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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 19<sup>th</sup> meeting of the ICP Waters Programme  
Task Force in Lugano, Switzerland, October 18-20, 2003

Prepared the ICP Waters Programme Centre  
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## 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 State Pollution Control Authority, has led the ICP Waters programme. The Norwegian State Pollution Control Authority (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 15 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 19<sup>th</sup> Task Force meeting of the ICP Waters programme, held in Lugano, Switzerland, October 18-20, 2003.

Oslo, June 2004

*Brit Lisa Skjelkvåle*  
Project manager

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# 1. ICP Waters monitoring programme in Canton Ticino, Switzerland

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Canton Ticino (TI) has a surface of about 2'812 km<sup>2</sup> with about 311'900 inhabitants. Its territory can be subdivided in two regions: the Sottoceneri (Southern region) is mostly characterised by hills, while the Sopraceneri (Northern region) has 50% of the territory lying above 1500 m, with mountains rising to over 3000 m a.s.l. Canton Ticino borders on the south with Italy, on the north with Cantons Valais (VS) and Uri (UR), and on the east with Canton Grisons (GR) (see figure 1).

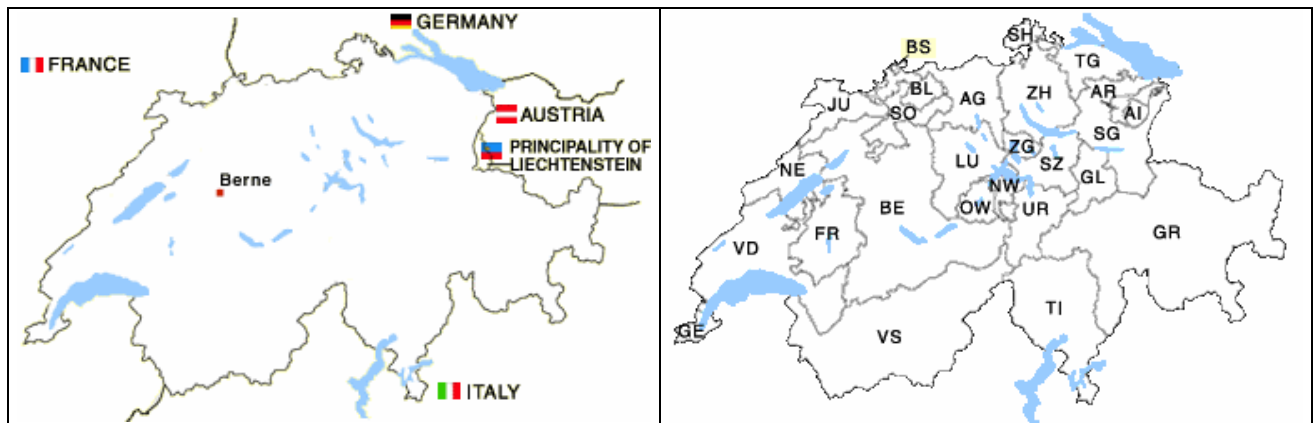


Fig. 1: Maps of Switzerland with neighbouring countries and Cantonal territories (<http://www.admin.ch/ch/e/schweiz/index.html>).

The geology of Sopraceneri (see figure 2) is characterised by crystalline rocks and by waters with low conductivity (20-50  $\mu\text{S cm}^{-1}$  in streams and less than 10-20  $\mu\text{S cm}^{-1}$  in Alpine lakes) and low alkalinity (streams with less than 50  $\mu\text{eq l}^{-1}$  and some Alpine lakes with negative ANC values). All these characteristics make the aquatic ecosystem particularly vulnerable to acidifying agents.

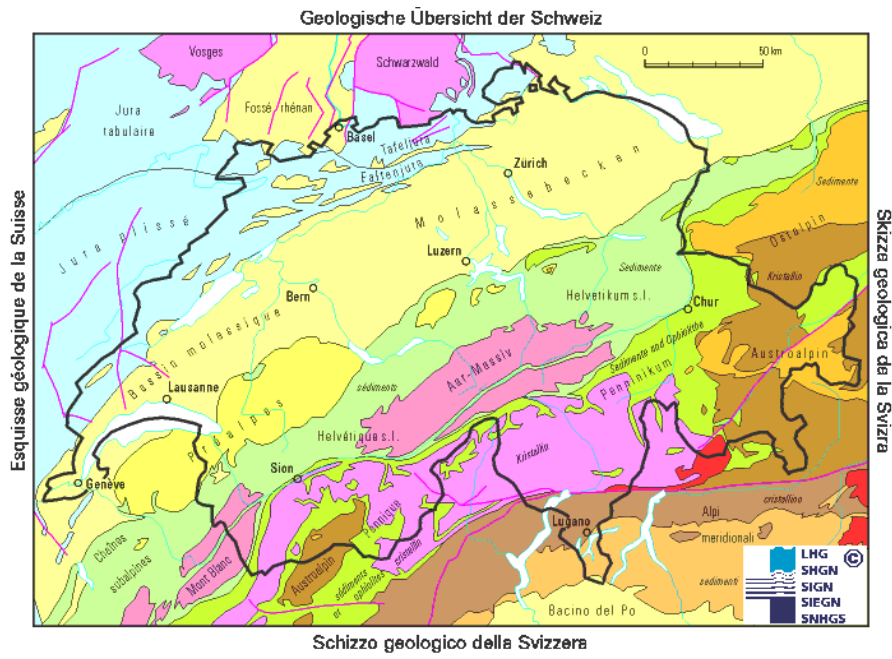


Fig. 2: Geological map of Switzerland ([www.admin.ch/lhg/karten/bilder/geokarte1.gif](http://www.admin.ch/lhg/karten/bilder/geokarte1.gif))

Canton Ticino is characterised by a mild climate with frequent and abundant precipitation, particularly in Spring and Autumn, especially close to the Alps (see figure 3). On average we have 25 – 35 weeks with precipitation events per year.

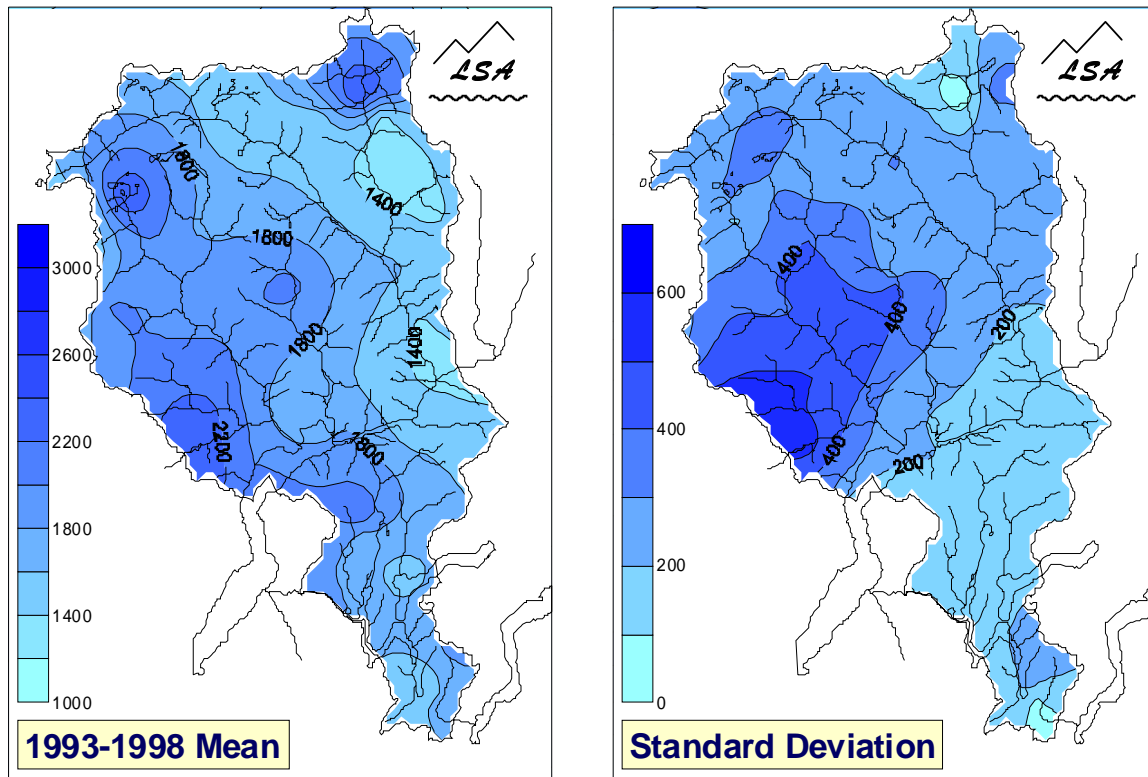


Fig. 3: mean distribution of precipitation in [mm] in Canton Ticino

Most of the air masses come from the south (see figure 4), and are laden with pollutants deriving from sources in the Po Plain (Northern Italy). Primary pollutants derive directly from the combustion of fossil fuels, which produces oxidised compounds of sulphur (sulphur dioxide) and nitrogen (nitrogen oxides). In addition pollutants are emitted from agriculture (use of mineral fertilisers) and manure production from cattle-breeding, both releasing considerable amounts of nitrogen in reduced form (ammonia).

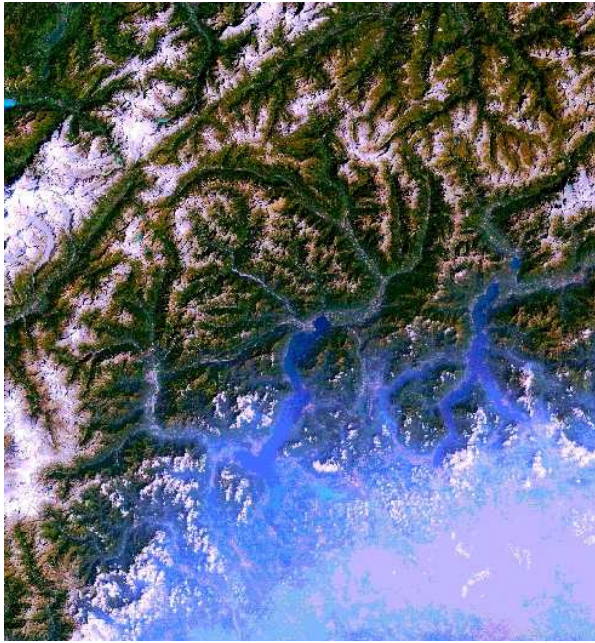


Fig. 4: Insubric Region: satellite picture of the southern arch of the Alps clearly showing the emissions of the Milan area.

(<http://npoc.ee.ethz.ch/Products/Posters/TM/pi43.jpg>)

Wet deposition began to be studied by the Cantonal Agency for Air, Water and Soil Protection (CAAWSP) in the early 80s, with weekly sampling and analysis of depositions at 7 stations located along the south-north axis of the Canton Ticino at various altitudes between 190 and 1890 m a.s.l.

Moreover, in the frame of ICPW Waters the CAAWSP began in 2000 to monitor three streams (Maggia, Vedeggio and Verzasca) and 20 alpine lakes (so-called survey lakes). In 2001 precipitation began to be collected at two further mountain stations, situated near the sampling point of the Maggia and Verzasca streams. In the same year another mountain stream, the Osura, was added to the monitoring programme. Besides chemical analyses, in these four streams investigations on macrobenthos are performed six times during the year.

Figure 5 indicates the location of all current sampling points and rain gauges with table 1 reporting the list of the 20 investigated Alpine lakes, which are sampled twice a year at the surface.

Tab. 1: Alpine lakes sampled at present in the frame of ICP Waters in Canton Ticino

| <b>ID</b> | <b>NAME</b>         | <b>Latitude North</b> | <b>Longitude East</b> | <b>Altitude (m asl)</b> |
|-----------|---------------------|-----------------------|-----------------------|-------------------------|
| 1         | Pozzöi              | 46.265                | 8.472                 | 1955                    |
| 2         | Sfille              | 46.265                | 8.496                 | 1909                    |
| 3         | Alzasca             | 46.267                | 8.585                 | 1855                    |
| 4         | Starlaresc da Sgiof | 46.276                | 8.777                 | 1875                    |
| 5         | Sascola             | 46.284                | 8.571                 | 1740                    |
| 6         | Schwarzsee (Poma)   | 46.335                | 8.504                 | 2315                    |
| 7         | Orsalia             | 46.340                | 8.524                 | 2143                    |
| 8         | Tomè                | 46.364                | 8.691                 | 1692                    |
| 9         | Crosa Grande        | 46.370                | 8.483                 | 2153                    |
| 10        | Porchieirsc         | 46.377                | 8.745                 | 2190                    |
| 11        | Antabia Grande      | 46.387                | 8.492                 | 2189                    |
| 12        | Barone              | 46.404                | 8.753                 | 2391                    |
| 13        | Gardiscio           | 46.429                | 8.757                 | 2580                    |
| 14        | Mognòla             | 46.431                | 8.690                 | 2003                    |
| 15        | Froda               | 46.441                | 8.559                 | 2363                    |
| 16        | Nero                | 46.449                | 8.541                 | 2387                    |
| 17        | Morghirolo          | 46.451                | 8.718                 | 2264                    |
| 18        | Leit                | 46.466                | 8.722                 | 2260                    |
| 19        | Superiore           | 46.477                | 8.587                 | 2128                    |
| 20        | Inferiore           | 46.477                | 8.594                 | 2074                    |

Furthermore, four of these Alpine lakes (Inferiore, Superiore, Tomè and Starlarescio), here defined as experimental lakes, are sampled twice on the profile for chemical parameters, in summer and in winter (below the ice cover). Table 2 reports the list of the parameters measured in the different water bodies. In addition macroinvertebrates samples are collected two to three times per year in the littoral zone and in the outflow of the experimental lakes.

