4		1.6	1.6
Autumn 2002	Fish number	22	19	14		11	15
	Weight (g)	76.3±7.8	62.2±23.0	92.9±25.4		135.5±21.8	94.0±22.2
	Length (g)	19.6±0.9	19.2±2.3	20.7±1.9		23.0±0.9	20.6±1.7
	C.I.	1.02±0.09	0.85±0.09	1.03±0.09		1.11±0.13	1.06±0.07
	age	32±5	33±6	40±8		40±6	35±5
	lipid (%)	1.5	0.7	1.4		2.3	1.8
Autumn 2003	Fish number	17	22	15	15	15	14
	Weight (g)	72.4±24.5	56.5±8.4	106.2±22.6	70.7±24.1	108.5±17.5	70.1±25.6
	Length (g)	19.2±2.3	18.3±1.3	22.5±1.9	19.0±2.1	21.8±1.0	18.7±1.9
	C.I.	0.99±0.09	0.92±0.11	0.93±0.07	1.00±0.08	1.04±0.08	1.03±0.10
	age	31±8	31±5	48±10	40±8	38±6	33±8
	lipid (%)	1.3	0.8	1.1	1.2	1.4	1.6

HCB, DDT's and PCB's concentrations in fish muscle

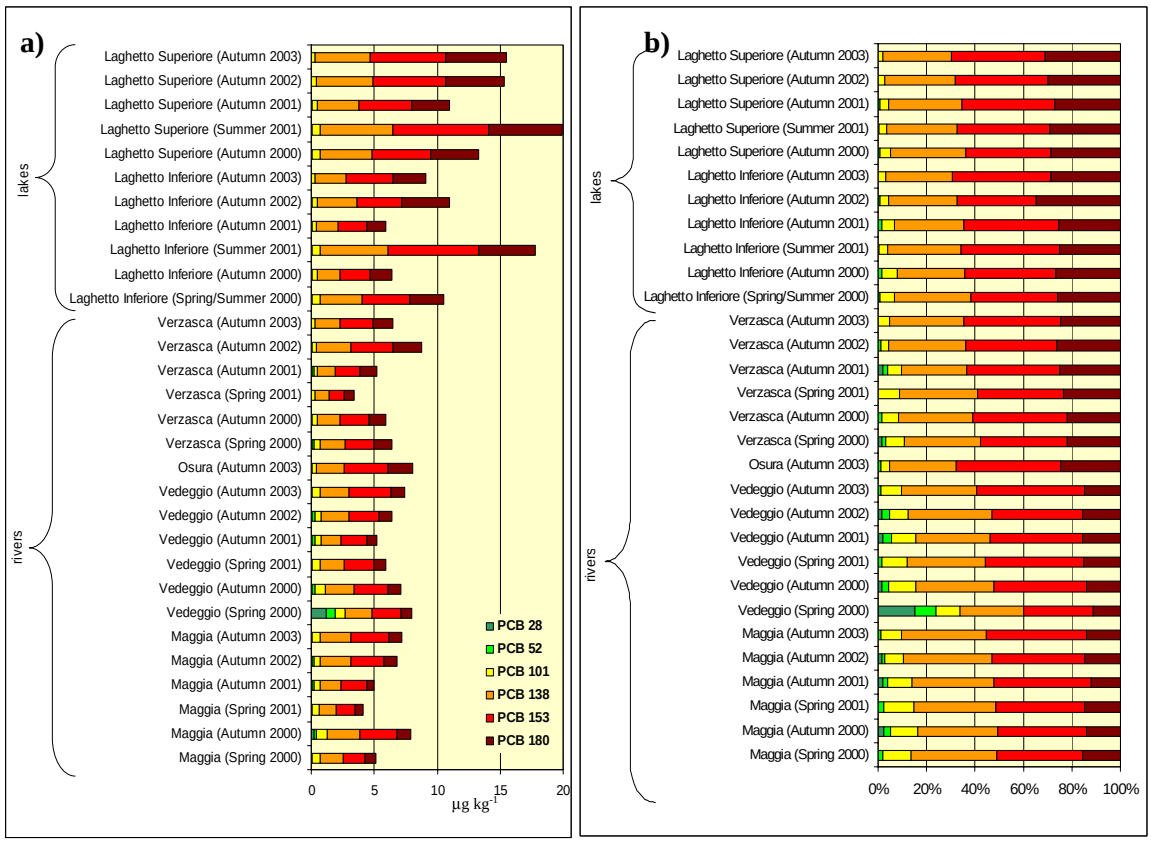
HCB concentrations in fish muscle of alpine rivers and lakes were low and ranged between 0.1 and 0.2 µg g^{-1} (Figure 2).

Figure 2: HCB concentrations in µg kg^{-1} wet weight in fish muscle of *Oncorhynchus mykiss* (in lakes) and *Salmo trutta fario* (in rivers) between 2000 and 2003.



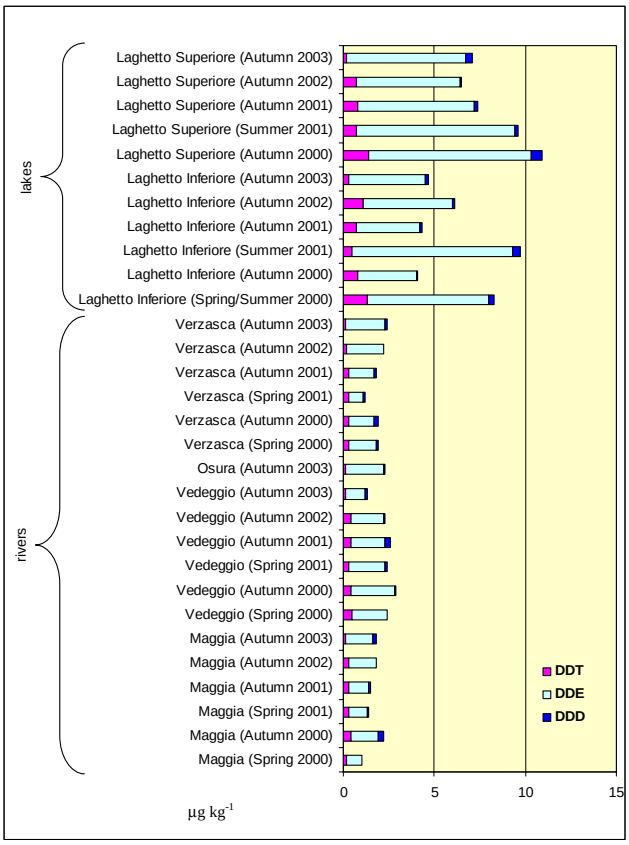
Total PCB concentrations ranged between 6 and 20 µg g^{-1} in lakes and between 3 and 9 µg g^{-1} in rivers (Figure 3a). Average concentrations were 15 µg g^{-1} in Laghetto Superiore, 10 µg g^{-1} in Laghetto Inferiore and 6 µg g^{-1} in the rivers Maggia, Vedeggio and Verzasca. Less volatile cogeners PCB 180, PCB 153 and PCB 138 prevailed either in lakes than in rivers (Figure 3b): in lakes the distribution was on average 28% PCB 180, 38% PCB 153, 29% PCB 138, 4% PCB 101, 1% PCB 52, 0% PCB 28 and in rivers 18% PCB 180, 38% PCB 153, 32% PCB 138, 8% PCB 101, 2% PCB 52, 2% PCB 28.

Figure 3: PCB's concentrations in µg kg^{-1} wet weight (a) and PCB's relative concentrations (b) in fish muscle of *Oncorhynchus mykiss* (in lakes) and *Salmo trutta fario* (in rivers) between 2000 and 2003.

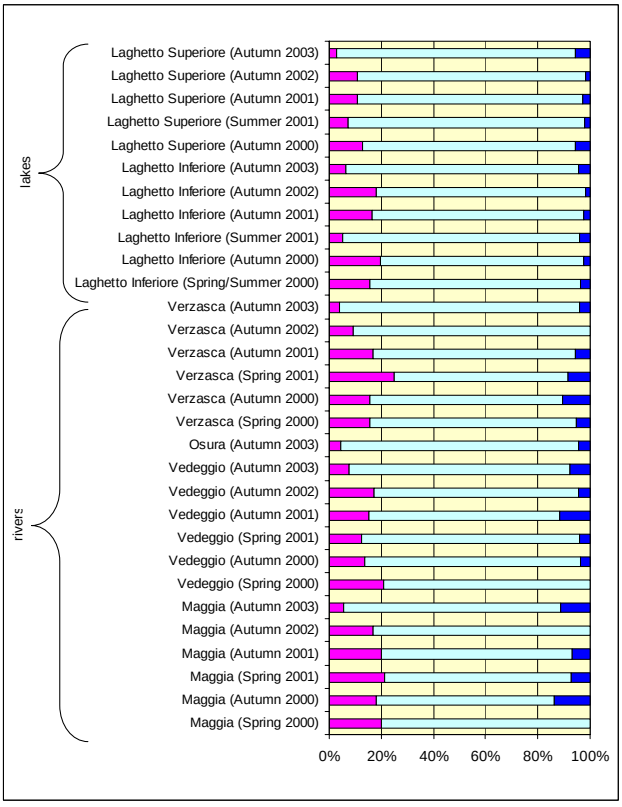


Total DDT concentrations ranged between 2 and 11 µg g^{-1} in lakes and between 1 and 3 µg g^{-1} in rivers (Figure 4a). Average concentrations were 8 µg g^{-1} in Laghetto Superiore, 6 µg g^{-1} in Laghetto Inferiore and 2 µg g^{-1} in the rivers Maggia, Vedeggio and Verzasca. DDE prevailed over DDT and DDD (Figure 4b): in lakes the distribution was on average 85% DDE, 11% DDT, 3% DDD and in rivers 80% DDE, 15% DDT, 6% DDD.

Figure 4: DDT's concentrations in µg kg^{-1} wet weight (a) and DDT's relative concentrations (b) in fish muscle of *Oncorhynchus mykiss* (in lakes) and *Salmo trutta fario* (in rivers) between 2000 and 2003.



a)



b)

Discussion and conclusions

Comparing our DDT and PCB data from the alpine lakes with those from alpine rivers it appears that concentrations in rivers were smaller. Unfortunately, this observation is difficult to interpret because rivers and lakes are two completely different ecosystems (different food web, sediments, morphology, temperature, …). However, the evidence of accumulation of contaminants like HCB, PCB's and DDT's in fish muscle originating from alpine rivers and lakes, far from local pollution, can in both cases only be explained by atmospheric deposition (cold condensation).

HCB, PCB's and DDT's concentrations in fish muscle from Laghetto Superiore and Laghetto Inferiore are in the same range as reported for other European mountain lakes (Grimalt et al. 2001, Hofer et al. 2001. Rognerud et al. 2001, Schmid et al. 2005, Vives et al. 2004). In particular, a good correspondence could be found for DDE concentrations predicted from the positive correlations between concentrations and latitude in Hofer et al. 2001 and with the concentrations of HCB, DDE and PCB predicted from the positive correlations between concentrations and altitude in Grimalt et al. 2001. Also the speciation of the before mentioned pollutants corresponds to literature data (Grimalt et al. 2001, Vives et al. 2004).

Schmid et al. 2005 concluded in their study that concentrations of PCB's in fish from water systems with (alpine lakes) and without input from water treatment plants (Swiss plateau lakes) are similar, indicating that the input to Swiss water systems is mainly caused by atmospheric deposition. We also compared our data from the alpine lakes Laghetto Superiore and Laghetto Inferiore with data from Lago Maggiore (Cipais, 2003), a close by situated lake (Figure 1), whose chemistry is influenced by inputs from water treatment plants and by DDT, Hg and As polluted groundwater originating from a Italian contaminated site, which is now in remediation. We compared fish from alpine lakes (*Oncorhynchus mykiss*) with fish species from Lago Maggiore with similar lipid content (*Scardinius erythrophthalmus, Leuciscus cephalus, Perca fluviatilis*).

HCB concentrations in fish from Lago Maggiore were on average 1 $\mu g\ kg^{-1}$ and varied between 1 $\mu g\ kg^{-1}$ and 17 $\mu g\ kg^{-1}$ and were therefore a factor 10 to 100 higher than in Laghetto Superiore and Laghetto Inferiore. HCB sources in the Lago Maggiore area may be the reason for this difference.

The sum of the PCB cogeners in Lago Maggiore were in the same range as measured in fish from Laghetto Superiore and Laghetto Inferiore and was on average 15 $\mu g\ kg^{-1}$ and varied between 3 $\mu g\ kg^{-1}$ and 49 $\mu g\ kg^{-1}$. Different than in alpine lakes was the speciation of PCB cogeners in Lago Maggiore. In fact, more volatile cogeners were more abundant in Lago Maggiore: 4% PCB 180, 19% PCB 153, 34% PCB 118, 15% PCB 101, 17% PCB 52, 11% PCB 28. Since more volatile PCB cogeners normally tend to accumulate at higher latitude (Wania and Mackay, 1993), our results suggest that there may be local pollution sources of PCB in the area of Lago Maggiore.