Fish catching for POPs analysis is performed once in autumn, both in the four streams and in two experimental lakes (Inferiore and Superiore).

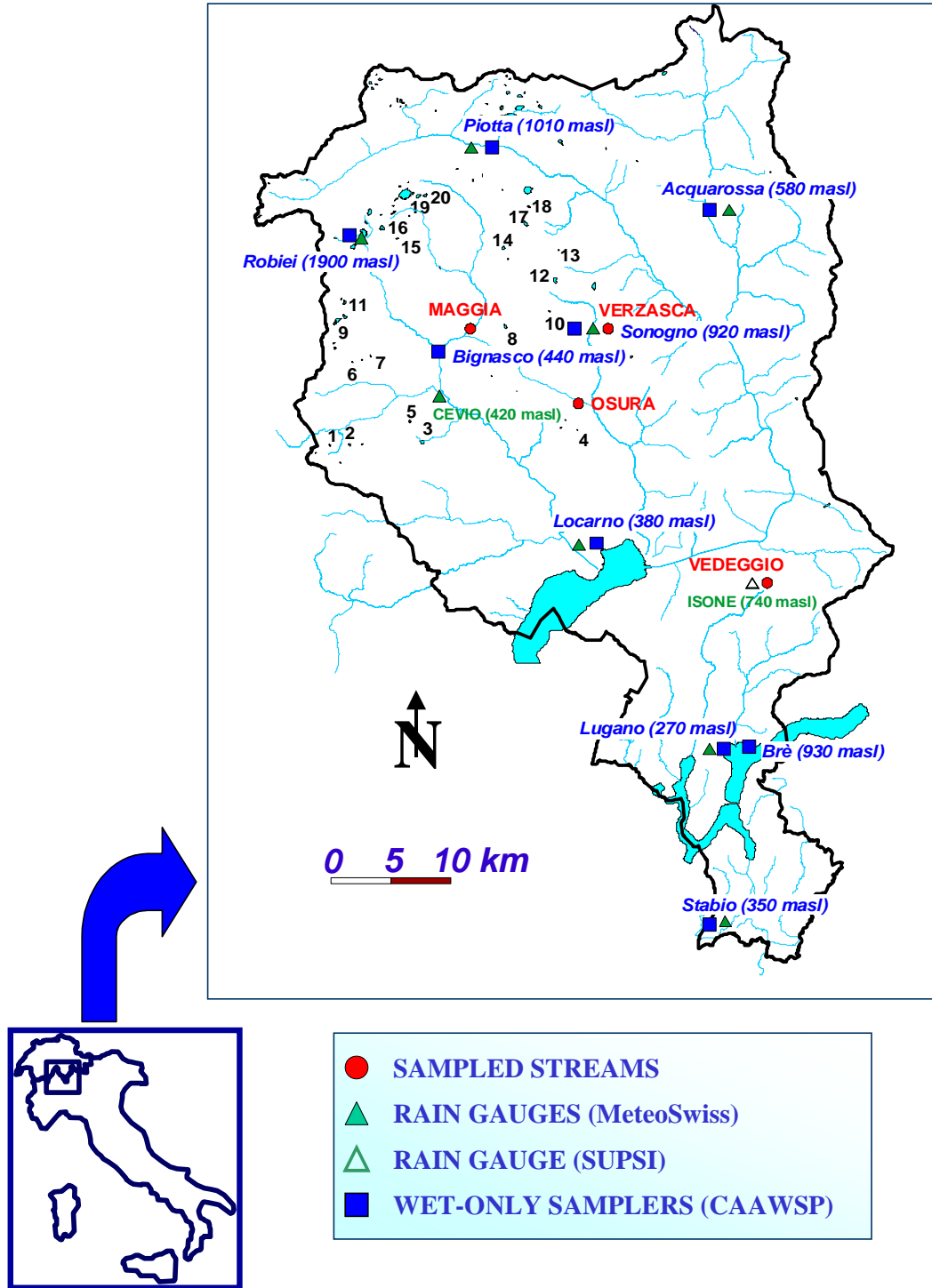


Fig. 5: Map of Canton Ticino with indication of sampled Alpine streams and lakes. Sites with rain gauges and precipitation collectors are also reported.

Tab. 2: List of parameters investigated in the different aquatic compartments

| Parameters                  | Methods  | Investigated water bodies |         |       |
|-----------------------------|--|---------------------------|---------|-------|
|                             |  | precipitation             | streams | lakes |
| pH                          | Potentiometric method  | X                         | X       | X     |
| Conductivity                | Kolrausch bridge (20°C)  | X                         | X       | X     |
| Alkalinity<br>(Bicarbonate) | Potentiometric titration, two end points 4.5 and 4.2 (Gran & Rodier method)                                | X                         | X       | X     |
| Sulphate                    | Ionic chromatography   | X                         | X       | X     |
| Nitrite                     | Automated method (reddish purple azo dye)  | X                         | X       | X     |
| Nitrate                     | Ionic chromatography   | X                         | X       | X     |
| Chloride                    | Ionic chromatography   | X                         | X       | X     |
| o-Phosphate                 | Automated method (molybdate blue, ascorbic acid reduction)   | X                         | X       | X     |
| Calcium                     | Ionic chromatography   | X                         | X       | X     |
| Magnesium                   | Ionic chromatography   | X                         | X       | X     |
| Ammonium                    | Automated method (Indophenol blue)   | X                         | X       | X     |
| Sodium                      | Ionic chromatography   | X                         | X       | X     |
| Potassium                   | Ionic chromatography   | X                         | X       | X     |
| Total Nitrogen              | Persulphate digestion (hydrolysis with $K_2S_2O_8$ + $H_3BO_3$ + NaOH, PSB), Spectrophotometry (UV 210 nm) |                           | X       | X     |
| TOC/DOC                     | UV/peroxodisulphate digestion  |                           | X       | X     |
| POC                         | Catalytic combustion   |                           | X       |       |
| Total Phosphorus            | Persulphate digestion (PSH), automated method (molybdate blue, ascorbic acid reduction)                    |                           | X       | X     |
| Aluminium                   | Automated method (Eriochrome Cyanine R method)   |                           | X       | X     |
| Reactive Silica             | Automated method (molybdenum blue, ascorbic acid reduction)  |                           | X       | X     |
| Oxygen                      | Winkler method   |                           | X       | X     |
| Chlorophyll a               | Ethanol 90% extraction, spectrophotometry (665 nm), cell path 4cm  |                           |         | X     |
| Lead                        | Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS)   |                           | X       | X     |
| Cadmium                     | GFAAS  |                           | X       | X     |
| Copper                      | GFAAS  |                           | X       | X     |
| Zinc                        | GFAAS  |                           | X       | X     |

## 2. Recolonisation of mayflies (Ephemeroptera) to decreased sulphur deposition in Sweden

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### Abstract

During the last decade the deposition of sulphur has decreased markedly in Sweden. This leads to a recovery of surface waters in Sweden. For example an increase in surface water alkalinity and ANC has been noted in the last decade. Increases in surface water alkalinity and ANC have resulted in positive biological responses of macroinvertebrate communities. For example, an acid index based on acid-sensitive species (HMI acid index) indicates recovery in a number of lakes. Some of the species behind the increases are the more frequent occurrence of three mayfly taxa: *Caenis horaria* (L.), *C. luctuosa* (Burmeister) and *Ephemera vulgata* (L.).

### 2.1 Introduction

During the last years the deposition of sulphur has decreased markedly in Sweden (Fig. 1), and as a consequence recovery in water chemistry can be seen (Wilander (1997, Skjelkvåle *et al.* 2001). As a result from this recovery acid sensitive species are now more common in the macroinvertebrate community in some Swedish reference lakes. This increase can be shown by the HMI acidity index. The HMI-index (Anonymous 1999) is a combination of acidity metrics or scored categories resulting in a composite indicator metric for acidity. The first category consists of the presence/absence of acid sensitive species of the orders Ephemeroptera, Plecoptera, and Trichoptera as well as the presence or absence of *Gammarus*. The second category consists of the presence/absence of groups of acid-sensitive indicator taxa (leeches, the coleopteran family Elmidae and molluscs). The third category is the ratio of *Baetis* to Plecoptera and the fourth is simply a score for taxa richness. Three scoring categories are recognized: 0 – 4 points indicate strong or very strong perturbation, 4 – 6 points indicate clear perturbation and 6 points is considered as no or insignificant perturbation.



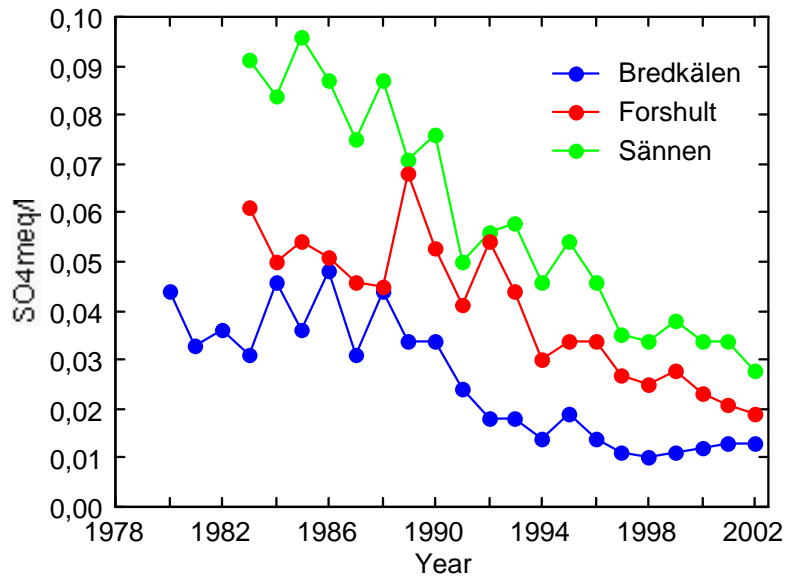


Figure 1. Deposition of sulphate (data IVL). Bredkälén is situated in north Sweden; north-west of Lake Tvärningen, Forshult in central north of Lake Vänern and Sännen close to Lake Sännen in southern Sweden (cf. Figure 2).



Figure 2. The geographic distribution of the eight lakes presented here.

## 2.2 Methods

Benthic macroinvertebrates have been collected from the littoral region (0-1 meter depth) in the Swedish reference lakes since 1984. Sampling has been performed annually, with spring samples taken from 1984 – 1994, whilst from 1995 to the present samples have been collected in September to October. Five replicate standardised kick-samples were taken from hard-bottom littoral regions using a handnet (0.5 mm mesh) and along a 1 m stretch during 20 seconds (SS-EN 27 828). Coincident with the biological sampling, surface water samples were collected and analysed for a suite of physico-chemical variables. In contrast to the macroinvertebrate samples that were collected once annually, water samples were collected from three to six times per year.

## 2.3 Results

Three lake groups were identified with respect to different phases of recovery:

(1) circum-neutral lakes that have never been acid, (2) naturally acid or acidified lakes that do not show any indication of biological recovery and (3) lakes that show biological recovery (Table 1).

*Table 1. Median pH (1986-2000) for eight lakes that are part of the Swedish monitoring programme. Results of regression of pH against time (1986 - 2000): \* = 0.05; \*\* = 0.01.*

|  | Median pH | Annual minimum value |
|--|-----------|----------------------|
| 1. Circum-neutral                                      |           |                      |
| Skärgölen  | 6.75      | 5.46-6.20            |
| Stora Envättern  | 6.51**    | 5.89-6.41            |
| 2. Acidified - showing no signs of biological recovery |           |                      |
| Härsvätten   | 4.49***   | 4.21-4.56            |
| Storasjö   | 5.43      | 4.67-5.48            |
| 3. Acidified - showing signs of biological recovery    |           |                      |
| Fräcksjön  | 6.34*     | 5.81-6.20            |
| Stensjön   | 6.34*     | 5.72-6.28            |
| Sännen   | 5.80**    | 4.81-6.01            |
| Tväringen  | 6.61      | 5.98-6.57            |

The effect of pH-value on biota indicated as HMI is apparent (Figure 3). While all lakes with a pH-value below 5 have index values below 6 do the two lakes with pH-values above 5,5 have index values higher than 6.

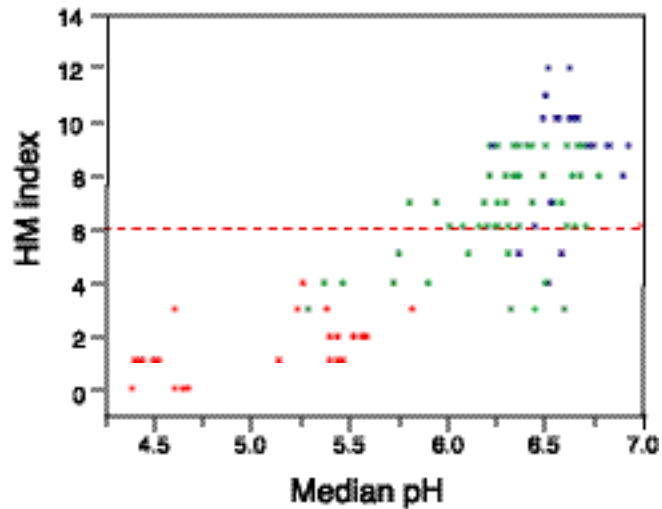


Figure 3. Acidity index regressed against median pH. Below a value of 6 (shown as the dotted red line) macroinvertebrate communities are expected to be affected by acidification. red = acid lakes ( $n = 2$ ), green = acid "recovery" lakes ( $n = 4$ ) and blue = circum-neutral lakes ( $n = 2$ ).

For the eight lakes the change in time of the littoral fauna as HMI index is presented in figure 4. The two circum-neutral lakes (blue) changed little with time, even though some increase may be seen. Apparent is the large variation between years in Stora Envättern. The four lakes in the "recovery" group (green) show steady increases in the index. As expected can little change be found in the two acid lakes (red).

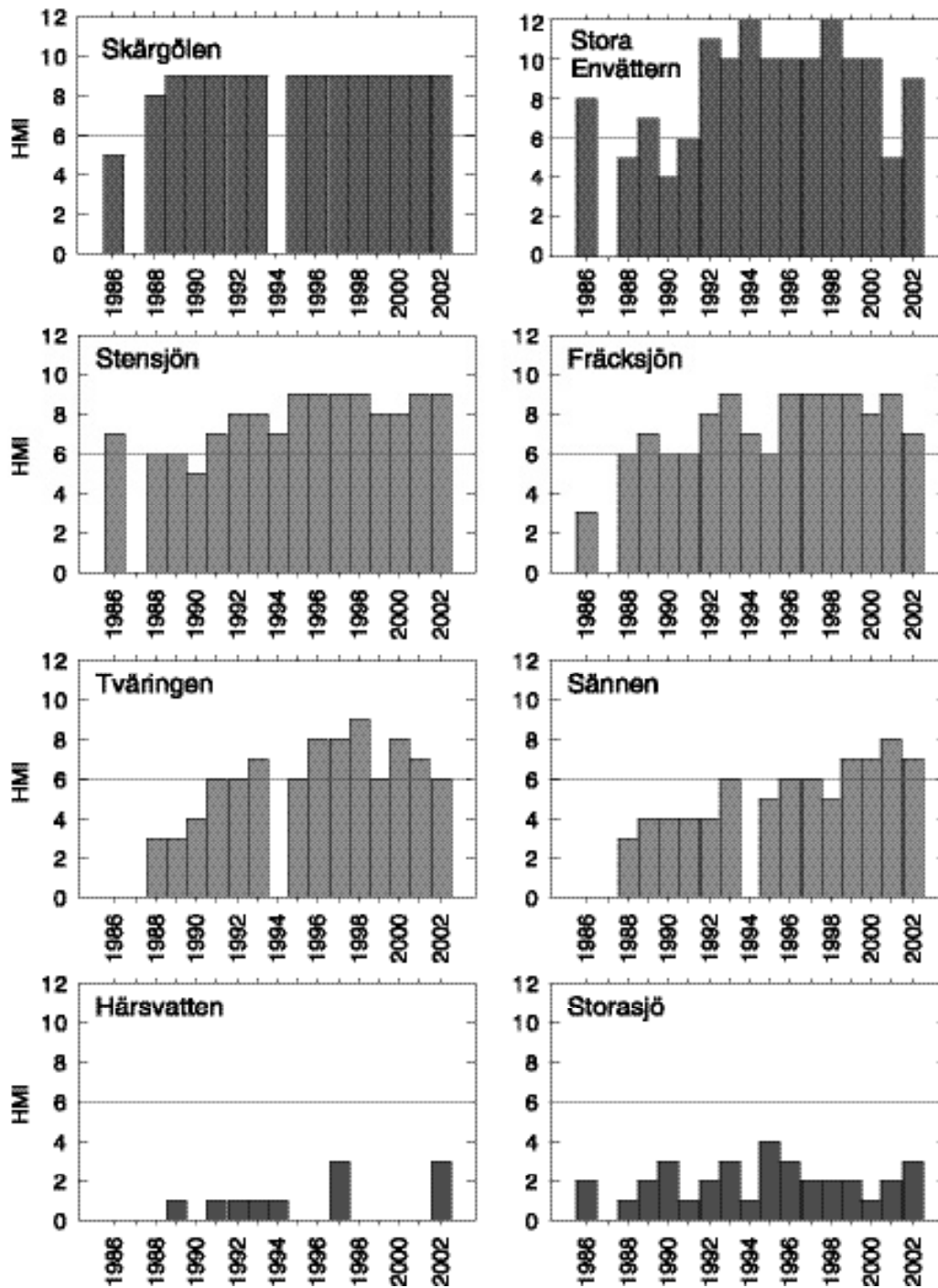


Figure 4. Time-series plots of the acid HM-index for eight reference lakes. Values <6 (denoted as the red line) indicate acid-stress, years 1986 – 2002.

Species causing an increase in the HMI index are the Ephemeropterans: *Caenis horaria*, *C. luctuosa* and *Ephemerella vulgata* (Table 2). After at least three years of absence (1988–1990) few individuals were collected until 1997. From that year both species have been found every year.

Table 2. Time-series for Lake Tväringen showing the number per sample of two acid-sensitive mayfly taxa becoming more abundant. No sample from 1994.

| Taxon           | 1988 | 1989 | 1990 | 1991 | 1992 | 1993 | 1995 | 1996 | 1997 | 1998 | 1999 | 2000 | 2001 | 2002 |
|-----------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| <i>Ephemera</i> |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| <i>vulgata</i>  | 0    | 0    | 0    | 1    | 0    | 1    | 0    | 0    | 10   | 2    | 2    | 2    | 8    | 13   |
| <i>Caenis</i>   |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| <i>horaria</i>  | 0    | 0    | 0    | 1    | 5    | 4    | 3    | 6    | 33   | 12   | 7    | 18   | 15   | 50   |

The possible effect of a change from sampling in the spring to autumn is important when evaluating the time series. During 1988 samples were taken in 18 reference lakes, acid as well as neutral, during four seasons; spring, early summer, late summer and autumn. Mean HMI index values for these four seasons are; spring = 4.7, early summer = 4.7, late summer = 4.3 and autumn = 4.1. The tendency for most lakes was that the spring HMI was higher (paired t-test  $p = 0.08$ ). The eight lakes presented here followed the same pattern. Hence, the change of sampling period from spring to autumn should not underestimate the assessment of trends using this dataset.

## 2.4 Conclusions

Thanks to decreased sulphur deposition in southern Sweden the pH has increased in some Swedish reference lakes. This increase has resulted in a notable biological recovery in the littoral macroinvertebrate communities. Taxa responsible for this recovery are the mayfly taxa *Caenis* spp. and *Ephemera vulgata*, both of which have become more common.

Although sulphur deposition has decreased in the last decade, the noted increase in pH could also to some extent be the result of a somewhat warmer climate during this time period (i.e. sharp peaks during snowmelt may also have resulted in lower pH).

## 2.5 References

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### 3. Seasonal change of metal concentration in Csórrét-reservoir, Hungary

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**Keywords:** heavy metal, reservoir

#### 3.1 Introduction

Csórrét reservoir has the smallest buffer capacity all of the Hungarian waters, hence the most sensitive water for airborne acidification. The reservoir is the Hungarian sampling area in the „International Cooperative Program on Assessment and Monitoring of Acidification of Rivers and Lakes” program (Hungarian ICP Water site).

The aim of our nearly two decades long survey series is to determine the sensitivity for airborne acidification of the abovementioned sampling area (Csórrét reservoir) and to determine its changing.

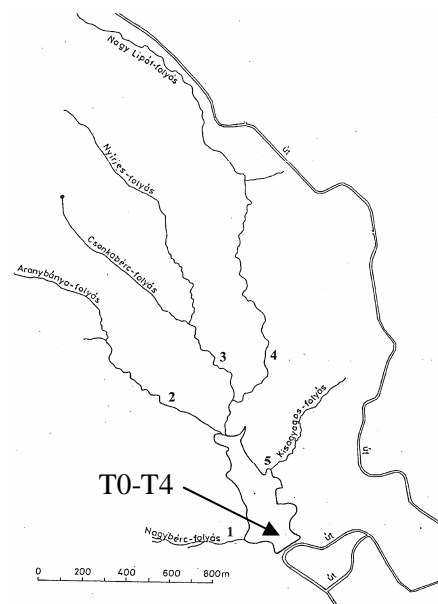
Besides acidification common water quality parameters and nitrogen household was investigated, as well as their variation in the light of seasonal and meteorological events.

Concentration of heavy metals present in the reservoir was measured continuously. In our work we looked for the reasons of concentration changes, accordingly not only the reservoir was investigated but all of its feeding creeks were measured, too. Thus in case of certain components it is determinable whether the concentration changes (practically increase) in the reservoir is caused by the feeding creeks or by internal load. The concentration variation of some heavy metals is determined by seasonal changes, while in case of other metals by short-term meteorological impacts. Seasonal and meteorological effects were investigated as well.

In May 2002 a new monitoring program was launched with monthly sampling. Exact dates of sample collections were harmonised with significant meteorological events instead of the earlier quarter-yearly sampling.

#### The Csórrét reservoir

The Csórrét Reservoir is located in the north-eastern mountain region of Hungary, at an altitude of 534 m. The reservoir was built in 1973 to supply drinking water to the nearby small villages. The surface of the reservoir at operating level is 12.8 ha, its maximum depth is 22 m and its volume is 1 million m<sup>3</sup>. The reservoir is fed by five perennial creeks and at time of larger rainfalls also by several temporary water-courses. Creeks are loading about 1.5 million m<sup>3</sup> water/year into the reservoir what is complemented with 0.3-0.4 million m<sup>3</sup> surface runoff and subsurface flow. About 1 million m<sup>3</sup>/year water is used for



drinking water supply. The 8.38 km<sup>2</sup> catchment area is vegetated by deciduous and coniferous forests in approximately equal ratio. The reservoir and its catchment are situated on volcanic bedrock.

There are no human activities on the catchment except tourism and forestry, so it is intact from direct anthropogenic pollution, only the airborne pollution can reach the reservoir.

### 3.2 Sampling

The monthly frequency sampling program was started in May 2002 and in this paper we show the results till November 2003. The samples were taken from the reservoir and from its five creeks. The samples from the reservoir were collected in 40 m distance of the dam at the water intake facility (see map). Five depths were sampled with a submersible pump (depths are relative to the bottom): **T4**: 1 m (bottom), **T3**: 3.5 m, **T2**: 7.0 m, **T1**: 10.5 m, **T0**: surface (14-16 m). The streams were sampled at a fixed section between 10-50 m from the mouth of the stream, to avoid the back-swell effect of reservoir. When sampling, much care was taken to exclude sediments from the water samples.

In the winter of 2002-2003 snow samples were taken from many different points of catchment.

### 3.3 Analyses

Immediately after sampling temperature, pH, and electric conductivity of the water sample were measured in situ. 200 ml of the sample was filtered through 0.45µm membrane filter for measuring suspended solids. The filtrate, and a sub-sample from the original sample were conserved with concentrated HNO<sub>3</sub> and stored for later analyses of dissolved and total heavy metal concentration, respectively.

The samples were analysed for the following conventional parameters: KOI<sub>ps</sub>, NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, organic nitrogen, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, alkalinity, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>. The concentrations of metals (Hg, Cd, Pb, Cu, Cr, Ni, Al, Zn, Fe, and Mn) were determined by atomic absorption spectrophotometry, using the graphite-furnace method.

### 3.4 Meteorological conditions

Before the monitoring program started there was a fairly long drought period, hence the water level of the reservoir was several meters lower than the normal operating level. At the end of July, beginning of August 2002 there was extraordinarily cold weather with extremely heavy rain (this rainy period caused serious floods in Czech Republic and Saxony, however in Hungary it caused only minor problems). The long, intensive rainfall filled up the reservoir, finally it even needed to deflate water. The next rainy period was at the end of September 2002 with cold rain. The first snowfall was in November 2002. The 2002-2003 winter was remarkably cold and extreme amounts of snow fell. Unusually there was no melt between two snowings, thus the snow cover remained during the whole winter. At March 2003 there was 70-80 cm deep snow on the catchment and according to the estimation it was equal to 1 million m<sup>3</sup> water. The snowmelt occurred at the end of March. After the usual spring (April-May) rainfall, there was no considerable precipitation and the summer was very hot.

### 3.5 Results

#### Temperature

Maximal depth of the reservoir is 22 m, average depth is about 10 m. The area of the reservoir is small and relatively protected from wind, so the wind can mix only the upper layer. Consequently stable thermal stratification evolves in the summer period. Because of the temperature changes the reservoir has two turnovers a year.

The surface of the reservoir freezes in winter, thickness of the ice in 2002-2003 reached 30-50 cm. The ice melted at end of March 2003. In the spring the upper water layers warmed up relatively fast, in May the water temperature reached 18-20 °C, what could increase to 22-24 °C by the middle of summer.