DDT concentrations in fish muscle from Lago Maggiore were a factor 3-4 higher than concentrations in Lago Superiore and Lago Inferiore. They were on average 23 $\mu g\ kg^{-1}$ and varied between 5 $\mu g\ kg^{-1}$ and 43 $\mu g\ kg^{-1}$. The speciation was also different: DDE was as important as DDD (12% DDT, 48% DDE, 41% DDD), while in alpine lakes DDE dominated. The higher DDT concentrations in Lago Maggiore are most certainly due to the influence of the contaminated site, mentioned before and the presence of important amounts of DDD may be caused be anaerobic degradation of DDT in the soil or in the sediments around and in Lago Maggiore (Cipais, 2003).

The fact, that the concentrations of HCB, PCB and DDT and the speciation of PCB and DDT in alpine lakes were in the same range as reported in literature for other European mountain lakes and different from what found in Lago Maggiore, suggests that local atmospheric pollution sources are neglectable in determining the HCB, PCB and DDT concentrations in fish from close by situated alpine lakes.

Acknowledgments
We are thankful to the Office of fishery and hunting of the Canton of Ticino for the collection and preparation of the fish and to the Laboratory of the Canton of Ticino for POP's analyses in fish.

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11. Trace Metal Measurements in the Italian ICP Waters Sites: Methodology and Preliminary Results

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Summary

The CNR Institute of Ecosystem Study (CNR ISE) has since 1995 acted as the National Focal Centre in Italy of the ICP Waters project, coordinated and directed by the International Environmental Protection Department of the Ministry of the Environment. In 1994, in addition to the continued monitoring of water chemistry at the ICP Waters sites, it launched a study on metal concentrations. The study was designed to cover lake and river waters, but was extended to atmospheric depositions with the aim of distinguishing between the portion of metals deriving from transport and the portion originating from weathering in the watershed. Atmospheric deposition analyses were performed in collaboration with researchers of the ARPA (Regional Environmental Protection Agency) in Piedmont, which meant that analyses could be conducted using two different instrumental methods: plasma emission spectrophotometry (ICP-OES), by the CNR ISE, and mass spectrometry (ICP-MS), by the ARPA. The second method has the advantage of being more sensitive, so that some metals could be quantified to a level below the detection limit for the ICP-OES; concentrations of other metals which had not initially been included in the project, such as mercury, were also quantified. Analyses were performed on samples of atmospheric deposition collected in three stations representing different environmental situations: Bellinzago, at the edge of the Po Plain in an industrialised area; Pallanza, a town in the subalpine area; Alpe Devero, a high mountain valley far from anthropogenic sources in a remote area of the Veglia-Devero Regional Nature Park (Fig. 1).
The sampling station with the highest concentrations was the subalpine station of Bellinzago, located close to industrial sites and urban centres. Nevertheless, the Alpine station, Alpe Devero, situated at an altitude of 1,600 m, also showed fairly high levels for most of the metals, with cadmium levels similar to those of the subalpine station. Measured fluxes of mercury, cadmium and lead were in good agreement with the fluxes estimated by the EMEP (2003) on the basis of the emissions of these metals in the atmosphere and according to dispersion models (Tab. 1). Generally speaking, the concentrations show high variability from one event to another. Concentrations in surface waters were determined solely using the ICP-OES technique, with which it was possible to quantify six metals; in more than 60% of cases, the other metals were below the detection limit. The concentrations of metals in surface waters (Fig. 2) were generally higher than those in atmospheric deposition, very likely due to the effect of runoff from the watershed (in the case of barium, for example). On the other hand, other heavy metals have the same concentrations in surface waters as those in atmospheric deposition, or even lower, due to adsorption by the soil.
Cluster analysis applied to the atmospheric deposition data, including some preliminary data obtained by ICP MS, revealed the common origin of a number of metals, for example between those of terrigenous origin (aluminium, boron, barium, iron, manganese and strontium) and those obviously of anthropogenic origin (copper, nickel and vanadium), traceable to metallurgical industries, road traffic and refuse incineration. The same analysis also revealed expected differences between the sampling sites. The station of Pallanza, which is affected by road traffic to a greater extent than the other two sites, showed up the link between palladium and rhodium, used as catalysers in the new generation of car exhausts.

The high variability of the concentrations in surface and atmospheric water, and the analytical precision required in achieving reliable results, make it essential to continue measurements for another year at least. It would also be advisable to compare results with the Italian working group on critical loads, to assess more exactly the damage to the environment which might be caused by the deposition of some of these metals. Any joint initiative of this kind should also involve the international working group of the ICP Waters and ICP Modelling and Mapping programmes, with a view to comparing the situation in Italy with that in other countries.

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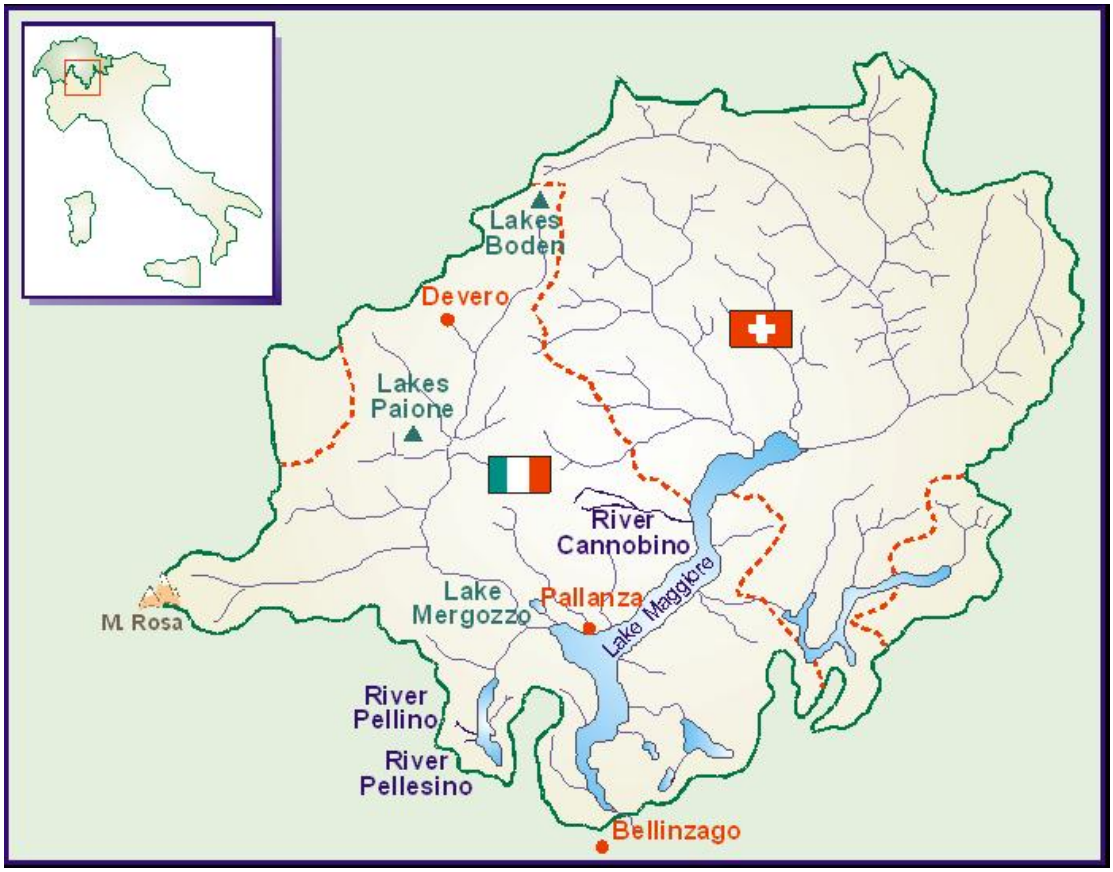

Fig. 1 – Location of the Italian ICP Waters sites in the watershed of Lake Maggiore.

Tab. 1 – Volume weighted measured concentrations and fluxes in the sampling stations compared with the EMEP (2003) estimated values.

		Lead	Cadmium	Mercury
Devero				
EMEP range conc.	µg L-1	0.387 – 0.647	0.007 – 0.013	0.007 – 0.010
Meas.concentrations	µg L^{-1}	0.548	0.03	0.003
EMEP range fluxes	g km^{-2} a^{-1}	0.58 – 0.97	0.011 – 0.02	0.010 – 0.015
Meas. deposition	g km^{-2} a^{-1}	0.827	0.046	0.005
Pallanza				
EMEP range conc.	µg L^{-1}	0.331 – 0.554	0.006 – 0.011	0.006 – 0.009
Meas.concentrations	µg L^{-1}	0.844	0.038	0.005
EMEP range fluxes	g km^{-2} a^{-1}	0.58 – 0.97	0.011 – 0.02	0.010 – 0.015
Meas. deposition	g km^{-2} a^{-1}	1.447	0.067	0.009
Bellinzago				
EMEP range conc.	µg L^{-1}	0.446 – 0.746	0.008 – 0.015	0.008 – 0.012
Meas.concentrations	µg L^{-1}	1.008	0.044	0.004
EMEP range fluxes	g km^{-2} a^{-1}	0.58 – 0.97	0.011 – 0.02	0.010 - 0.015
Meas. deposition	g km^{-2} a^{-1}	1.339	0.058	0.005

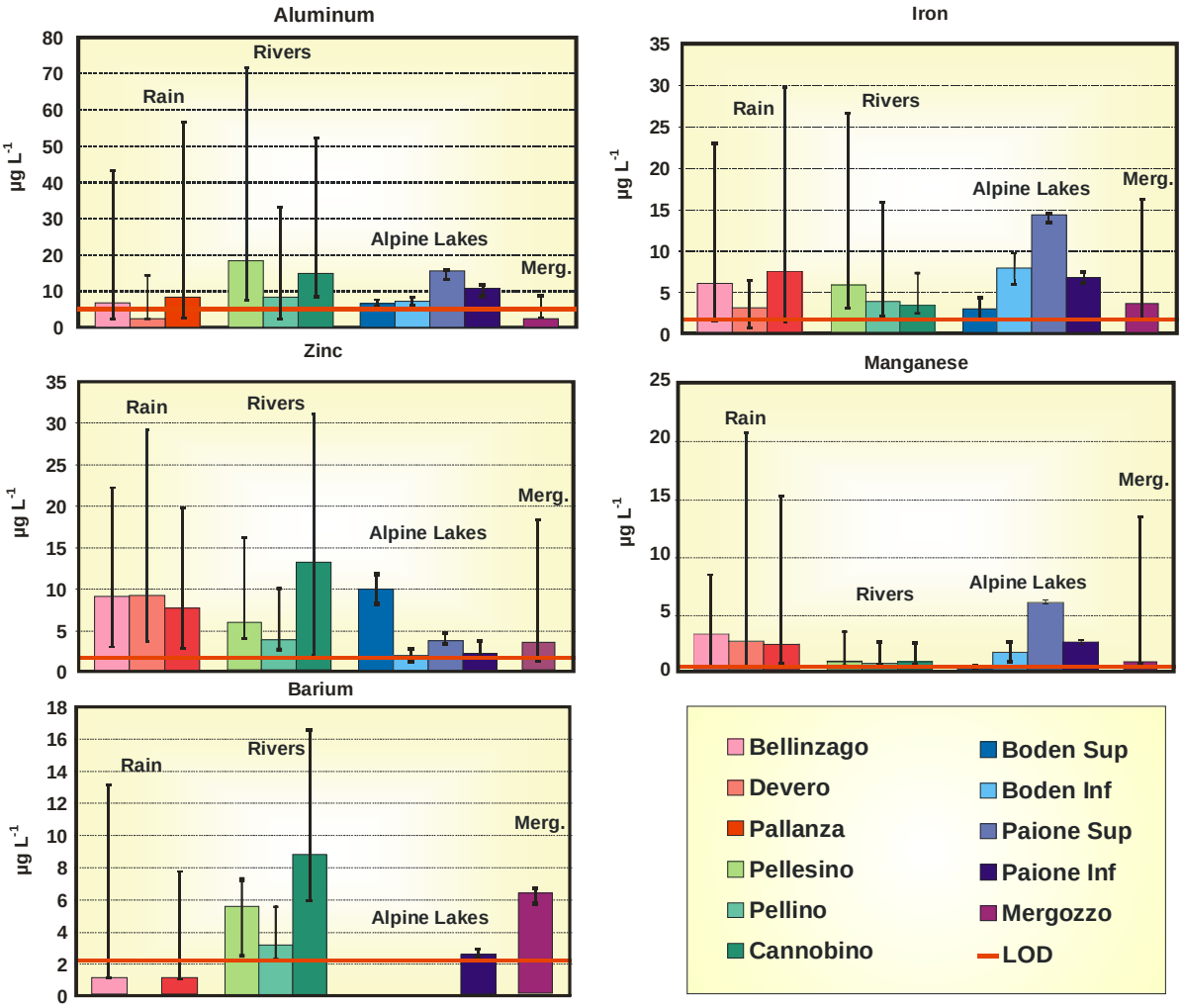

Fig. 2 – Mean volume weighted concentrations in atmospheric deposition and mean concentrations in rivers and lakes. Ranges indicate 95% CL, LOD= Limit of detection.

12. Workshop on alkalinity

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12.1 Introduction and aim of the workshop on alkalinity. Anders Wilander, Sweden

Mr Wilander introduced the workshop and indicated some points for discussion. Estimations of the buffer capacity of freshwater have been performed in several different ways. These may give systematically different results. The intention of the mini-workshop was to discuss these methods; their advantages and disadvantages and also to which extent the results can be used as chemical indicators for effects on biota. Here, a summary of the workshop is presented based on seven contributions.

12.2 Intercalibration of alkalinity. Haavard Hovind, Programme centre

Mr Hovind presented results from the NIVA's Intercomparison 0418. 21 out of 46 participants used the recommended Gran plot titration method, which is defined as the reference method (1 lab excluded, 11 totally).
End point titration was used by nearly all of the other laboratories:

pH 4,5 and 4,2 (6 labs, 4 excluded)
pH 4,5 (14 labs, 3 excluded)
pH 5,4
pH 5,6 (1 lab)

Very few laboratories are using a colorimetric method. These methods give more or less different results compared to the Gran plot results

12.3 Chemical-biotic relationships observed on the UK Acid Waters Monitoring Network: 1983–2003. Don Monteith, UK

The presentation of Mr Monteith is shown elsewhere in the proceedings of the Task Force meeting. Here, only the parts relevant for the alkalinity workshop are presented.

Mr Monteith presented an alternative definition of ANC, i.e. "alkalinity based ANC":

$ANC = [Alkalinity]\ (\mu eq\ l^{-1}) + F*[DOC]\ (mg\ l^{-1}) - 3*[labile\ Al](\mu mols\ l^{-1})$
where F = 4.5 (pH<5.5) or 5.0 (pH>5.5)

Advantages and disadvantages of "alkalinity-based ANC" (alk-ANC) versus base cation-based ANC (BC-ANC) were discussed:

- BC-ANC involves 7 components – with consequently a potential for high compound errors, as opposed to alk-ANC
- Potential errors in BC-ANC for sites on west coast of UK particularly high after seasalt episodes
- 5% error on Cl can result in a 30 $\mu eq\ l^{-1}$ error in BC-ANC estimate
- DOC does not have a constant charge density, which is an disadvantage for using it to calculate alk-ANC

- Alk-ANC trend strength more strongly correlated with xSO4 trends than BC-ANC
- Alk-ANC trends significant at any site showing a trend in one or more of: pH, labile Al or Alkalinity – which means that Alk-ANC acts as a generic acidity indicator

The relevancy of ANC for biological trends:
- Macroinvertebrate trends more closely linked to ANC than any other variable – both spatially and temporally
- Juvenile brown trout have appeared for the first time at all sites which have crossed the 0 μeq l^{-1} ANC threshold over the monitoring period
- ANC threshold as effective as an alkalinity threshold in "explaining" recent appearance of aquatic macrophyte species
- No strong statistical link between ANC and epilithic diatom communities

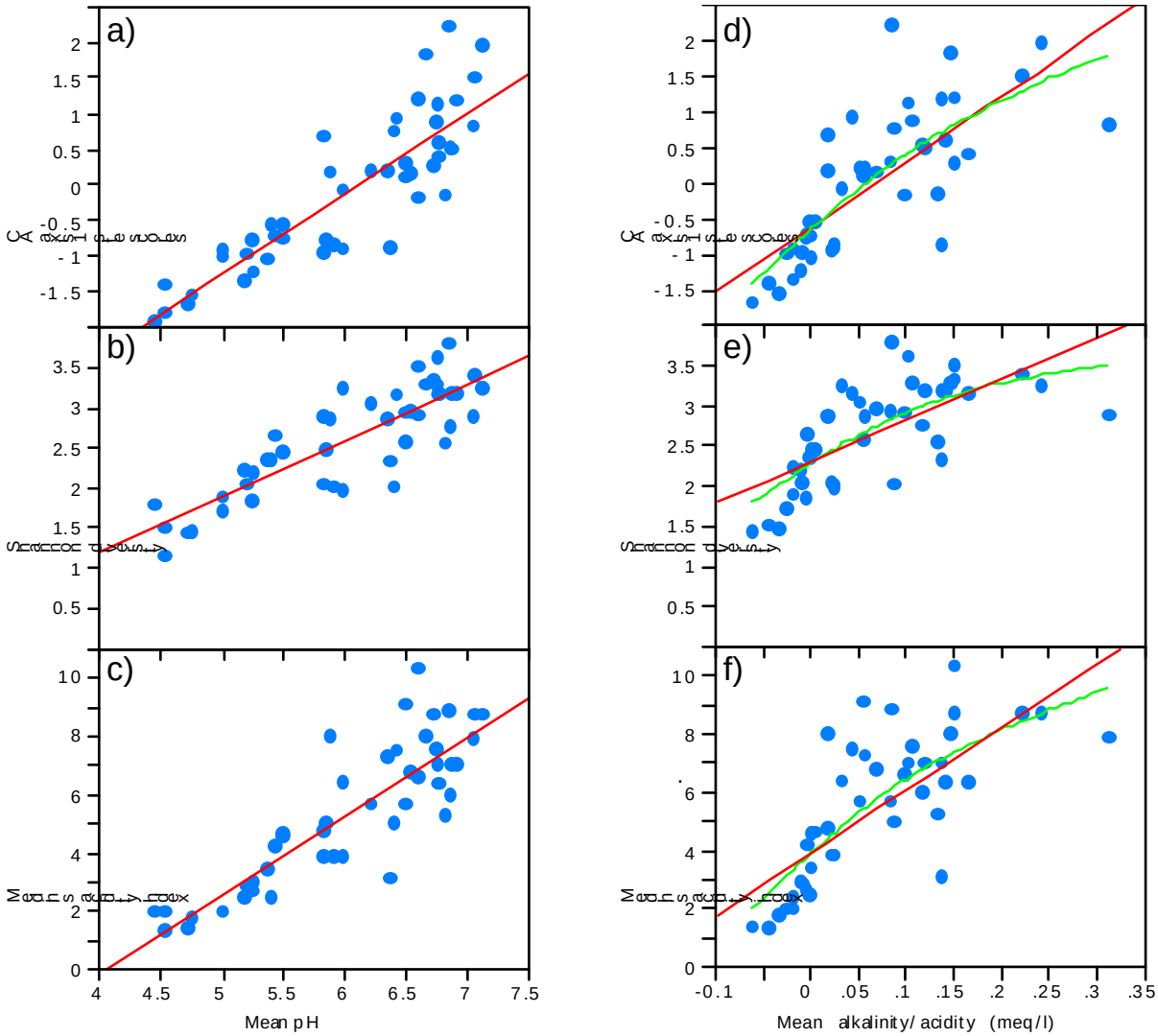
12.4 Assessing acidity and acidification. Jens Følster, Sweden

Mr. Fölster presented the work on the revision of the Swedish environmental criteria for acidity/acidification. So far the work has been limited to reference lakes sampled four times a year. The intention is to set acidity classes related to effects on biota (litoral fauna and fish). In the case of litoral fauna a Swedish acidity index (Medin's) was used. Several alternative parameters have been tested; pH, Ali (inorganic Al), alkalinity (carbonate), ANC and ANC/H^+). For these parameters median and extreme values were tested, not only for the year of interest but also with a lag of one or two years. The reasoning behind this was that biota (litoral fauna and fish) might react either on an extreme condition or on a longer period with a high acidity. Also their reaction may be immediate but it could be delayed one year as well. The results indicated that pH was the best chemical indicator. Sometimes carbonate alkalinity (acidity) gave better results than ANC. However, all acidity indicators are correlated.

Summary of quadratic relation between benthic fauna and acidity indicators in Swedish forest lakes

	pH	Alkalinity/acidity	ANC	Ali (WHAM)
CA scores axis 1 R^2	0.74	0.63	0.59	0.46
Medin's index R^2	0.71	0.62	0.62	0.46

For the classification of acidification was MAGIC modelling used to determine an ANC_0 value, which can be compared with a present day ANC_t Since pH-value was found to be stronger correlated to effects on biota were these ANC-values transferred to pH-values under identical TOC and pCO2 conditions. Acidification was thereafter identified as a diminution in pH-value greater than 0.4 units.



Regression plots of three biological metrics (CA scores, Shannon diversity and Medin's acid index) against lake water pH and alkalinity/acidity for lakes situated in the mixed forest ecoregion. Curved lines show smoothed spline fits with lamda = 0.01.

12.5 Report on experience on alkalinity measurements in the AQUACON project and on the results from the first Working Ring Test 2002 performed in the framework of the ICP Forests, Expert Panel on Atmospheric deposition. Rosario Mosello, Italy

Mr. Mosello presented the study of the chemistry of atmospheric deposition within the ICP Forests, done in 513 permanent plots in 31 countries. Within this work an intercomparison was performed. From the results of the intercomparison exercise we realized as "weakness" in the analyses the measurement of low values of alkalinity. Total alkalinity was measured both for natural and synthetic samples (solutions of $NaHCO_3$).
Results showed that although most of the analyses are based on acidimetric titration, many analytical methods were used to detect the inflection or end point:

- colorimetric indicators (different dyes);
- one end-point (pH 4.3 or pH 4.5);
- two points (0.3 pH units of difference, normally 4.2 and 4.5);
- Gran's titration.

The different analytical techniques showed typical systematic errors, with an overestimation of true values given by the colorimetric and one end point titration.
Based on the results of the intercomparison, in agreement those of analogous exercises and with well established analytical concepts, the indication given in the manual for the measurement of low alkalinity values is as follows:

The measurement of low alkalinity values is reliable when the following analytical methods are used:

- Gran's titration;
- two end points titration (e.g. pH 4.5 and pH 4.2);
- titration at pH 4.5 (or 4.3) and correction for the extra acid added.

12.6 Acid lake chemistry in Northern Alberta. Dean Jeffries, Canada

Mr. Jeffries gave a presentation on alkalinity and organic anions observations from northern Alberta in Canada. Most lakes had high alkalinity and high DOC. The interpretation of the alkalinity measurement is that some must be attributed to weak organic acids.

12.7 Measuring ANC and alkalinity – how variable are the protocols? John Stoddard, USA

Mr. Stoddard discussed the results of a simple test of protocols

- Gran titration
- Single endpoint (pH = 4.5) titration
- Double endpoint (pH = 4.5, 4.2) titration
- "ANC" – calculated as cations minus anions
- Calculated alkalinity from pH and DIC

The presentation focused on "bias" and "precision".

Bias was defined as the difference between measured alkalinity variability and "true" value from calculated alkalinity (from DIC and pH).