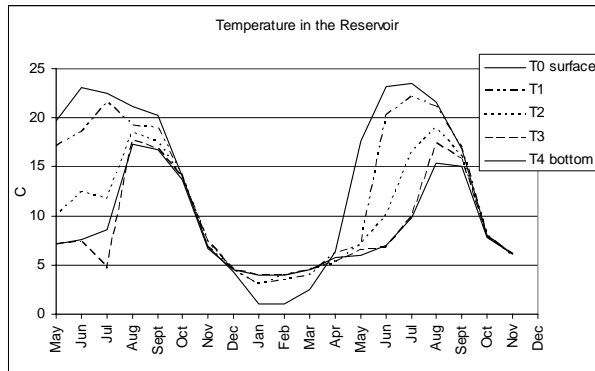


Figure 1. Temperature in the reservoir

Due to lack of mixing the temperature of the lower layer increased very slowly, thus at end of June, beginning of July the temperature difference between the surface and the bottom could reach 15 °C (Fig. 1). The water was the warmest in August, this time the lowest layer warmed up to 15-18 °C. The air and water temperature started to decrease in the relatively cool September (what is typical at our climate) and the thermal stratification ceased at the beginning of October and the temperature fell rapidly until freezing in December. In the frozen reservoir a small-scale stratification was observable, from the bottom up to T1 layer the water temperature is 4 °C, while in the uppermost layer the temperature decreased continuously to 0 °C.

#### pH

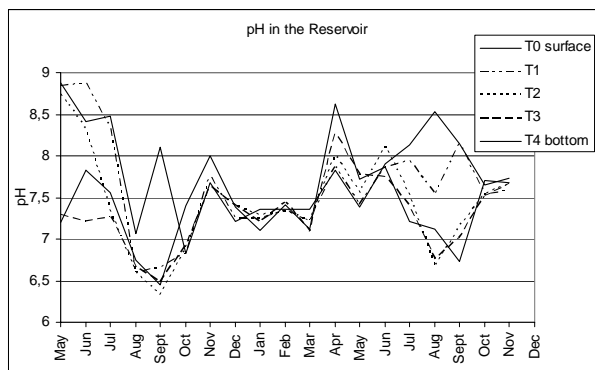


Figure 2. pH in the reservoir

At the beginning of the investigation period – the water level of the reservoir was low, and thermal stratification evolved – significant pH differences were measured between the upper and the lower water layers (Fig. 2). In the lower layers 7.3-7.5 pH was measured, in the near surface layer the pH was



around 8.5. The drastic pH fall perceptible in August 2002 is a result of a huge amount of acid characteristic rain. After this remarkable decrease and some small fluctuation the pH stabilized around 7.3 which characterized the whole winter period. This pH changed in the beginning of spring (April 2003) in form of a short-term but significant pH increase, when the pH of the lower layers increased to 8-8.5 (the reason of this increase is not known). In May-June the pH of different layers was equalized at 7.8-8.0 level. From June to September significant pH differences developed between the water layers. The pH of the upper layers increased in small-scale, whilst in the lower layers (T2-T4) the pH decreased considerably, more then one unit. The pH increase of the upper layer can be explained with the algal activity, but the reason of the pH decrease in the lower layer is not known. In October thermal stratification ceased, the water mixed up, what extinguished the pH stratification also. The pH of reservoir was same in October and November 2003 and based on the experience of previous year, it is presumable, that significant pH change will not happen until March 2004.

### Alkalinity, conductivity

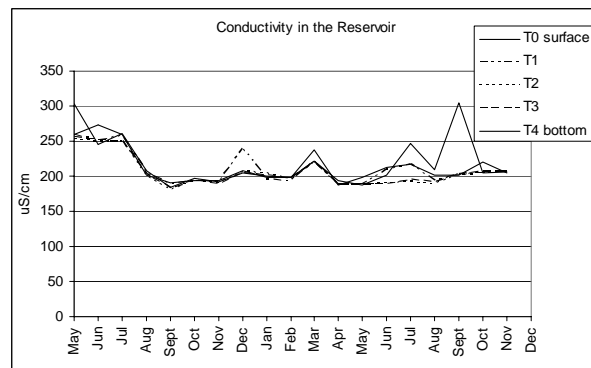
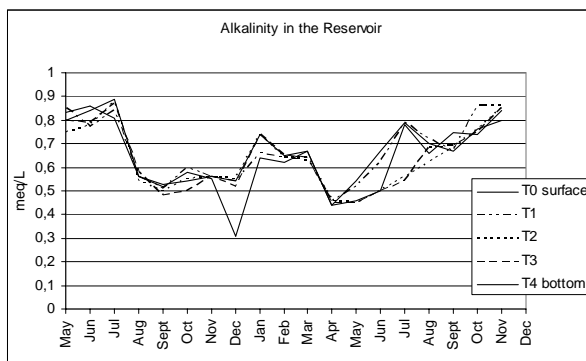


Figure 3. Alkalinity in the reservoir      Figure 4. Conductivity in the reservoir

The alkalinity of the reservoir was 0.8-0.9 meq/l at the beginning of the investigation period (Fig. 3), what was dropped to 0.5-0.6 meq/l by the effect of precipitation filled up the reservoir. The alkalinity increased (relatively slowly) in dry periods, because the alkalinity of feeding creeks was almost two times higher than that of the reservoir. Snowmelt at March 2003 caused a drastic alkalinity decrease again. In the rainy periods alkalinity decreased in proportion to the diluting effect of rain. In aspect of alkalinity, stratification is not detectable. From May to July 2003 in T2 and T3 layers the alkalinity was lower than in the other layers, though this phenomenon is not really understandable.

The conductivity of the reservoir was 250  $\mu\text{S}/\text{cm}$  in the beginning of the investigation period (Fig. 4), and decreased to and stabilized at 200  $\mu\text{S}/\text{cm}$ . The conductivity is equal in all water layers, „stratification” is not detectable.

### Chemical oxygen demand ( $COD_{ps}$ )

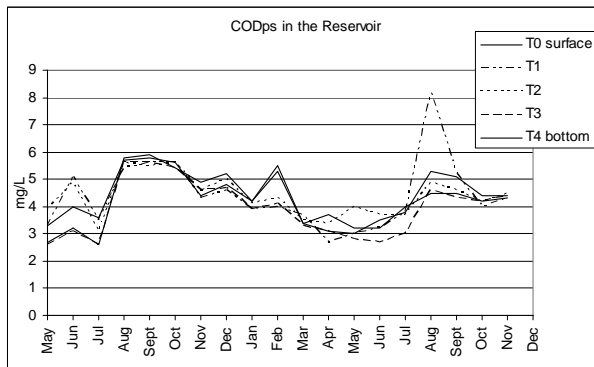


Figure 5.  $COD_{ps}$  in the reservoir

COD showed stratification in the beginning. This stratification ceased at July 2002 and COD was about 3 mg/L in the reservoir (Fig. 5). In August, by the effect of heavy rain, the creeks transported huge amounts of organic matter into the reservoir, accordingly the COD increased to 6 mg/L. After this, COD decreased slowly to 3 mg/L till May 2003. From June COD started to increase again up to 4.5 mg/L. In 2003 autumn COD showed a moderate decrease.

The salient high COD value (8.2 mg/L) measured in T1 layer in August 2003 is explainable with a large algal biomass present in the reservoir.

The organic matter present in reservoir is transported by creeks, generally in relatively small concentration, what can grow up dramatically at time of large runoffs. Organic material degrades relative slowly in the reservoir (to decrease from 6 mg/L to 3 mg/L needed half year). In the reservoir less than 3 mg/L or more than 6-7 mg/L COD concentration is not likely to occur according to experiences.

### Mercury

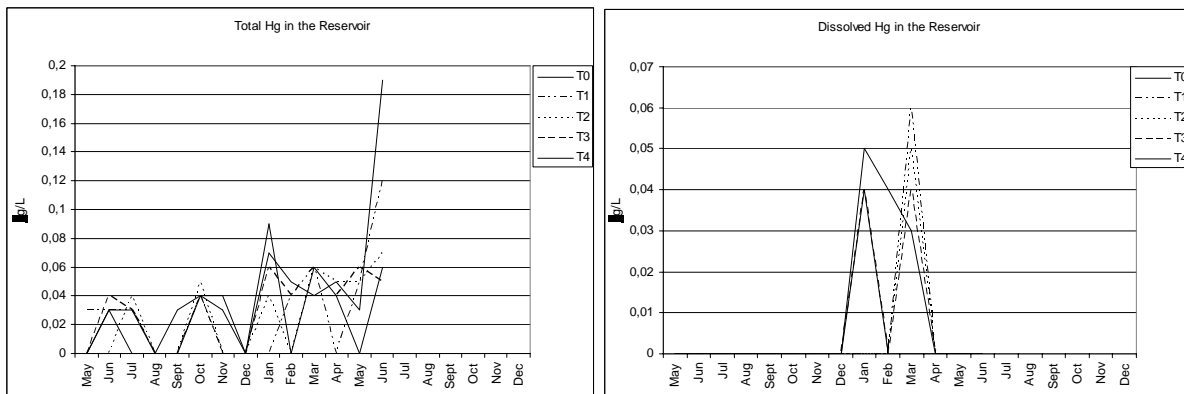


Figure 6.: Total and dissolved mercury in the reservoir

Mercury in the reservoir was present just above the detection limit (0.03 µg/L). The measurable mercury nearly in full amount was present in solid state, dissolved form was measurable only in some cases (Fig. 6).

Contrarily in the snow samples the mercury concentration was relatively high, the highest value of total mercury was 2.5 µg/L (limit for drinking water: 1 µg/L) and the concentration of dissolved form reached 0.7-0.8 µg/L. The estimated volume of the accumulated water in snow form on the catchment of the reservoir was approximately 1.0-1.1 million m<sup>3</sup> which is equal to the volume of the reservoir (1 million m<sup>3</sup>). Thus theoretically at snowmelt a total water change could take place and it could cause a

drastic mercury concentration increase. Contrarily after snowmelt only a small-scale dissolved mercury concentration increase was observable (adjudication of “small-scale increase” is very relative: the *ratio* of increase is approximate 100% so it is very significant, but the “high” *absolute* concentrations are very low, only 1/10 of the allowed amount in drinking water (1.0 µg/L) so it is not significant increase) and total mercury concentration increase was also small. The reason of this phenomenon is that mercury precipitates rapidly and settles, eventually accumulating in the sediment.

### Cadmium

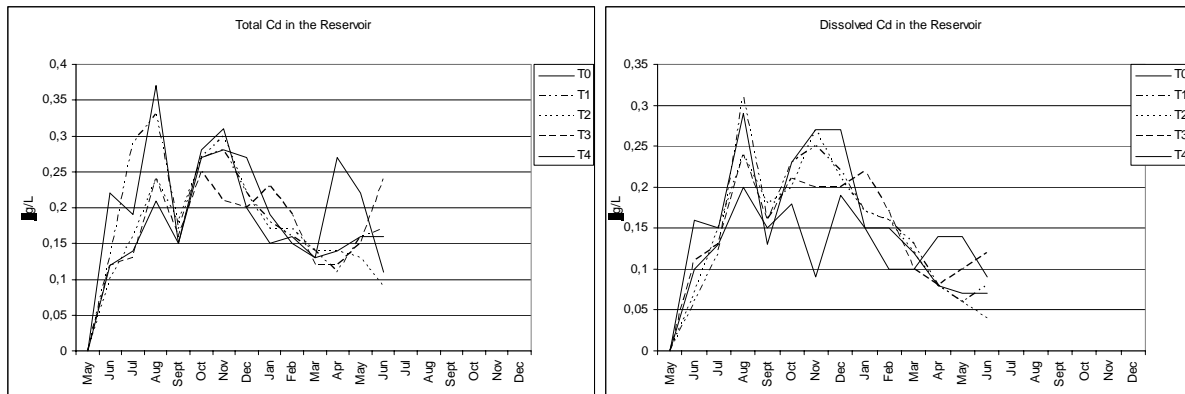


Figure 7.: Total and dissolved cadmium in the reservoir

Cadmium was almost entirely in dissolved form in the water of the reservoir (Fig. 7). Its concentration was increasing in the beginning of the study period up until 0.37 µg/l. (The limit in drinking water is 5.0 µg/l.). This increase was stopped by the heavy rains in mid-summer, when the concentration fell to 0.15 µg/l in each depth. After this event the concentration increased again until November, up to 0.3 µg/l. From November to April it decreased gradually to 0.10-0.15 µg/l. From June it increased again slightly. No vertical gradient was detected in the cadmium concentration.