Precision was calculated in two ways:
as the standard deviation of bias values = $\sqrt{\frac{\sum(measured - calculated)^2}{n}}$

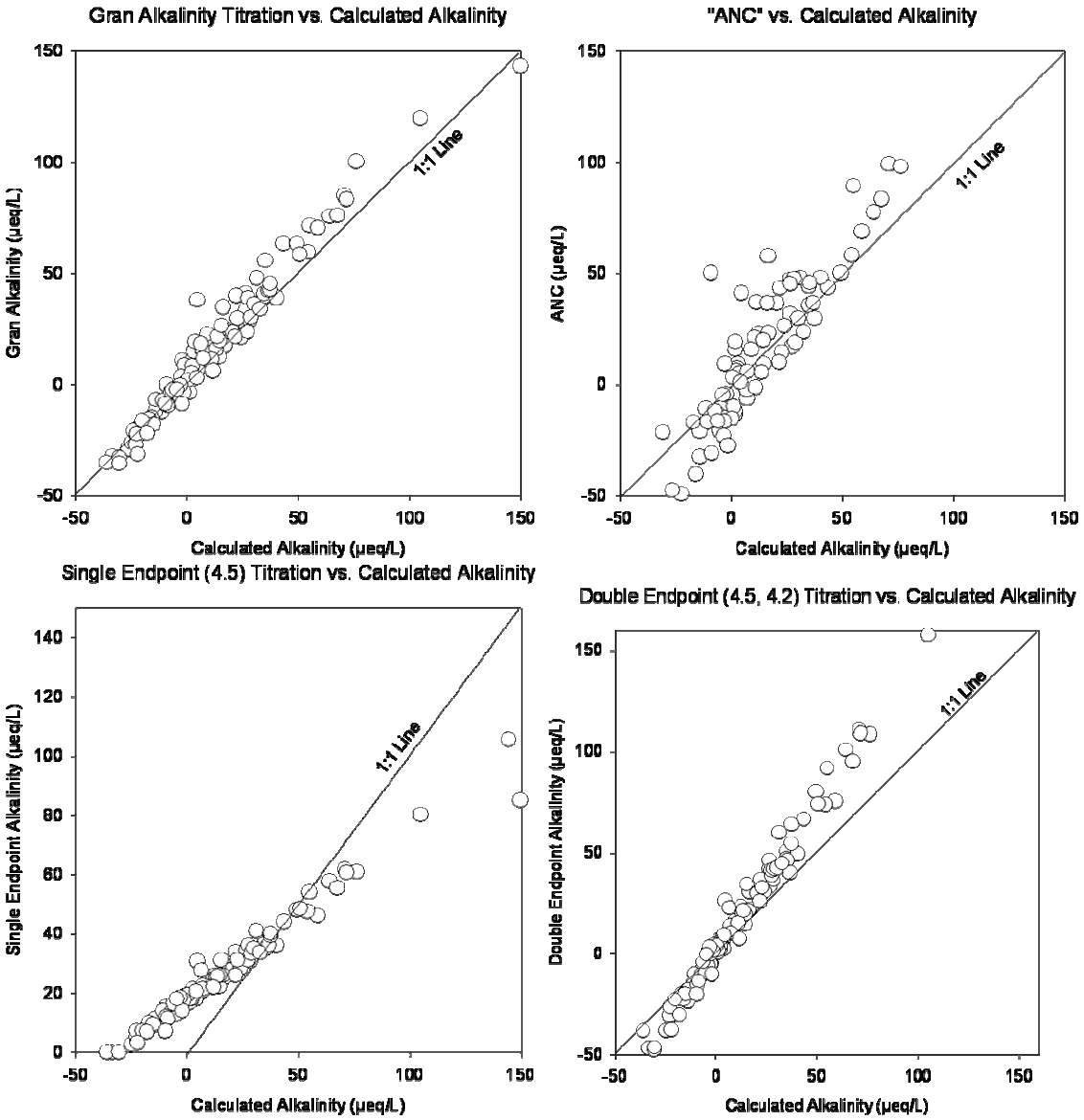
as the standard deviation of duplicate measurements = $\sqrt{\frac{\sum(duplicate\#1 - duplicate\#2)^2}{2n}}$

- Bias affects our ability to assess current acidification status of surface waters
- Precision affects our ability to detect significant trends in acidification

For 112 low alkalinity stream samples the following analyses were done:

- Gran titration (20-40 points) between pH 4.5 and 3.0
- single endpoint titration to pH 4.5
- dual endpoint titration to pH 4.5 and 4.2 (doubling of H^+)
- a calculation of alkalinity as: $HCO_3^- + CO_3^{2-} + OH^- - H^+$
  where all variables calculated from standard equilibrium constants and measured Dissolved Inorganic Carbon and pH
- calculated ANC as: $(Ca^{2+} + Mg^{2+} + Na^+ + K^+) – (SO_4^{2-} + NO_3^- + Cl^-)$
- Repeated all measurements (except for ANC) on 23 duplicate samples

Results



Relationships between alaklinity measured in different ways and calculated alkalinity.

Evaluation of results in terms of bias and precision

	Method	Bias (mean of)	Precision #1 (s.d. of bias estimates)	Precision #2 (s.d. of duplicates)
"Good"	Gran titration	4.7	7.6	2.1
	Dual endpoint	7.1	14.4	2.5
"Bad"	Single Endpoint	12.1	14.4	3.2
	"ANC"	18.1	77.1	??

12.8 Alkalinity -the role of suspended solids. Istvan Licsko, Hungary

In most cases only dissolved compounds are taking into consideration when discussing alkalinity.

- Is there any effect of suspended matter?
- Quality (originating) of suspended solids: Silica type rocks, Sedimentary rocks
- Surface charge (electric) of SS (negative in all cases). Negatively charged particles – possibility to provide a weak bond with cathions, rather the H^+ ions
- Some types of clay particles have ion exchange (cation) capacity – possibility to change the surface bonded cathions into H^+ ions
- Particles originating from sedimentary rocks– binding the H^+ ions
- **Conclusion:** Suspended particles have a H^+ ion capture effect
- The level of this effect; strong or weak was studied in an experiment using sediment from Csorret Reservoir. The collected sediment was dried. Measured amounts of suspended solids were mixed with water (Csorret Reservoir).

After continuous mixing alkalinity measurements were made.

Results show an influence of suspended matter on the alkalinity.

Suspended matter added (mg/L)	Alkalinity increase (meq/L)
0	0
10-50	0,03
10-50	0,04
100-200	0,04
250	0,05

12.9 Discussions – Conclusions of the workshop on alkalinity. Anders Wilander, Sweden.

Several different definitions for the buffer capacity in water have been published. Many of them are similar, providing that all determinations and constants are correct. However, as shown by many of the participants the choice of method affects the results sometimes significantly. According to electro-neutrality the values for ANC and base-cation based alkalinity (Cbalk) should be equal. This rarely happens mainly due to systematic errors and also to low precision of the chemical analysis. The precision as judged from the ICP Waters data and NIVA Intercomparison (NIVA 0014) data indicate a lower standard deviation for the ANC estimate than for the CBalk. However the systematic error (Anders: you mean bias? accuracy) of the two estimates is more important. It is evident from the interlaboratory comparisons that there are substantial differences for many of the determinands used in both these calculations. This implies that results from different laboratories have to be compared with caution. However, it is likely that trends still can be well described for the different stations.
It is important to realise that the Gran plot finds the equivalence point for the “dominant” protolyte and determines the amount of acid consumed (alkalinity) to reach this pH-value.

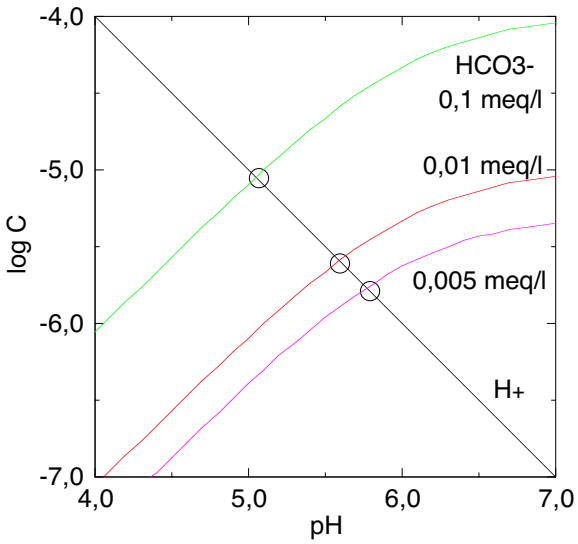


Figure . The equivalence point for the titration of hydrogen carbonate at different concentrations.

Whenever other protolytes than the hydrogen carbonate system dominate (as in acid waters) will the result be based on other protolytes as aluminium ions and organic anions.
The use of a variable end-point for the titration (the equivalence point) can be judged as a deviation from one alternative definition for ANC: “the amount of acid required to reach a set pH-value”.
The challenge to find a generally accepted chemical criterium for effects on biota remains. One presentation favours ANC while another indicates that pH-value is better.

References

Assessing the Suitability of Acid Neutralising Capacity as a Measure of Long-Term Trends in Acidic Waters Based on Two Parallel Datasets. Evans C.D.; Harriman R.; Monteith D.T.; Jenkins A.Water, Air, and Soil Pollution, August 2001, vol. 130, no. 1-4, pp. 1541-1546(6)

13. Chemical-biotic relationships observed on the UK Acid Waters Monitoring Network: 1988-2003

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Environmental Change Research Centre
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Overview location of streams and lakes in monitoring network

Biological parameters (sampled annually)

- Epilithic diatoms: 3 samples from fixed locations. 300 diatoms per sample counted to species level
- Macroinvertebrates: 5 x1 minute kick-samples. All individuals collected and counted in laboratory
- Aquatic macrophytes: Shoreline survey and fixed transects
- Salmonids: Electrofishing of streams and lake outflows (3 x 50 survey stretches)

Chemical parameters

- streams – monthly
- lakes – 3 monthly
- sulphate, nitrate, chloride, pH, alkalinity, conductivity, base cations (Ca2+, Mg2+,Na+,K+), aluminium (total, and labile), dissolved organic carbon, nutrients (phosphate, silica)

Acid Neutralising Capacity

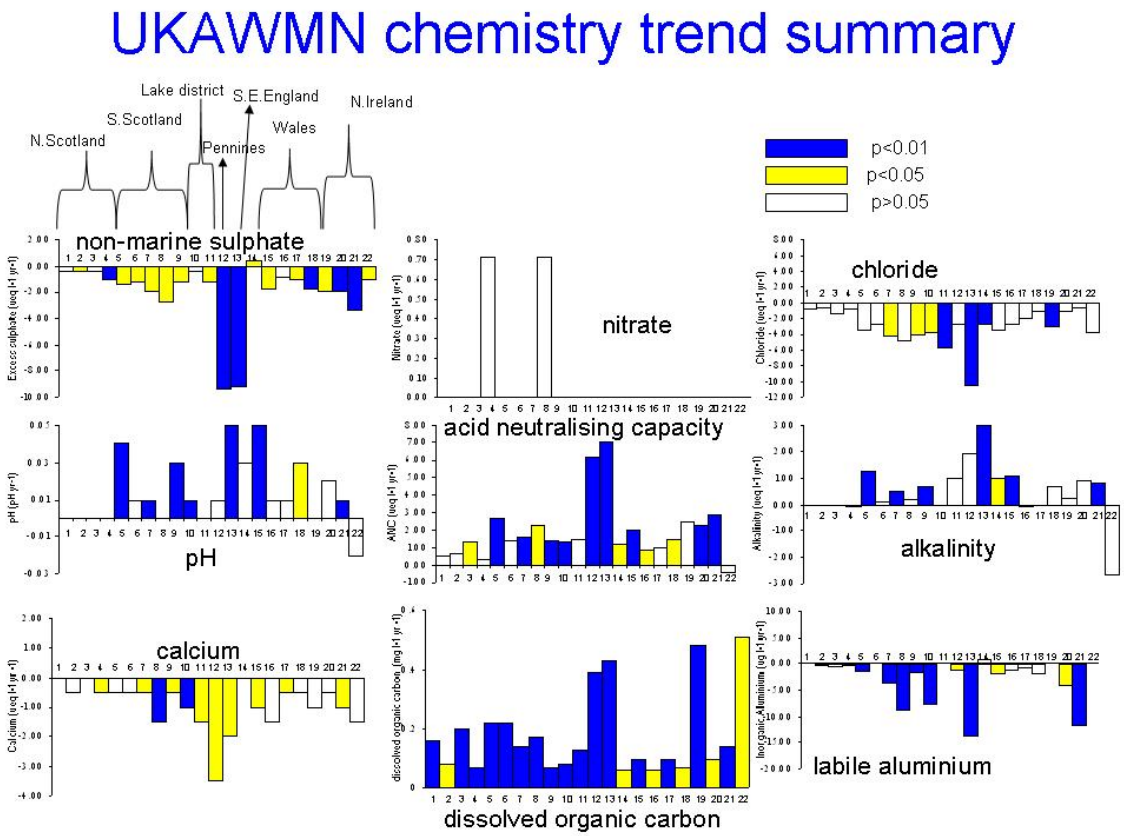
calculated as: [Alkalinity] (µeq l^{-1}) + F*[DOC] (mg l^{-1}) – 3*[labile Al](µmols l^{-1})
Where F = 4.5 (pH<5.5) or 5.0 (pH>5.5)

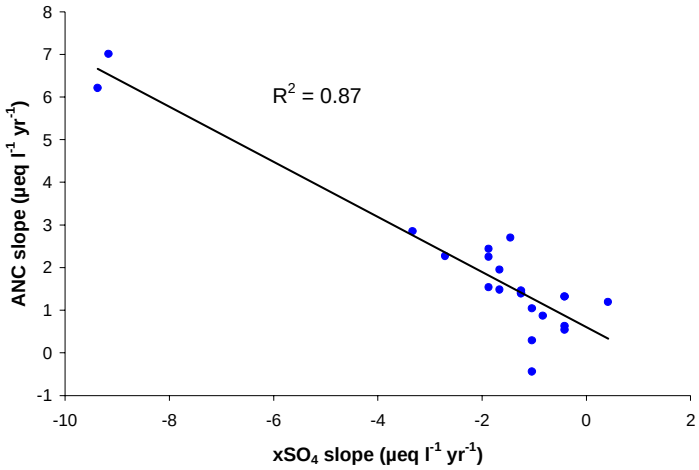
(Assessing the Suitability of Acid Neutralising Capacity as a Measure of Long-Term Trends in Acidic
Waters Based on Two Parallel Datasets. Evans C.D.; Harriman R.; Monteith D.T.; Jenkins A.Water, Air, and Soil Pollution, August 2001, vol. 130, no. 1-4, pp. 1541-1546(6))

Why Alkalinity based ANC rather than base cations – acid anions?

- BC-AA involves 7 components – with consequent potential for high compound errors
- Potential errors for sites on west coast particularly high after seasalt episodes
- 5% error on Cl can result in a 30 µeq l-1 error in ANC estimate

UKAWMN chemistry trend summary





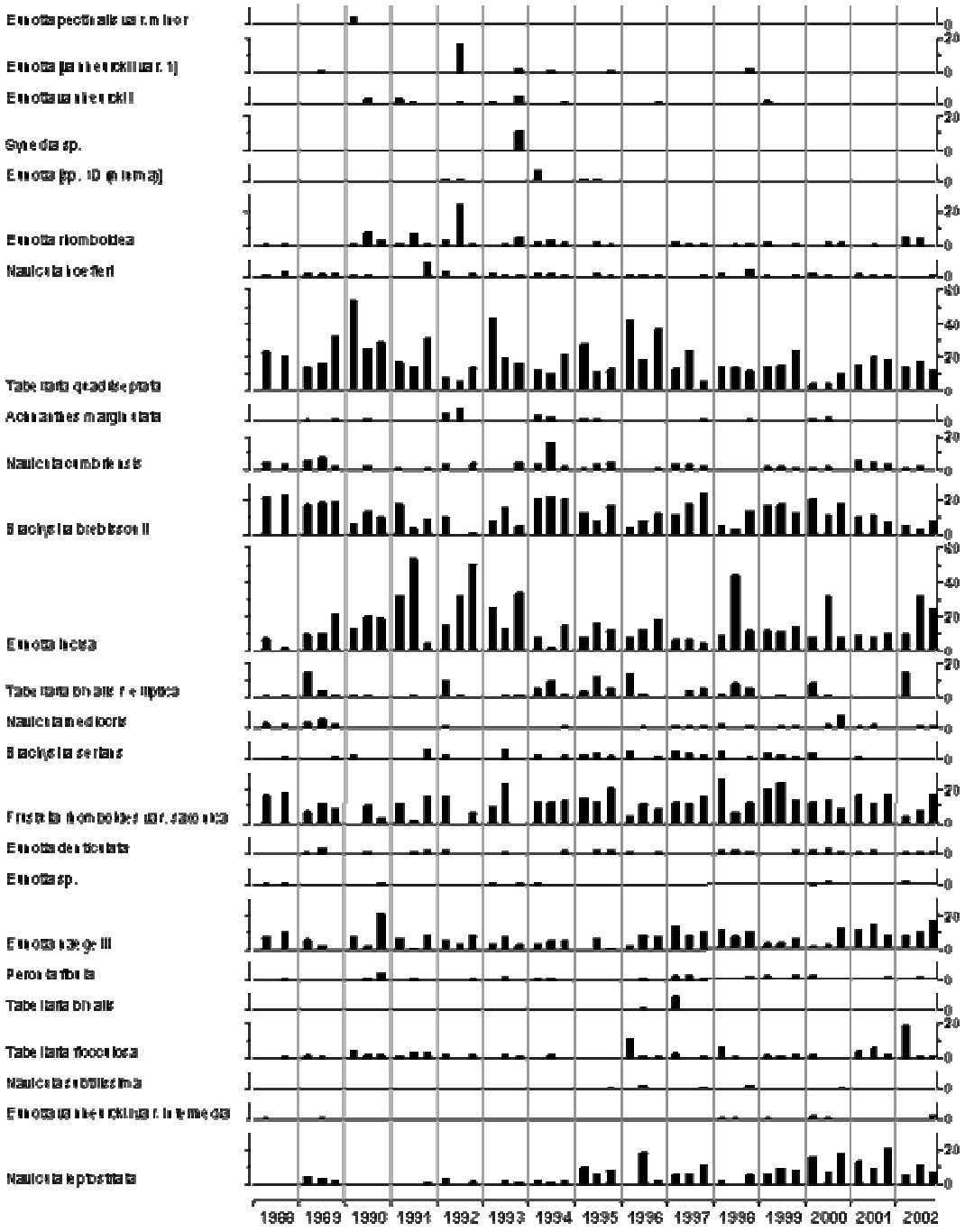
Non-marine sulphate v ANC

Biological recovery?

- Have populations changed over the monitoring period?
- If so, what is changing?
- Is there a geographical link between sites showing trends in biology and those showing trends in chemistry?
- Is there a temporal link between biological change and chemical change?
- Are the biological changes consistent with our understanding of the chemical preferences of these species?

Have populations changed over the monitoring period?

	Epilithic diatoms		Macroinvertebrates		Aquatic macrophytes		brown trout density			
							0+ group		>0+ group	
Site	λ_1RDA$_{year}$	p restricted test 999 perms	λ_1RDA$_{year}$	p restricted test 999 perms	λ_1RDA$_{year}$	p restricted test 999 perms	r	p	r	p
Loch Coire nan arr	**12.9**	**0.016**	18.1	0.052	**30.1**	**0.010**	**-0.70**	**0.010**	**-0.71**	**0.009**
Allt a' Mharcaidh	**10.9**	**0.016**	4.9	0.182	33.9	0.060	0.18	0.521	0.38	0.157
Allt na Coire nan Con	**10.7**	**0.011**	**9.7**	**0.006**	35.4	0.052	**-0.55**	**0.032**	0.37	0.180
Lochnagar	4.2	0.210	6.5	0.416	22.8	0.166	-0.36	0.200	-0.41	0.139
Loch Chon	**18.9**	**0.016**	**10.0**	**0.040**	23.4	0.142	-0.05	0.875	-0.45	0.106
Loch Tinker	6.3	0.139	8.2	0.138	19.5	0.330	-0.47	0.102	**-0.59**	**0.035**
Round Loch Glenhead	9.1	0.057	2.9	0.434	6.7	0.476	0.11	0.714	0.11	0.708
Loch Grannoch	**29.3**	**0.018**	**11.3**	**0.024**	21.2	0.426	no fish caught		0.04	0.886
Dargall Lane Burn	**15.2**	**0.047**	9.2	0.198	27.3	0.095	0.01	0.917	0.03	0.920
Scoat Tarn	**6.7**	**0.022**	**8.2**	**0.018**	23.9	0.290	0.52	0.057	0.09	0.763
Burnmoor Tarn	**12.3**	**0.011**	**14.2**	**0.014**	19.7	0.174	0.15	0.605	-0.06	0.830
River Etherow	6.6	0.286	**10.7**	**0.020**	35.6	0.076	no fish caught		no fish caught	
Old Lodge	6.0	0.302	**10.6**	**0.020**	**41.2**	**0.034**	**0.61**	**0.023**	**0.84**	**0.001**
Narrator Brook	6.0	0.360	6.0	0.114	8.4	0.936	-0.10	0.712	-0.36	0.191
Llyn Llagi	**24.6**	**0.011**	**14.6**	**0.038**	28.1	0.102	-0.26	0.396	-0.25	0.420
Llyn Cwm Mynach	**9.7**	**0.031**	**14.1**	**0.004**	49.8	0.060	0.36	0.206	0.02	0.961
Afon Hafren	**19.4**	**0.016**	3.8	0.530	2.4	0.666	-0.04	0.927	0.35	0.403
Afon Gwy	**9.1**	**0.036**	**5.3**	**0.016**	11.9	0.168	-0.22	0.481	0.08	0.800
Beagh's Burn	8.3	0.314	9.6	0.224	20.6	0.492	0.08	0.761	0.12	0.675
Bencrom River	6.9	0.079	**6.6**	**0.012**	23.3	0.140	-0.21	0.460	0.42	0.115
Blue Lough	5.7	0.224	**22.0**	**0.018**	4.7	0.806	0.55	0.054	**0.70**	**0.008**
Coneyglen Burn	7.0	0.254	9.8	0.172	9.2	0.350	0.01	0.961	0.33	0.276


Eunotia pectinalis var. minor
Eunotia [Jannei Ruckii var. 1]
Eunotia Jannei Ruckii
Synedra sp.
Eunotia [sp. 10 (minima)]
Eunotia rhomboidea
Navicula hoefleri
Tabellaria quadriseptata
Achnanthes marginulata
Navicula cumbriensis
Brachysira brebissonii
Eunotia incisa
Tabellaria binalis f. elliptica
Navicula mediocris
Brachysira serians
Frustulia rhomboides var. saxonica
Eunotia denticulata
Eunotia sp.
Eunotia naegelii
Peronia fibula
Tabellaria binalis
Tabellaria flocculosa
Navicula subtilissima
Eunotia Jannei Ruckii var. intermedia
Navicula leptostriata
1988 1989 1990 1991 1992 1993 1994 1995 1996 1997 1998 1999 2000 2001 2002

Site	Taxa showing temporal change	mean % per sample		SWAP pH optima mean (1 s d)		difference in mean pH optima between increasing and decreasing groups
		1988-1992	1998-2002	increasing taxa	decreasing taxa	
Loch Coire nan Arr	***Achnanthes marginulata***	0.15	0.94	5.65	5.63	+0.02
	Achnanthes minutissima	12.45	29.42	(0.55)	(0.59)	
	Achnanthes pusilla	0.00	0.95			
	Cymbella perpusilla	0.27	1.01			
	Eunotia exigua	0.35	2.07			
	Nitzschia gracilis	0.04	0.96			
	Cymbella microcephala	3.51	0.53			
	Frustulia rhomboides var. saxonica	6.35	3.31			
	Tabellaria flocculosa	20.91	8.76			
Allt a' Mharcaidh	***Eunotia incisa***	0.20	1.40	5.10	6.15	-1.05
	Fragilaria vaucheriae	18.35	10.11		(0.21)	
	Hannaea arcus	8.43	0.00			
Allt an Coire nan Con	***Eunotia incisa***	2.16	10.97	5.10	5.70	-0.60
	Achnanthes saxonica	58.01	25.41			
Loch Chon	***Brachysira brebissonii***	2.67	12.36	5.70	x = 5.0	+0.70
	Brachysira vitrea	6.63	24.67	(0.25)	std = 0.19	
	Cymbella lunata	0.05	1.33			
	Nitzschia gracilis	0.00	0.66			
	Nitzschia perminuta	0.02	0.30			
	Achnanthes marginulata	10.21	1.62			
	Eunotia denticulata	0.64	0.04			
	Eunotia incisa	7.81	3.22			
	Fragilaria [cf. oldenburgiana]	3.19	0.26			
	Navicula leptostriata	20.37	9.46			
Round Loch Glenhead	***Navicula leptostriata***	1.04	9.67	x = 5.10		na
Loch Grannoch	***Brachysira brebissonii***	0.17	2.43	x = 5.20	x = 5.08	+0.12
	Eunotia vanheurckii* var. *intermedia	0.16	1.11	std = 0.26	std = 0.19	
	Tabellaria quadriseptata	1.24	58.17			
	Achnanthes altaica var. *minor*	8.10	0.47			
	Asterionella ralfsii	6.85	0.00			
	Eunotia rhomboidea	5.98	1.14			
	Frustulia rhomboides var. *saxonica*	11.72	1.54			
	Pinnularia irrorata	1.17	0.10			
	Pinnularia subcapitata var. *hilseana*	9.06	0.33			
Dargall Lane Burn	***Peronia fibula***	26.19	52.88	x = 5.3	x = 5.05	+0.25
	Eunotia incisa	16.29	7.23		std = 0.07	
	Eunotia naegelii	16.16	4.27			
Scoat Tarn	***Navicula subtilissima***	0.15	2.26	x = 5.2	x = 5.2	no change
	Eunotia tenella	0.51	0.00			
Burnmoor Tarn	***Cymbella cesatii***	0.38	3.75	x = 6.03	x = 5.70	+0.33
	Denticula tenuis	0.96	6.20	std = 1.00	std = 0.00	
	Navicula cumbriensis	0.00	1.56			
	Cymbella lunata	2.28	0.63			
	Nitzschia perminuta	3.70	1.41			
Llyn Llagi	***Brachysira vitrea***	0.97	6.45	x = 5.70	x = 4.90	+0.80
	Cymbella lunata	0.18	1.69	std = 0.25		
	Nitzschia gracilis	0.00	0.82			
	Nitzschia perminuta	0.89	18.60			
	Peronia fibula	0.94	4.28			
	Tabellaria quadriseptata	18.91	1.03			
Llyn Cwm Mynach	***Navicula madumensis***	0.00	1.24	x = 5.10	x = 4.95	+0.15
	Navicula tenuicephala	1.83	7.53	std = 0.28	std = 0.17	