### Lead

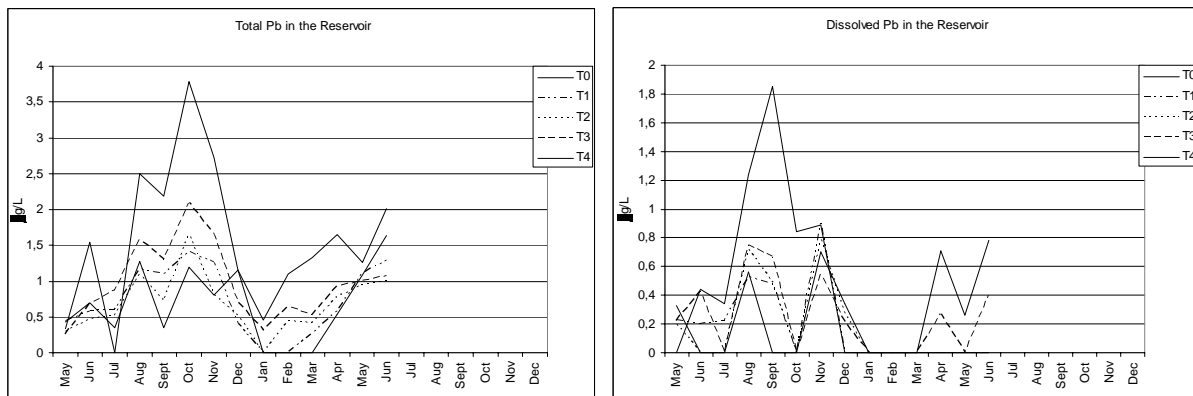


Figure 8.: Total and dissolved lead in the reservoir

One third – half of the lead was in dissolved form (Fig. 8). The particulate fraction showed significant variation mainly in the deepest water layer. In the winter, after the reservoir was ice covered, concentration of the lead decreased to its minimum, most probably due to settling. The concentration of the dissolved fraction ranged between the detection limit (0.2 µg/l) and 0.5 µg/l and it did not show any specific temporal variation. The only feature to be mentioned is that by the time the reservoir got ice-cover, concentration of dissolved lead decreased below the detection limit. Dissolved lead was

detectable only in the deepest, i.e. near-sediment layer, which suggests that the lead was desorbed from the sediment.

## Zinc

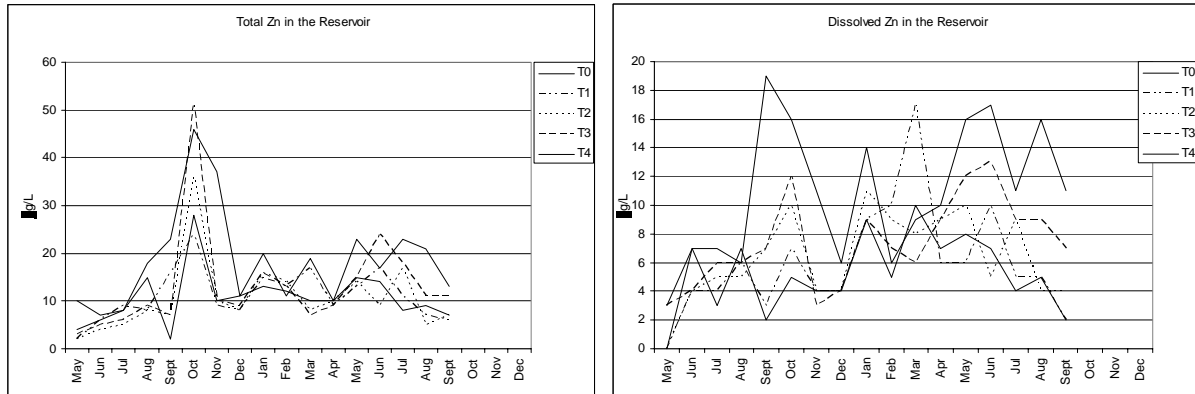


Figure 9.: Total and dissolved zinc in the reservoir

Dissolved zinc accounted for a little more than half of the total zinc measured in the reservoir (Fig. 9). In October, 2002 following a heavy storm there was a sharp increase in the zinc concentration. After this event the concentration decreased rapidly and stabilized at a lower value. No further tendency or important change in zinc concentration occurred later on.

## Aluminum

There were two peaks in the total Al concentration – one during the summer 2002 rainstorms and one during the snowmelt next spring (Fig. 10). This was just the opposite compared to what has happened to pH and alkalinity in the same period. At the same time in the inflowing creeks Al concentration multiplied, 2500 µg/l being the highest measured value. Thus, it can be assumed that the Al concentration increase in the reservoir was caused by the Al load coming with the inflowing creeks. As these peaks occurred during high-flows, when soil erosion is also significant, it is possible that the Al was washed from clay-minerals.

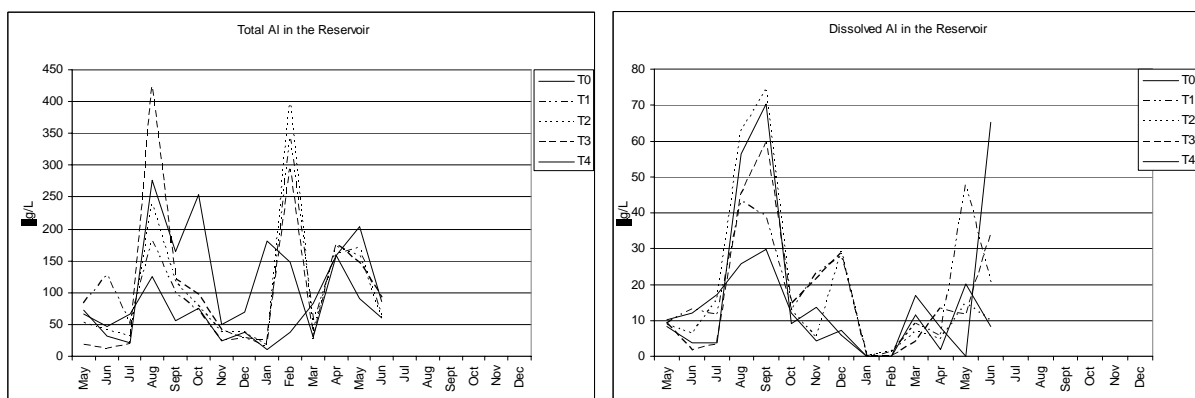


Figure 10.: Total and dissolved aluminium in the reservoir

Less than 20% of the total Al was in dissolved form. Its concentration increased only for short periods and parallel to the particulate fraction. However, when the total Al concentration increased, there was always an increase in the dissolved fraction, too. The concentration of dissolved Al never got close to 200 µg/l, which is the limit for drinking water. The particulate form, on the other hand, is easily removed by the treatment technology provided.

### Suspended solids

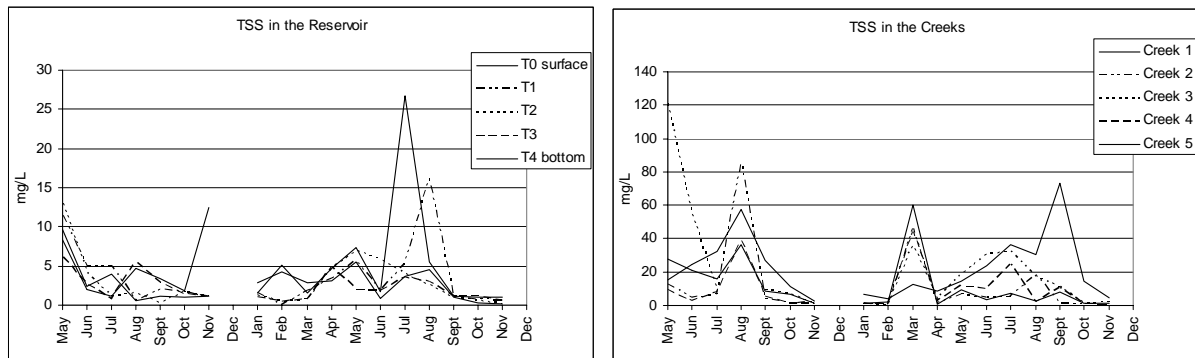


Figure 11.: Suspended solids in the reservoir and creeks

Suspended solids concentration in the reservoir was low, usually lower than 5 mg/l (Fig. 11). This is in accordance with that the reservoir is deep, and the sediment cannot be stirred up by the wind. In some cases higher suspended solids concentrations were measured, but due to the uncertainty of the sampling, we should not draw any further conclusion from it.

Sampling of the creeks, mainly at the time of low-flow, was quite problematic, because of the easily suspending sediment, which could be stirred up during the sampling. This, in turn, might have biased suspended solids measurements. Keeping this in mind, typical suspended solids concentrations in the creeks were between 5-40 mg/l. During high-flow, concentrations well exceeded this range. Reasonably, no other temporal variation could be detected.

### Iron and manganese

Iron and manganese behaved rather similarly. In the warm period their concentration increased significantly in the water layers near the sediment (but only there) and decreased during cooling and the turnover of the reservoir.

In the sediment of the reservoir there was oxidized Fe(III). During the summer period, after stratification of the reservoir, there was a very limited supply of oxygen into the water layers near the sediment. At the same time, the dissolved oxygen pool was depleted quickly by degradation processes. Anaerobic conditions developed, and Fe(III) was reduced to Fe(II). This latter dissolves easily in water, thus there was a supply of dissolved iron from the sediment to the water (Fig. 12). If in contempt of the stratification Fe(II) reaches the overlying water layers, it is oxidized to Fe(III) by the dissolved oxygen present there, and precipitates and settles.

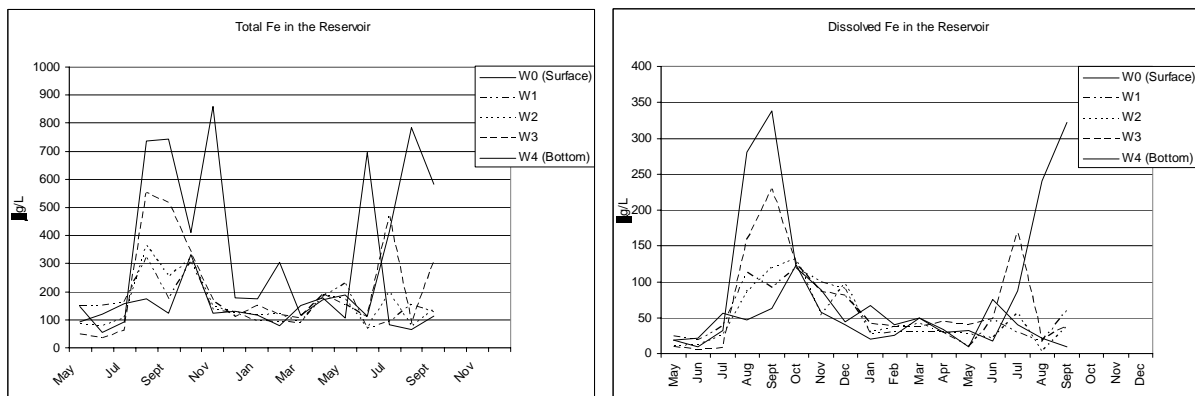


Figure 12: Total and dissolved iron in the reservoir

Thus dissolved iron can be present only near the sediment. Total iron in the reservoir was split into dissolved and particulate form in a 1:2 ratio. (This is not in disagreement with the preceding, as solution and precipitation occurs simultaneously.) Compared to the drinking water standard (200 µg/l), total iron almost always exceeded it, dissolved iron exceeded it regularly in the summer only in the deepest water layer.

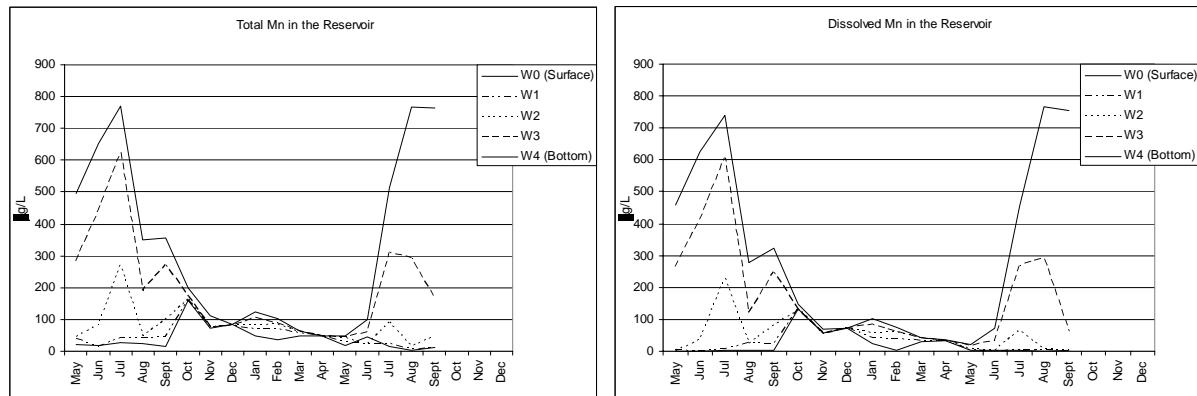


Figure 13: Total and dissolved iron in the reservoir

Manganese behaved very similarly to iron. Depending on the redox circumstances manganese is present in the Mn(II) or in the Mn(IV) form and the manganese concentration changes accordingly (Fig. 13). Manganese could be found almost entirely in the dissolved form in the reservoir. In the near-sediment water layers manganese concentration was almost always above the drinking water standard (50 µg/l), in the end of the summer values grew as high as 800 µg/l.

In the inflowing creeks both iron and manganese were present in lower concentration than in the reservoir. It refers to that the high dissolved iron and manganese content in the deepest water layer came from internal load.

### 3.6 Conclusion

The water quality of the Csórrét-reservoir was grossly affected by seasonal variation of the meteorological conditions. However, in case of some components this was overwhelmed by extreme episodic events, such as heavy rainstorms.

Temperature stratification and turnovers (dimictic reservoir) affected the temporal variation of most of the measured components.