Site	Taxa showing temporal change	mean % per sample	
		1988-1992	1998-2002
Allt an Coire nan Con	***Heptagenia lateralis*** (E)	1.06	3.34
	Siphonoperla torrentium (P)	1.99	3.90
	Oreodytes sanmarkii (C)	0.10	13.12
	Brachyptera risi (P)	6.70	0.39
	Protonemura sp. (P)	1.72	0.04
	(*Isoperla grammatica* (P))	6.01	0.00
Loch Chon	***Leuctra nigra*** (P)	0.13	6.49
	Enallagma cyathigerum (O)	0.03	1.18
	Oulimnius tuberculatus (C)	0.16	1.51
	***Cyrnus* sp.** (T)	0.08	1.18
	Ischnura elegans (O)	1.95	0.00
	Hesperocorixa sahlbergi (CX)	2.49	0.00
	(*Callicorixa praeusta* (CX))	0.28	0.00
Loch Grannoch	***Cyrnus* sp.** (T)	0.00	2.47
	Chironomidae	15.08	41.80
	Empididae	0.02	1.00
	Oulimnius tuberculatus (C)	5.67	0.00
Scoat Tarn	***Polycentropus* sp.** (T)	0.00	0.57
	***Cyrnus* sp.** (T)	0.00	0.51
	Limnephilidae (T)	0.05	1.02
	***Halesus* sp.** (T)	0.00	0.62
Burnmoor Tarn	**Leptophlebiidae** (E)	20.43	36.19
	Caenis horaria (E)	0.00	17.40
	Caenis luctuosa (E)	0.00	12.74
	OLIGOCHAETA	26.85	3.15
River Etherow	***Brachyptera risi*** (P)	0.07	9.58
	Elmis aenea (C)	0.00	0.45
Old Lodge	SIMULIIDAE	32.04	8.27
Llyn Llagi	***Oulimnius tuberculatus*** (C)	0.75	4.71
	***Mystacides* sp.** (T)	0.00	5.74
	Nemoura spp. (P)	4.24	0.08
Llyn Cwm Mynach	***Pisidium* sp.** (E)	0.00	5.07
	Chironomidae	23.50	69.11
	(***Sigara scotti*** (CX))	1.38	4.83
	LEPTOPHLEBIIDAE (E)	47.35	11.66
	Polycentropus sp. (T)	3.46	0.00
	(*Anabolia nervosa*) (T)	0.57	0.00
Afon Gwy	***Isoperla grammatica*** (P)	1.55	4.66
Bencrom River	***Siphonoperla torrentium*** (P)	1.85	7.95
Blue Lough	**Leptophlebiidae**	11.36	45.51
	***Polycentropus* sp.** (T)	0.42	6.99
	(***Glaenocorisa propinqua*** (CX))	0.35	3.31
	OLIGOCHAETA	9.13	0.94
	CHIRONOMIDAE	64.95	36.56
	(Potamonectes griseostriatus) (C))	3.95	0.63

Increasing proportions of macroinvertebrate predators

- Caddisflies increasing proportionally in Loch Chon, Loch Grannoch, Scoat Tarn, Llagi, and Blue Lough
- Predatory net-spinners (*Cyrnus* or *Polycentropus*) increasing in Loch Chon, Loch Grannoch, Scoat Tarn and Blue Lough

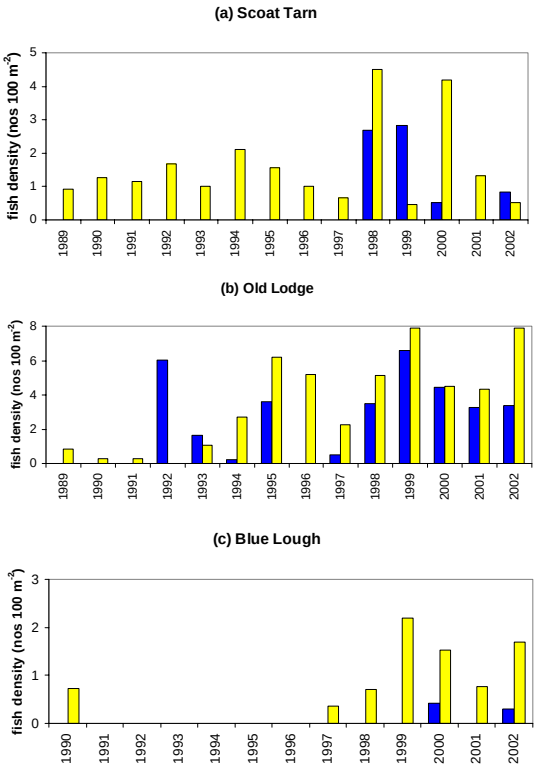
Increasing proportions of predators

- Predatory stoneflies *Isoperla grammatica* in Afon Gwy, *Siphonoperla torrentium* in Allt an Coire nan Con and Bencrom River
- Damselfly *Enallagma cyathigerum* in Loch Chon

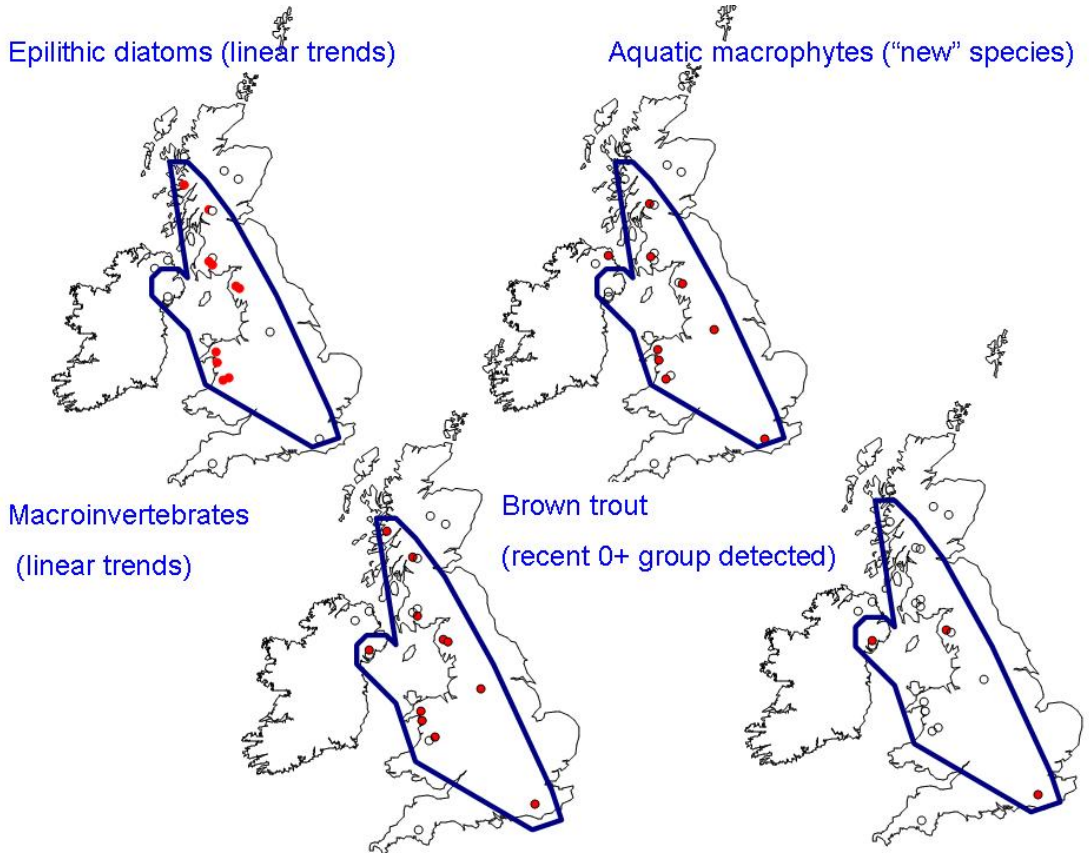
Aquatic macrophytes: recent appearances

site	species	sample years								
		95	96	97	98	99	00	01	02	03
LAKES										
Loch Chon	*Elatine hexandra*	✓	•	✓	•	✓	•	X	•	X
	Subularia aquatica	✓	•	✓	•	✓	•	✓	•	✓
	Chara virgata	X	•	X	•	✓	•	✓	•	✓
Round Loch of Glenhead	*Myriophyllum alterniflorum*	X	•	X	•	X	•	X	•	✓
Burnmoor Tarn	*Chara virgata*	X	•	X	•	X	•	X	•	✓
Llyn Llagi	*Callitriche hamulata*	X	X	X	X	✓		✓		✓
Llyn Cwm Mynach	*Scirpus fluitans*	X	•	X	•	✓	•	✓	•	✓
	Isoetes lacustris	X	•	X	•	✓	•	✓	•	✓
STREAMS										
River Etherow	*Fontinalis antipyretica*	X	X	X	X	X			X	X
Old Lodge	*Hyocomium armoricum*	X	X	X	X	X	✓	✓	X	✓
Afon Hafren	*Hyocomium armoricum*	X	X	X	X	X	X	X	✓	✓
Beagh's Burn	*Hygrohypnum luridum*	X	X	X	X	X	X	X	✓	✓

Salmo trutta density



Is there a geographical link between sites showing trends in biology and those showing trends in chemistry?



Chi^2 contingency table: chemical trends v biological trends

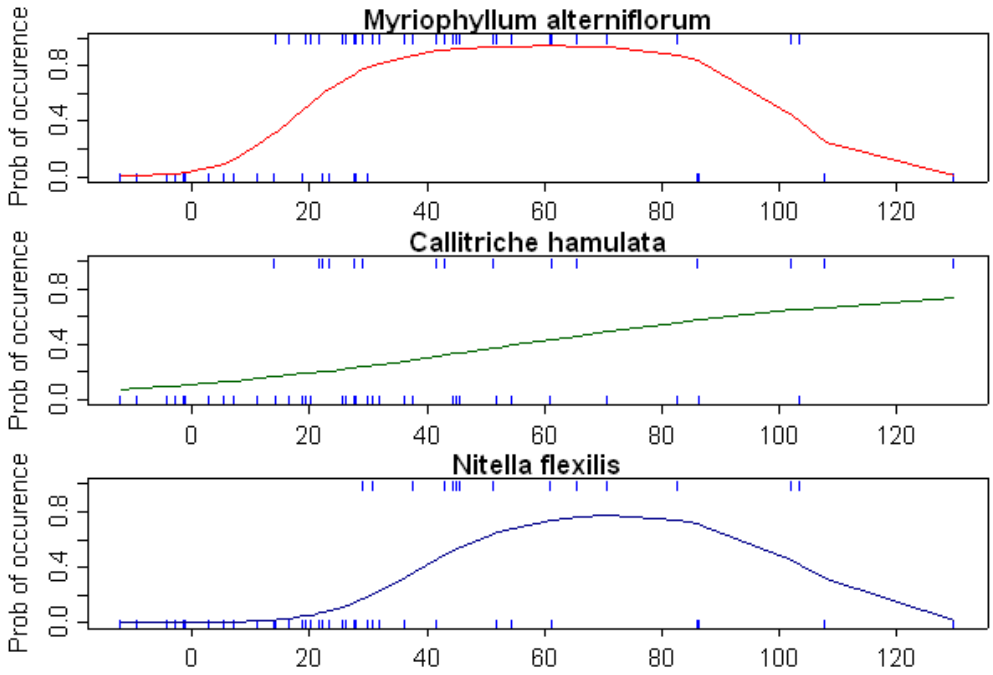
	Frequency							
Biological group	**Chemical determinand**	**Biological trend**	**Chemical trend**	**Biological and chemical trend**	**Biological trend – no chemical trend**	**Chemical trend – no biological trend**	**No biological or chemical trend**	**χ^2 statisitic significance at p<0.05 denoted in bold**
Epilithic diatoms	pH	12	8	6	2	6	8	2.12
	alkalinity	12	6	4	2	8	8	0.49
	ANC	12	13	9	4	3	6	2.76
	Al_{lab}	12	10	7	3	5	7	1.76
	calcium	12	10	7	3	5	7	1.77
Aquatic macrophytes*	pH	9	8	4	4	5	9	0.43
	alkalinity	9	7	4	2	5	11	2.26
	ANC	9	13	6	7	3	6	0.36
	Al_{lab}	9	10	5	5	4	8	0.63
	calcium	9	10	4	6	5	7	0.006
Macroinvertebrates	pH	12	8	6	2	6	8	2.12
	alkalinity	12	6	4	2	8	8	0.49
	ANC	12	13	11	2	1	8	**11.59**
	Al_{lab}	12	10	8	2	4	8	**4.79**
	calcium	12	10	7	3	5	7	1.77
brown trout	pH	3	8	3	0	5	14	**6.08**
	alkalinity	3	7	2	1	4	15	2.71
	ANC	3	13	3	0	10	9	2.40
	Al_{lab}	3	10	3	0	7	12	**4.17**
	calcium	3	10	1	2	9	10	0.21