Electric conductivity was rather stable in the reservoir, only huge extra inflows could reduce it significantly. On the other hand, it got back to the original values slowly.

The alkalinity was low, which was further decreased by the vast inflow in the summer 2002 rainstorm and in the spring 2003 snowmelt. After these events alkalinity increased slowly. When compared to other areas in Hungary, alkalinity of the water of the reservoir is low, however, it cannot be considered as sensible to airborne acidification.

This is supported also by the pH measurements. The pH of the reservoir was almost always above pH 7. In the summer pH showed a vertical gradient. The upper water layers could more than 1 unit higher pH than the deeper water layer, probably due to the effect of the algae grown near the surface of the water.

Chemical oxygen demand in the water of the reservoir ranged between 3-6 mg/l. During significant precipitations the inflowing creeks brought higher amounts of organic material in the reservoir,

increasing the COD concentration in the reservoir, too. After these events COD concentration decreased slowly, due to the slow breakdown of organic material.

Concentration of different heavy metals and the variation in their concentration varied notably. Mercury was present in very low concentrations and dissolved mercury was usually below the detection limit. At the same time we can assume that there was a significant airborne mercury load, which assumption is based on the measurements of snow-samples. Concentration as high as 2 µg/l was found in the snow, which was magnitudes higher than those measured in the water of the reservoir. However, the snowmelt increased the mercury concentration of the reservoir slightly, as mercury precipitates and settles quickly.

Cadmium was present also in very small concentration, and almost all of it was in dissolved form. Changes in its concentration can not yet be explained.

Concentration of lead in the reservoir was always just above the detection limit. Dissolved lead made up one third – half of the total lead concentration. Changes in its concentration were not affected either by seasonal variation or episodic meteorological events.

Zinc had very stable concentration during the study period, only the October 2002 rain caused a notable increase in its concentration. Half of the total zinc could be found in dissolved form.

As the sediment of the reservoir is not stirred up regularly, suspended solids concentration in the water was low. After significant precipitations the inflowing creeks brought large amounts of suspended solids.

Aluminum was mainly bound to particulate matter, only 20% was in dissolved form. The Al concentration of the reservoir was determined mainly by the inflowing creeks. The Al concentration of the creeks correlated well with the flow, which implies that Al was transferred in the creeks by erosion. The scale of erosion is affected by the scale of the precipitation. It means that the Al concentration was defined mostly by the meteorological conditions.

Iron and manganese got into the water of the reservoir mainly by internal load. The concentration of both components increased sharply in the summer in the near-sediment water layers. This was due to that organic material degrading processes deplete the dissolved oxygen pool, thus anaerobic conditions developed. Under these circumstances poorly soluble Fe(III) and Mn(IV) in the sediment were reduced to highly water soluble Fe(II) and Mn(II). The autumn turnover ceased the oxygen deficiency, thus iron and manganese were oxidized, precipitated and settled. As a result, the concentration of iron and manganese was low in the winter.

## 4. Recovery from acidification – Plešné Lake in the Bohemian Forest; in Czech with English abstract

Vrba, J., Kopáček, J., Nedbalová, L. (2003): Zotavování šumavských jezer z acidifikace – příklad Plešného jezera ( ). *Acta Universitatis Ecologiae* **10**, Suppl. 1: 59–61.

### Abstract

During the last decade, we observed a recovery of phytoplankton in a strongly acidified lake, following a drop of atmospheric sulphur and nitrogen deposition in the Bohemian Forest. A statistical comparison of seasonal data (1994, 1998, and 2001; Kruskal-Wallis test) showed significant decreases in total reactive aluminium ( $Al_T$ ) and extracellular acid phosphatase activity and, in parallel, significant increases in total phosphorus, chlorophyll, and phytoplankton biomass. Our results suggested a key role of  $Al_T$  in overall phosphorus availability in acidified lakes, in particular for the phytoplankton. Hence, the decrease in  $Al_T$  likely controls the level of lake recovery.

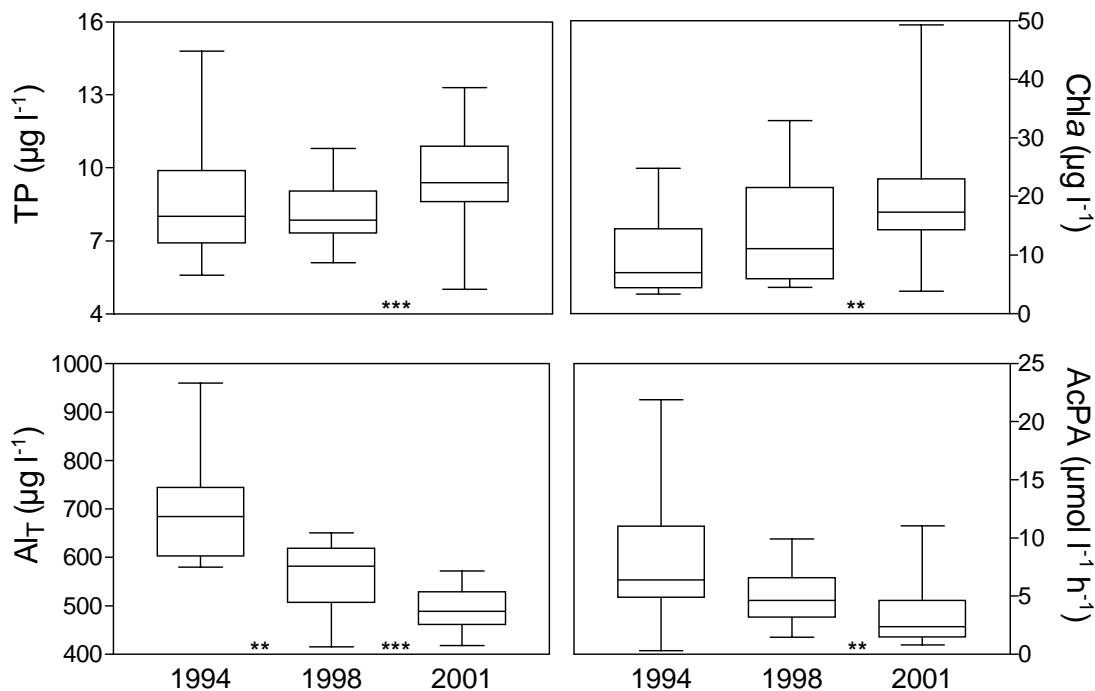
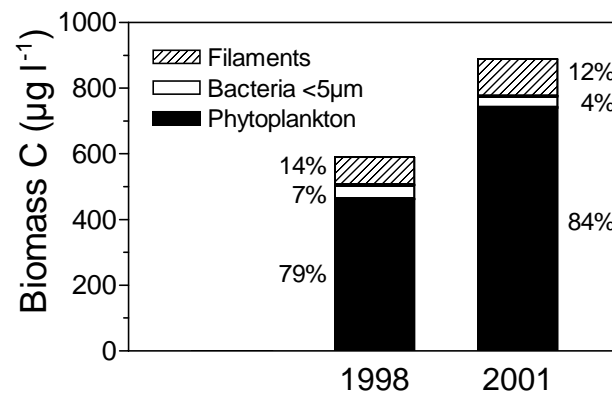


Fig. 1. Comparisons of data on total phosphorus (TP), total reactive aluminium ( $Al_T$ ), chlorophyll a (Chla), and extracellular acid phosphatase activity (AcPA) in Plešné Lake during three seasons (median, quartiles, minimum and maximum). Changes of all parameters are significant (\*\*  $P < 0.01$ , \*\*\*  $P < 0.001$ ).





*Fig. 2. A comparison of total plankton biomass and proportions of phytoplankton, unicellular and filamentous bacteria (%) in the epilimnion of Plešné Lake during two seasons (mean values).*

## 5. Some results from the Swedish national lake and river survey in 2000.

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### 5.1 Introduction

In Sweden seven national surveys of lakes have been performed until now (Table 1). The first took place in August 1972 and covered a little more than 1000 lakes. At that time no national lake register was available, so each of the 25 counties was asked to select 50 "representative" lakes for the study. Even though the counties had various preferences e.g. eutrophication or acidification, this survey gave a good overview of those aspects and in addition to also to water colour and organic matter. This survey also included sampling of phytoplankton.

When the third national lake inventory was planned a lake register was available covering the bulk of lakes with an area  $>0,01 \text{ km}^2$ . Thus a statistical selection of lakes to sample could be performed. In connection with the survey in 1990 a Nordic co-operation was initiated regarding a common evaluation of acidification (Henriksen *et al.* 1990). The outcome of this and later surveys have been to Swedish contribution to LRTAP.

For the 1995 inventory the three Nordic countries; Finland, Norway and Sweden joined forces and used uniform methods for selection of lakes, determinations and evaluations (Henriksen *et al.* 1996). The physico-chemical part of the study was implemented in co-ordination, while Sweden only included biodiversity. Also Northern Kola and Russian Karelia participated.

*Table 1. National lake surveys in Sweden. Number includes regional surveyed lakes (Wilander *et al.* 2003).*

| <b>Date</b> | <b>Number of lakes</b> |
|-------------|------------------------|
| August 1972 | 1250                   |
| Spring 1975 | 1000                   |
| 1977-1980   | 8000                   |
| Winter 1985 | 6900                   |
| Winter 1990 | 4018                   |
| Autumn 1995 | 4113                   |
| Autumn 2000 | 3465                   |

### 5.2 Survey

Sites were randomly selected (stratified with respect to size and acidification/county) and used to determine the status of the country's surface waters with respect to general ecological quality, with emphasis on the assessment of acidification, eutrophication, metal concentrations, and biodiversity (benthic macroinvertebrates). Autumn sampling, during the mixing period, was selected to obtain a representative whole-lake sample (i.e. decreasing the variation that might be introduced by sampling stratified lakes). For both lakes and streams a stratified, statistical selection based on the national lake and stream registers (SMHI, Swedish Meteorological and Hydrological Institute) was chosen. Five

lake surface area classes ( $>0.04 \text{ km}^2$ ) and county were used in the stratified selection of lakes. This resulted in a sample of 3025 lakes, which corresponds to about 3% of the population. For stratifying streams two catchment area classes (15 – 50 and 50 – 250  $\text{km}^2$ ) were used, out of which 700 streams were sampled. The same lakes and streams were sampled both in 1995 and 2000. The stratified sample (with respect to lake area and location) and knowledge of the population enables a destratification resulting in an estimate of the condition for the entire lake population. Data are available on [http://info1.ma.slu.se/max/www\\_max.acgi\\$Project?ID=Intro](http://info1.ma.slu.se/max/www_max.acgi$Project?ID=Intro)

### 5.3 Results

Two problems are of special importance when evaluating acidification of Swedish surface waters; one is the unusual high concentration of humic substances and the other is the extensive liming. The TOC concentration in Sweden as median is 6,1 mg/l; a little bit less than that for Finland with 7,6, but substantially higher the value for Norway of 1,9 mg/l (Skjelkvåle *et al.* 2001). Most of the lakes and streams reported to ICP-Waters also have lower concentrations ( Skjelkvåle, 2003). Liming is quite intensive in Sweden. Out of the sampled lakes 20% were limed and an additional 9% affected by liming upstream. When evaluating national surveys a correction for the lime treatment was made by estimating the pre-liming Ca of limed lakes using the expected (natural) Ca/Mg ratio for nearby lakes and assuming that the Mg-concentration was not affected by liming (Henriksen *et al.* 1990, Wilander *et al.* 1998).

Sulphate is generally considered as the major source of acidity ( $\text{H}^+$ ) and to a lesser degree nitrate. However, due the high concentrations of organic matter in many Swedish lakes organic anions can explain a considerable proportion of the acidity (Figure 1). For the most acid lakes are concentrations of organic anions higher than the  $\text{H}^+$  concentration and thus can alone explain the acidity. Only in three cases does sulphate correspond to the entire acidity. Of course the effect of each anion can not entirely be singled out. This condition, which will be further accentuated thanks to reduced S deposition, makes it even more difficult to separate anthropogenic acidity from natural (humic acids).

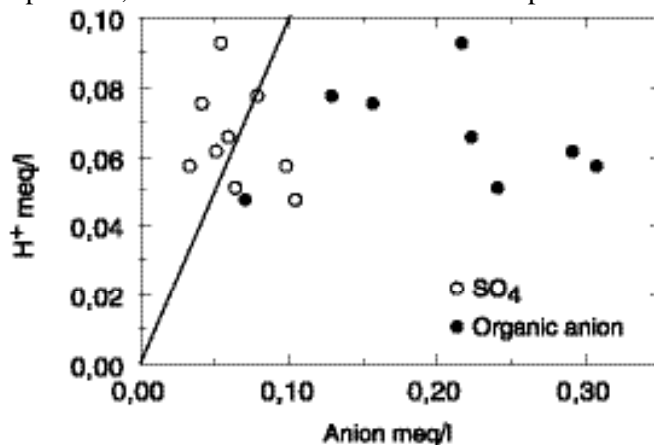


Figure 1. The relation between concentration of  $\text{H}^+$  (from pH-value) and the two dominant acid anions sulphate and organic anions (humic acids). Data for the most acid lakes. Lake survey 2000.