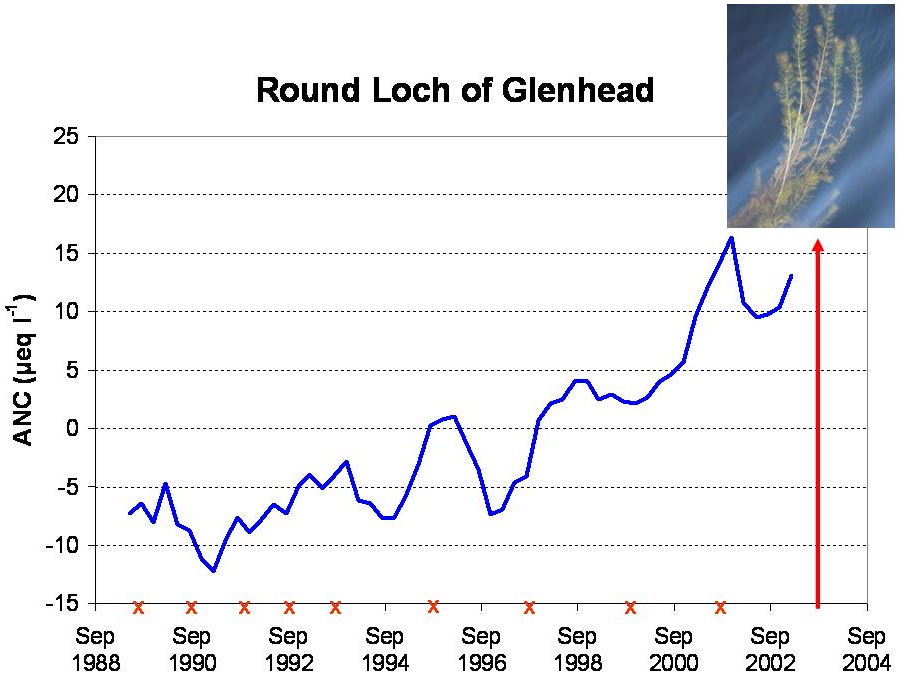
Statistically significant relationships between biology and chemistry

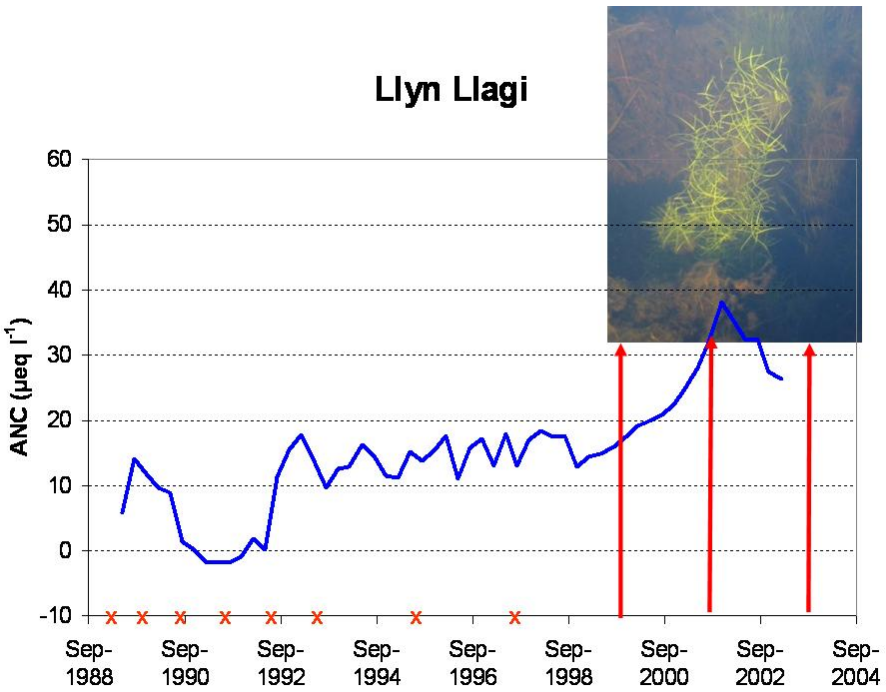
	λ_1RDA								variance shared with time as % total temporal variance							% variance explained when time covariable					
site	TIME	pH	alk	Al	Ca	ANC	DOC	all chem	pH	alk	Al	Ca	ANC	DOC	all chem	pH	alk	Al	Ca	ANC	DOC
Loch Coire nan Arr	**12.1**						6.0	6.0						28.1	28.1						
Allt a'Mharcaidh	**10.6**		5.5				10.1	11.1		0.0				83.0	92.5						5.8
Coire na Con	**9.0**				1.6		7.8	10.6				17.8		11.1	11.1						6.8
Lochnagar	3.8																				
Loch Chon	**16.5**	8.5	10.1	8.6		12.8	12.4	24.4	45.5	48.5	44.2		67.9		64.8						
Loch Tinker	**6.9**																				
RL Glenhead	**9.1**	7.4	7.6	6.7	5.6	8.4	8.1	22.6	50.5	52.7	50.5	23.1	74.7	67.0	76.9						
Loch Grannoch	**29.9**			11.9	26.0	9.5		30.5			33.8	70.9	28.1		71.9				4.7		
Dargall Lane	**18.2**																				
Scoat Tarn	6.0	5.9	5.4				5.0	14.0								4.4	4.3				4.9
Burnmoor Tarn	**10.4**				5.6	6.1		11.0				8.7	32.7		39.4				4.7		
River Etherow	10.8	4.4		6.1														5.9			
Old Lodge	5.4																				
Narrator Brook	**15.1**		8.1			9.2		11.8		29.1			29.1		31.8						
Llyn Llagi	**19.5**		5.6		15.2	8.0	7.6	26.7		0.0		67.7	21.0	22.1	60.5		6.0			3.9	
Llyn Cwm Mynach	**8.7**				3.8		4.4	8.2				1.1		31.0	31.0				3.8		
Afon Hafren	**19.1**				10.5	9.0		20.7				28.8	25.7		40.3						
Afon Gwy	**9.4**			9.2	6.6		8.1	21.3			20.2	29.8			71.3			7.3			5.8
Beagh's Burn	**10.7**	9.6	7.8		12.0	7.5	11.0	42.3	0.0	0.0		0.0	5.6	29.9	82.2	9.7	7.8		12.6	6.9	7.8
Bencrom River	**6.7**	8.4	8.8	5.2	6.0		5.7	28.3	4.5	6.0	7.5	1.5		0.0	28.4	8.1	8.4	4.7	5.9		5.8
Blue Lough	6.2	7.7	6.5	7.7		7.1	9.4	28.6													6.3
Coneyglen Burn	6.1																				

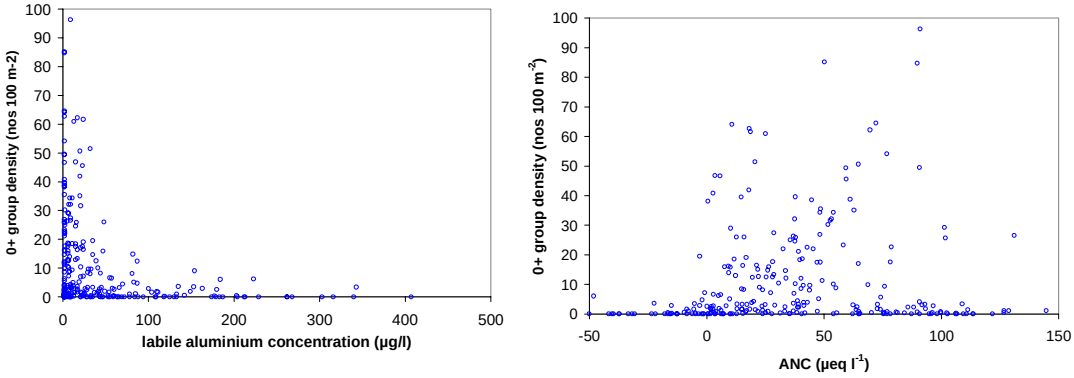
- Epilithic diatoms show strongest correlations with DOC and Ca
- Macroinvertebrates show strongest correlations with ANC and labile Al

Elodeid macrophyte probability of occurrence on an ANC gradient (Generalised linear model)

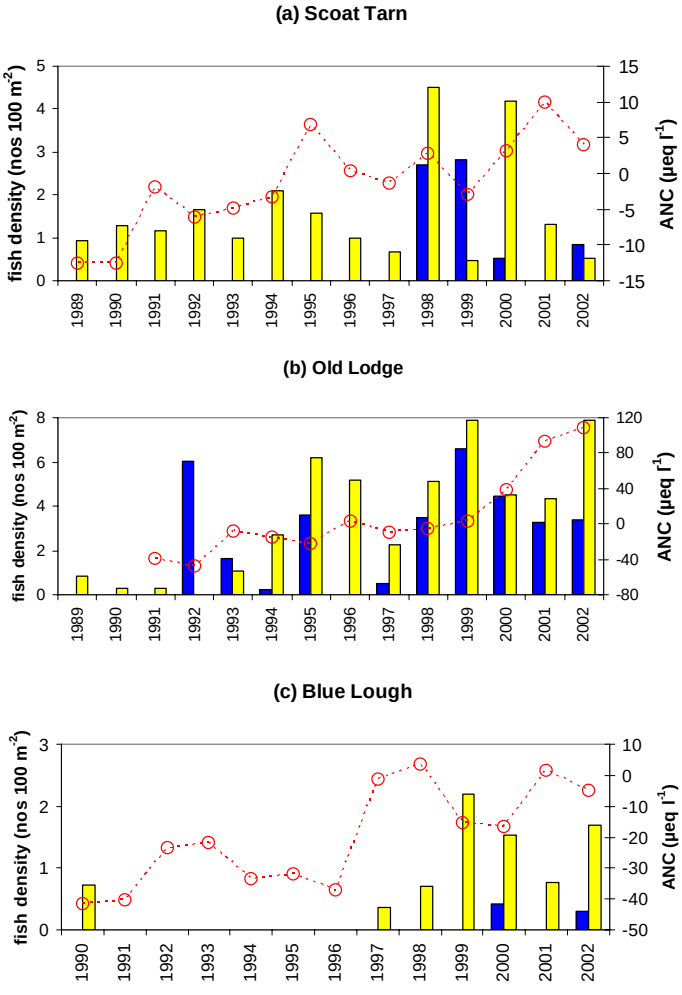



Round Loch of Glenhead
ANC (µeq l-1)
25
20
15
10
5
0
-5
-10
-15
Sep 1988
Sep 1990
Sep 1992
Sep 1994
Sep 1996
Sep 1998
Sep 2000
Sep 2002
Sep 2004


Llyn Llagi
ANC (µeq l-1)
60
50
40
30
20
10
0
-10
Sep-1988
Sep-1990
Sep-1992
Sep-1994
Sep-1996
Sep-1998
Sep-2000
Sep-2002
Sep-2004



Brown trout density (<1 year old) v.labile Al (left) and ANC (right) for all years at all AWMN sites



Brown trout density and ANC with time

Conclusions - chemistry

- Alkalinity-based ANC appears to be less susceptible to noise than BC-AA method
- (although still subject to uncertainties re. actual charge density)
- Alkalinity-based ANC trend strength more strongly correlated with xSO4 trends
- Alkalinity-based ANC trends significant at any site showing a trend in one or more of: pH, labile Al or Alkalinity – acts as a generic acidity indicator

Conclusions – ANC v biology

- Macroinvertebrate trends more closely linked to ANC than any other variable – both spatially and temporally
- Juvenile brown trout have appeared for the first time at all sites which have crossed the 0 µeq l-1 ANC threshold over the monitoring period
- ANC threshold as effective as an alkalinity threshold in "explaining" recent appearance of aquatic macrophyte species
- No strong statistical link between ANC and epilithic diatom communities

14. ICP Waters and EC-Water Framework Directive (WFD) – a view to the future water assessment monitoring in Germany

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Water assessment monitoring - general situation in Europe

The new European water law forces EC-member states to increase activities in water assessment monitoring. These demands raise problems in a number of EC- members e.g. Germany for the reason of decreasing availability of money depending on economical reasons. Consequences can be, that other monitoring activities get a status of minor interest. In Germany, some federal states want to retire from ICP-Waters monitoring.

1. Water framework directive

The future water assessment monitoring of the EU-Member-States will be mainly focussed on the new water law, the Water Framework Directive (WFD), driven into force in the year 2000 (EC 2000).