### 5.4 The 2000 lake survey in perspective

National lake surveys describe various conditions in surface water over the entire nation. The lake inventory in 2000 revealed lower pH-values than for the previous in 1995. Why do we find no recovery? However, samplings with long time intervals are not useful to outline changes over time. Thus an interpretation of these data must be supported by other, more intense, monitoring programmes. Here will the results of surveys will be discussed in that perspective. First presented are data for the close to 500 lakes, which have been sampled at five lake surveys (Figure 2).

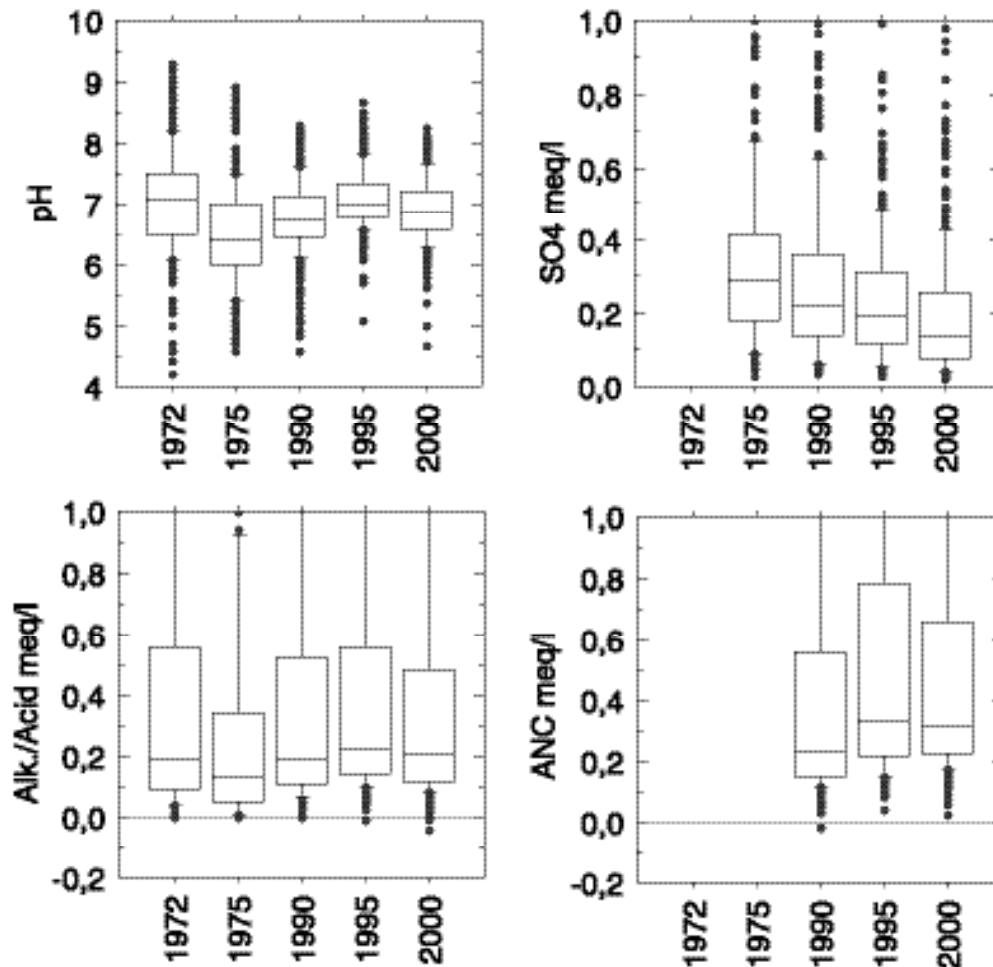


Figure 2. Results for lakes sampled at five lake surveys (n=470). The box presents the 25, 50 and 75 percentiles. Whiskers show the 10 and 90 percentiles. The graphs may be cut.

There is no straightforward increase in pH-values from 1972 to 2000. Instead the highest values were measured in 1972. This is quite contradictory to the decline in sulphate. But it is the sampling during the summer of 1972 that causes this pattern. In 1990 the sampling took place in the winter, often in ice-covered lakes. Thus part of the pattern is a result of seasonal variation and not a temporal change. In the summer photosynthesis leads to uptake of  $\text{CO}_2$ , while mineralisation of organic matter during winter, often under the ice, produces  $\text{CO}_2$ . From 1975 to 1995 the pH-values increased, but in 2000 this positive trend was broken. Other acidity indicators as alkalinity and ANC also diminished in 2000. Again, this is in contrast to the change in sulphate, which decreased substantially throughout the period, even in 2000.

Both alkalinity and ANC diminish with a supply of strong acid as sulphuric acid or nitric acid. Humic acids reacts differently; it lowers the carbonate alkalinity but has little effect on ANC. ANC thus is a more distinct indicator of anthropogenic acidification than alkalinity. Organic matter increased from 1990 to 2000 (Figure 3). Thus here one cause for the diminution in alkalinity between 1995 and 2000 can be found.

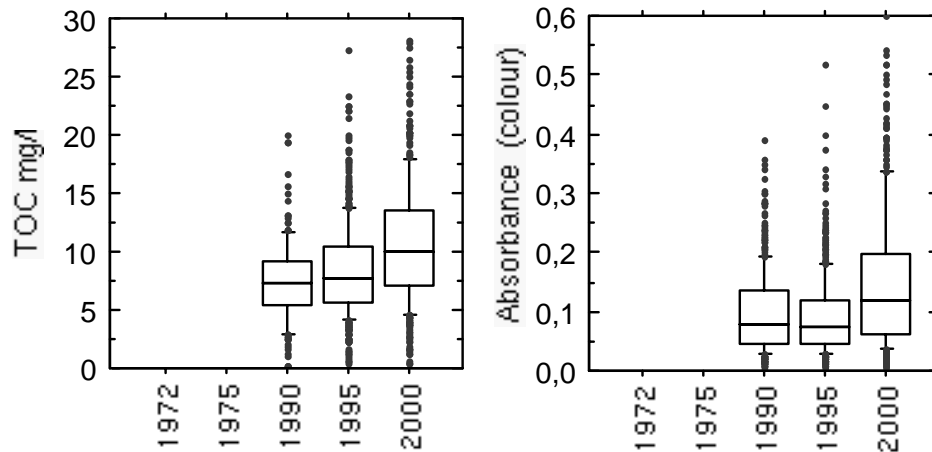


Figure 3. Organic matter as TOC and water colour (absorbance at 420 nm). Results for lakes sampled at five lake surveys ( $n=470$ ). The box presents the 25, 50 and 75 percentiles. Whiskers show the 10 and 90 percentiles. The graphs may be cut.

Not only sulphate and alkalinity diminished between 1995 and 2000 but also the concentrations of calcium, magnesium, sodium and chloride. Simultaneously concentrations of organic matter (absorbance), silicate and nitrate increased (Figure 4). The decrease in alkalinity is not anticipated – concentrations were lower in 2000 than in 1995. We will look at this contradiction more in detail.

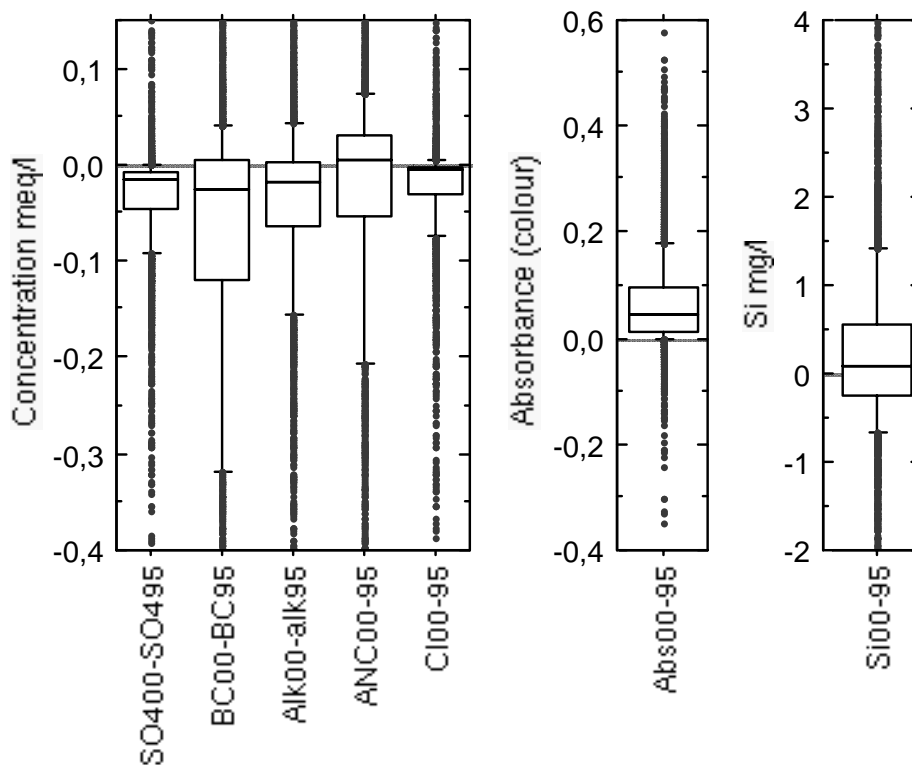


Figure 4. Differences between the surveys in 2000 and 1995 for  $SO_4$ , base cations (BC), alkalinity, chloride, absorbance (colour) and silica. Negative values imply lower concentrations in 2000. The graphs may be cut.

Year 2000 was an extremely rainy year (Figure 5). No other lake survey encountered such a situation. The lower concentrations are due to dilution created by the heavy rains. High groundwater levels forced the flow of water to take more surficial paths, reducing the effect of weathering and at the same time increasing leaching of humic substances. Concentrations of sodium and chloride, which mainly emanate from seasalt in the precipitation diminished less, and not significantly.

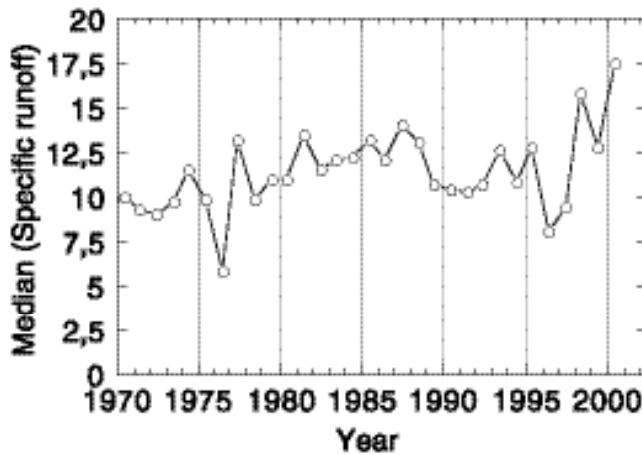


Figure 5. Specific run-off ( $l/km^2,s$ ) for the period 1970–2000 (median values for 27 small streams).

A large part of the rains fell at the end of the year (November–December) when sampling was going on in the southern part of the country (Figure 6). But the high precipitation in July and August did not seem to substantially affect the water chemistry when sampling in September in southern Norrland.

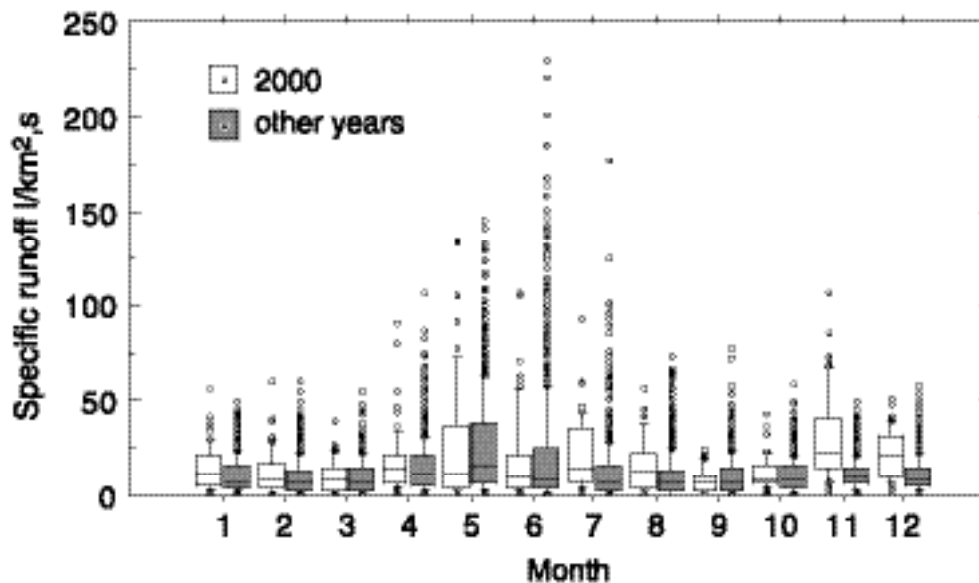


Figure 6. Monthly specific runoff for 64 small streams. Year 2000 and, as a comparison, other years (1970–2001).

The extreme precipitation in 2000, especially in the autumn, is thus one cause for the unexpected lower concentrations of many components. As can be seen did the run-off in general increase throughout the whole period.