The demands for monitoring concerning the WFD are

- ecological status has to be determined for water body types of
  - Rivers (> 10 km² catchment area)
  - Lakes (> 0,5 km² surface area)
  - Transitional waters
  - Coastal waters

- ecological status has to be determined with the four biological quality elements
  - phytoplankton
  - macrophytes & phytobenthos
  - macroinvertebrates
  - fish

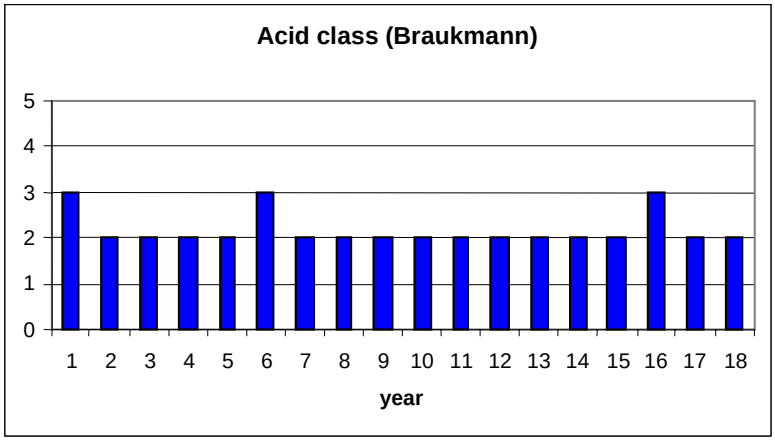
The classification should describe the difference between reference conditions (status 1) and degraded conditions (status 2-5). The target of the WFD is to reach the good Status (= 2) until 2015.

Chemical and hydromorphological elements are to be used as supporting elements for the ecological classification.

In addition a chemical status has to be determined.

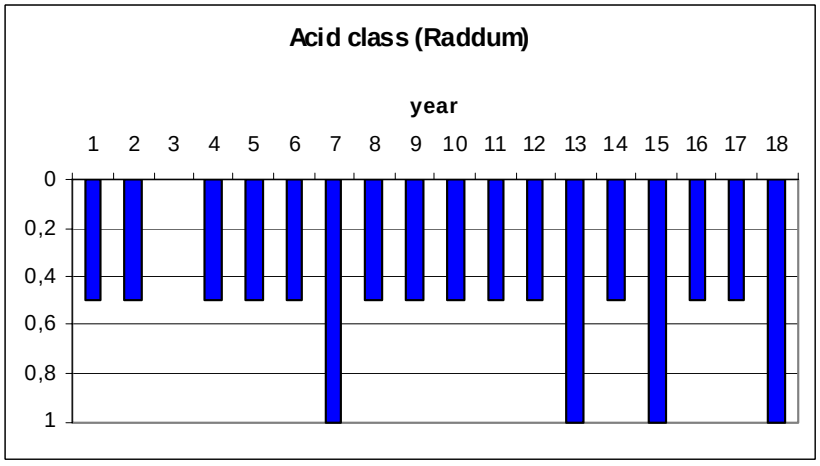
2. ICP-Waters monitoring – some problems

In the last decades a lot of acidification monitoring has been done. The recovery from acidification needs long time periods. The visible results of decreasing acidification (success) depend mainly on changes of the chemical situation in the waters. Biological recovery often cannot be recognized yet. This leads to the question if the current practiced biological methods are useful for the targets of the monitoring of acidified surface waters and if there are alternatives. Especially the acidification index on the basis of macroinvertebrate fauna, which has been used in Germany so far does not indicate much biological response to chemical changes as can be seen from the following example: Hinterer Schachtenbach (Figs. 1, 2).



Values	
1	not acidic, pH > 6.5, most sensitive species are present
2	slightly acidic, pH > 5.5, most sensitive taxa are missing
3	temporarily clearly acidic, pH < 5.5, only tolerant species are present
4	chronically acidic, pH < 5.5 often < 4.3, only a few resistant Indicators are present

Fig. 1: Development of acid class (Braukmann 1994) from 1983 to 2002



Values	
0	Indicators that tolerate acidity to pH < 4.7
0,25	Indicators that tolerate acidity pH 4.7
0,5	Indicators extinct at pH 5.0- 5.5
1	Indicators extinct at pH 5.5- 6.0

Fig. 2: Development of acid class (Fjellheim & Raddum 1990) from 1983 to 2002

In many cases the used biological methods are less sensitive and often do not show any development of the biocoenosis. Alternatives could be to include more benthic fauna metrics and more biological quality elements. The following examples from the same German stream show, that there are more sensitive metrics, which could be used for acidification monitoring (Figs. 3, 4, 5).

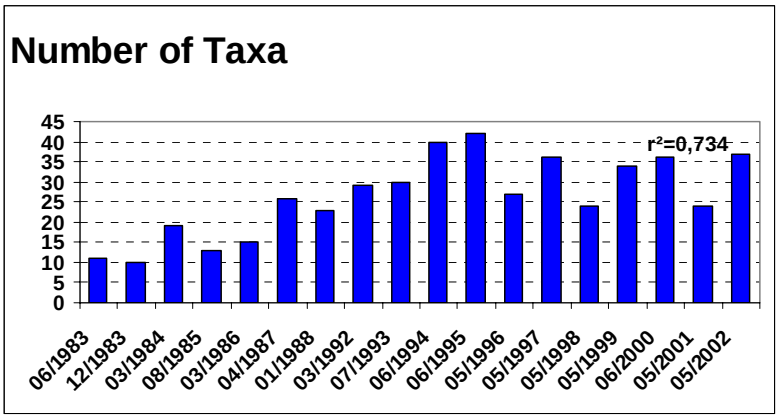


Fig. 3: Development of number of taxa from 1983 to 2002

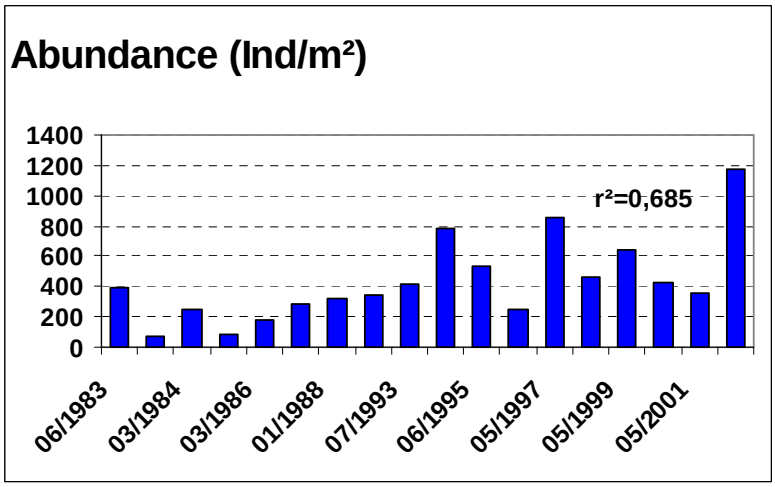


Fig. 4: Development of taxa abundance from 1983 to 2002

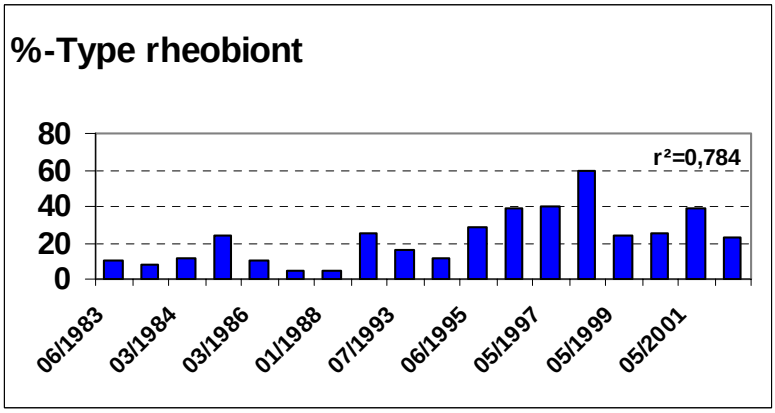


Fig. 5: Development of rheobiont taxa from 1983 to 2002

Proposal for solutions – exemplary activities in Germany

The future way to fulfil all water monitoring demands in Germany will be the combination of monitoring activities where ever possible. With an ecological status classification for the WFD it also should be possible to get information about biological recovery of acidified waters. The WFD classification methods combine the four biological elements. With these elements we should get information about the main pressures on our surface waters including organic pollution, eutrophication, salinisation, acidification and hydromorological degradation. In Germany classification systems for the demands of the WFD are under development. Metrics which are sensitive to acidification are included in the classification systems for the biological elements macroinvertebrates and macrophytes & phytobenthos. For macroinvertebrates an adapted Index (Braukmann & Biss 2004) is used, for macrophytes and phytobenthos new metrics for sensitive mosses and diatoms were developed (Schaumburg et al. 2004).

The current ICP-Waters activities in Germany are:

- 2004: Test of metrics sensitive to acidification at the Bavarian ICP Waters sites
- evaluation of the results and conclusions in the next German ICP Waters report which covers the years 2003/2004
- 2005: further investigation at additional German sites
- results, conclusions and suggestions at the next task force meeting

One problem of the combination of monitoring activities are the sizes of water bodies, which are to be assessed. The acidified waters in many cases are smaller, than the given size borders of the WFD. Thus the WFD-methods will be developed only for larger waters. In Germany, many rivers and streams which meet the sizes of the WFD are acidified and therefore the WFD-methods probably can be used. Acidified German lakes on the other hand are all smaller than 0,5 km². Therefore no WFD lake method can be used for acidified German lakes because no sufficient methods will be developed.

The demands for the future monitoring in Germany are

- with the new assessment systems we should be able to cover most of the monitoring programs, not only the WFD
- with the used metrics we should be able to classify the main degradations of waters
- the classification systems should be sensitive enough to detect major changes in water quality (including acidification)

An overview on the status of the recently developed biological classification systems for the WFD in Germany can be found in Limnologica 34/4, special issue (Dec. 2004). This issue contains 12 articles about the macroinvertebrates in rivers, Macrophytes & Phytobenthos in rivers & lakes. The detailed method for macrophytes an phytobenthos can be downloaded from the homepage of the Bavarian Water Management Agency: www.bayern.de/lfw/projekte.

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15. The European Water Framework Directive and ICP-Waters

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The European Union Water Framework Directive (WFD) is being implemented in a great number of European countries since 2000. Its goal is to guarantee the future use of water resources for all possible uses, e.g. drinking water, nature, recreation, agriculture, etc. Its concerned with both surface waters and groundwaters. Its target is that all waters are in a good chemical and (if applicable) in a good ecological status by the year 2015. The WFD discriminates between four types of waters: rivers, lakes, coastal zone and estuarine waters. Furthermore, waters should be assigned to three categories: natural waters, (hydro-morphologically) heavily modified waters and artificial waters. For natural waters a good ecological status is derived from a natural reference situation. For heavily modified and artificial waters a good ecological potential is defined, taking into account the other functions assigned to the waters. The ecological status and ecological potential is measured using four or five quality elements which are based on characteristics (species composition, abundance) of different species groups, e.g. phytoplankton, macrophytes and phytobenthos, macrofauna and fish. For implementation purposes, waters are delineated into so-called water bodies, where each water body can contain adjacent waters of equal category and equal quality status. The WFD is valid for all waters (and groundwater). For reporting purposes, individual small water bodies may be left out of the reports to the EU, i.e. rivers with a catchment of less than 10 km2 and lakes with a surface area of less than 0.5 km2. However, the results reported should be representative of all the waters the WFD applies to. The monitoring needed to assess the ecological status doesn't need to be performed in all water bodies: a representative set for each water body type should suffice.
Because of monitoring and reporting activities, individual countries within the EU take their own decisions concerning the implementation of the WFD. One of the phenomena is the discarding of small lakes (and other small individual water bodies) in the process of the implementation. However, certain environmental issues are especially important in these small water bodies, e.g. acidification. This is the case not only for the Dutch heathland lakes, but for similar lakes in northern Germany and Denmark, high-altitude lakes in the Alps and a number of lakes in Southern Sweden as well. Thus, according to the current status of the implementation of the WFD, acidification tends to be left out of the reports on ecological status as an important environmental issue although acidified waters may still be present.

It was discussed how the ICP-Waters could play an active role in:
- initiating the cooperation between ICP-Waters and the individual countries on the level of uniformity in metrics to assess the effects of acidification on the ecological status; and in
- increasing the awareness of the European Commission towards acidification as the EU itself is a member of the Convention on Long-Range Transboundary Air Pollution.

16. Reports and publications from the ICP-Waters Programme

All reports from the ICP Waters programme from 1987 up to present are listed below. All reports are available from the Programme Centre.

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Norwegian Institute for Water Research, 1992. Data Report 1990. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1992. Evaluation of the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes. Programme Centre, NIVA, Oslo.

Hovind, H. 1993. Intercalibration 9307: pH, k_{25}, HCO_3, NO_3 + NO_2, Cl, SO_4, Ca, Mg, Na, K, total aluminium, reactive and non-labile aluminium, TOC and COD-Mn. Programme Centre, NIVA,Oslo. NIVA-Report 2948-93.

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