## 5.5 What would the conditions be if the rains had not fallen?

For the about 180 reference lakes a higher sampling frequency (3-8 times a year) is kept. Many of these lakes showed some recovery for the period 1984–1997 (Wilander and Lundin, 1999). Some of these are included in the national report to ICPWaters. Those results may contribute to the understanding of the causes for the situation. The median pH value for year 2000 was 6,31 but for 2001 it fell to 6,18; the lowest for the period. Other water quality conditions show similar patterns (Figure 7). Base cation concentrations were somewhat higher in 2000 than the years before and after. However, the alkalinity fell from 2000 to 2001, while the colour (absorbancy) increased. The cause for this unexpected result is that these lakes were sampled latest in October. As a consequence the effects of the 2000 autumn rains did first show up in 2001.

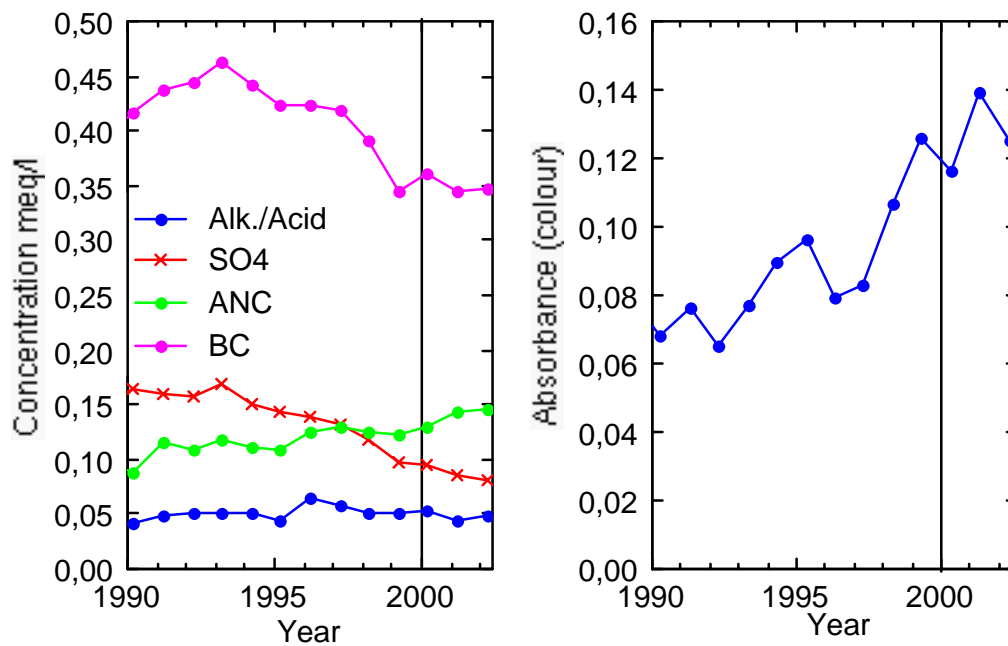


Figure 7. Temporal changes for some parameters. Reference lakes (unaffected by point sources and agriculture) sampled four times per year ( $n=118$ ).

Changes with time may be followed more in even more detail using the small streams with monthly monitoring. An example describing this development is the sampling station Kringlan at River Rastälven in central Sweden (Figure 8). It has a drainage area of 294 km<sup>2</sup>, mainly forested, and just downstream of Lake Sängen with an area of 0,73 km<sup>2</sup>. While the lake area is relatively “normal” for the survey lakes is the drainage area large; about 90% of the sampled lakes have a smaller drainage area. The extreme flow during the late autumn is concentrated to November–December; both September and January the following year are more normal (Table 2).

Table 2. Flow of water at Kringlan (m<sup>3</sup>/s). Monthly mean values.

| Year                 | August | September | October | November | December | January    |
|----------------------|--------|-----------|---------|----------|----------|------------|
| 1985–2002 (median)   | 1,20   | 1,75      | 2,90    | 3,65     | 3,75     | 3,50       |
| 1985–2002 (90 perc.) | 5,14   | 5,52      | 5,40    | 9,74     | 6,32     | 7,11       |
| 2000                 | 4,7    | 1,8       | 5,3     | 20       | 11,9     | 6,8 (2001) |

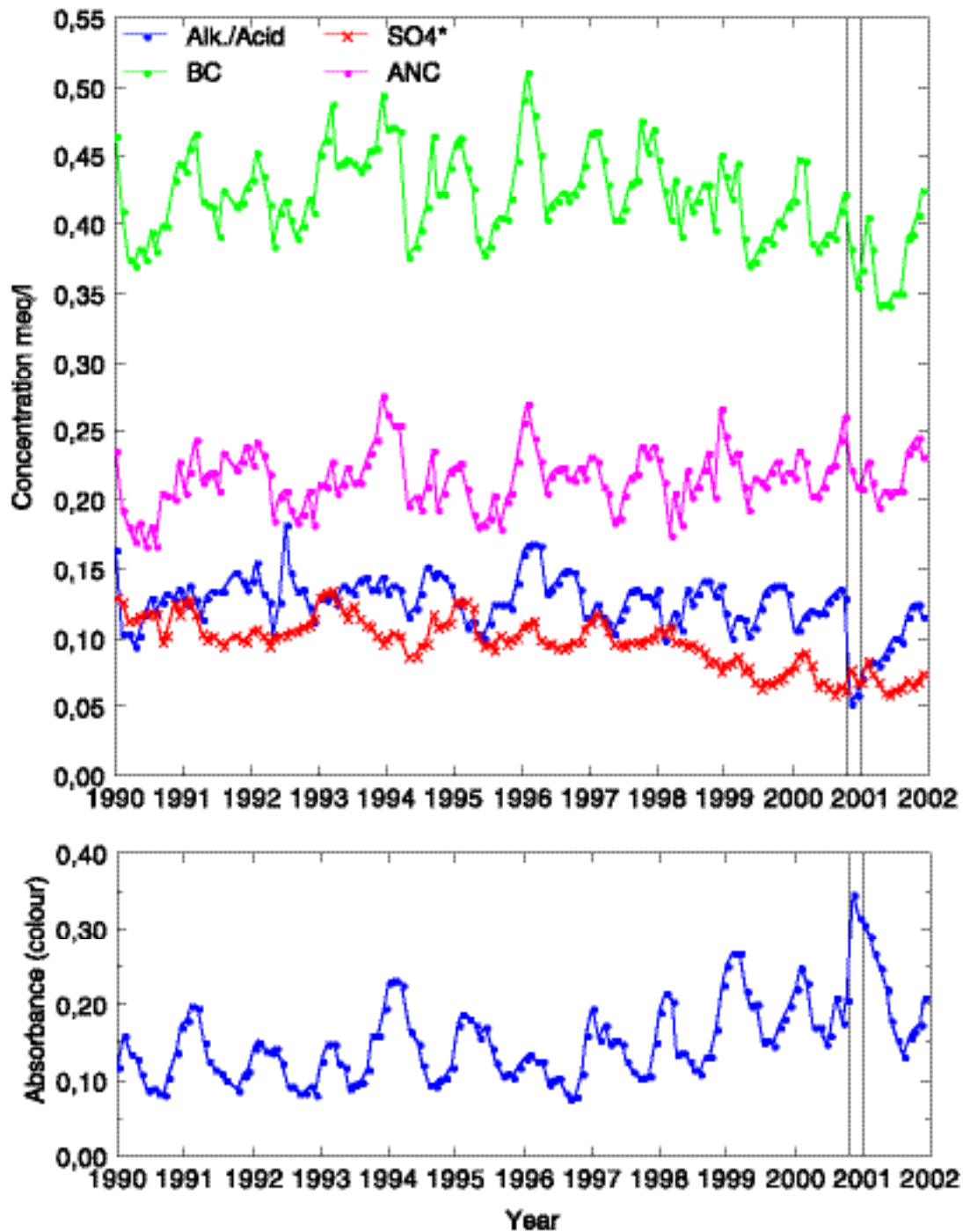


Figure 8. Time-series for selected water chemistry parameters at Kringlan (Rastälven: a stream in south central Sweden). The vertical lines delineate the period for sampling in southern Sweden for the lake survey.

During the autumn 2000 the conditions changed quickly. Alkalinity fell from 0,128 meq/l in October to about half that in November–December. This contrasts to the situation during the survey in 1995, when the concentration was quite stable (0,12 meq/l) during these months. In 2000 the pH-value was the lowest during the decade. At the same time the colour increased by about 50%, which induced the lowering of both pH and alkalinity.



If the change in base cations (BC) is selected as a measure of dilution due to the rains (in a broad sense) then the dilution could explain a diminution of concentrations by 17%. This corresponds well to the decrease in ANC. As the alkalinity decreased by about 60% it is thus possible to allocate 20% to dilution effects and the remainder due to an increased supply of humic acids. Nothing similar was seen in the time for the 1995 survey. Then the pH-value was lower at the beginning of the sampling year than in the autumn while the colour diminished.

### 5.6 Is it possible to compensate for such extreme conditions?

Among the latest three surveys it is only that in 2000 when the precipitation drastically deviates from "normal" hydrological conditions (cf. Figure 5). As indicated above may normalisation (corrections) for large variations be very difficult. The intricate conditions as reflected by the situation at the stream Kringlan are probably only representative for lakes in the vicinity. In the case of the lake survey in 2000 does both the large variation in time, within a few months, as well as in area make any normalisation unreliable. Despite this it may often be necessary to normalise as correct as possible.

### 5.7 References

Data can be found on [http://info1.ma.slu.se/max/www\\_max.acgi\\$Project?ID=Intro](http://info1.ma.slu.se/max/www_max.acgi$Project?ID=Intro)

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## **6. Evidence for the recovery of freshwater lakes and streams in the UK from acidification, based on the analysis of data from the UK Acid Waters Monitoring Network (1988-2003)**

*Don Monteith,  
Environmental Change Research Centre,  
University College London,  
UK.*

The UK Acid Waters Monitoring Network (AWMN) was established to determine the ecological impact of acidic emissions abatement policy in 1988 by the UK Department of the Environment. The chemistry of run-off and the species composition of a range of biological groups from 22 acid-sensitive lakes and streams have been routinely monitored ever since. Analysis of the first 15 years of data from the AWMN has recently been completed and is due to be reported shortly.

Over the period of assessment (1988-2003), data from the UK's Acid Deposition Network show that the deposition of sulphur (S) from non-marine sources has fallen by approximately 50% over much of the UK. The largest absolute reductions are centred in southeastern and central England and fall in magnitude in northerly and westerly directions. Over the same period there has also been a smaller reduction in nitrogen deposition but significant declines are mostly restricted to the central England. The decline in non marine sulphate ( $xSO_4$ ) in deposition is reflected in concentrations of  $xSO_4$  in run-off from AWMN sites with little evidence for any time lag. Significant declines in run-off are observed in all but the north of Scotland where S deposition has historically been very low. No trends have been observed in nitrate ( $NO_3$ ) concentration, but recently elevated spring peaks can be linked to a recent series of colder, drier winters associated with a relatively low North Atlantic Oscillation Index. At some sites the recent elevation in  $NO_3$  is of the same magnitude as the decline in  $xSO_4$ .

Declines in the  $SO_4$  anion are predominantly balanced by declines in the concentration of base cations (particularly calcium and magnesium). However, 13 sites have experienced one or more of the following changes which are considered biologically favourable: an increase in pH; an increase in alkalinity; and, a decline in labile (biologically toxic) aluminium. Acid neutralising capacity (ANC), a calculated expression of the acid-base balance has been determined according to the calculation:

$$[ANC] (\mu eq \text{ l}^{-1}) = [Alkalinity] (\mu eq \text{ l}^{-1}) + 4.5 [DOC] (\text{mg l}^{-1}) - 3 [Labile Aluminium] (\mu\text{mols l}^{-1})$$

ANC has increased at all 13 sites where one or more of the above changes has been identified and this may therefore be seen as a generic indicator for trends in acidity. The rate of increase in ANC is linearly related to the rate of decline in  $xSO_4$  and those sites which fail to show any change in ANC are mostly those experiencing the smallest declines in  $xSO_4$ . Noise generated by climatic effects, particularly due to inter-annual variability in precipitation, sea-salt deposition and nitrate leaching has masked improvement in acidity at some sites where changes in  $xSO_4$  are only modest.

Dissolved Organic Carbon (DOC) concentration has increased substantially at all 22 sites. The mechanism for this increase, which is similar to that observed in other regions of the ICP Waters network, are as yet unclear. However, work in progress seems to suggest a dual influence of declining S deposition and a climatic effect (related to long-term warming and/or increased occurrence of drought). ANC trends are most pronounced at sites where  $xSO_4$  declines are greatest, suggesting that they are integral to the recovery process. The decline in strong "mineral" acids may therefore be being partly balanced by an increase in "weak" organic acids and this should be biologically favourable.

However, strong increases in DOC in north Scotland amount to a net increase in acidity and can only be explained by climatic effects.

The species composition of epilithic diatom (single celled algae which grow attached to rock surfaces) and aquatic macroinvertebrates (largely representing insect larvae and beetles) has changed significantly at approximately half of all sites. The relationship between those sites showing trends in these biological groups and those showing trends in ANC is statistically significant. Where epilithic diatom communities have changed, acid sensitive species have usually increased proportionally relative to acid tolerant species. There is also evidence for an increase in the proportion of some known acid sensitive macroinvertebrate taxa, while there has been a notable increase in the representation of predatory animals, which is consistent with an expansion of the aquatic chain. Acid sensitive mosses and higher plants have been found for the first time in the last five years at several sites, mostly those where ANC has increased. In contrast, positive changes in salmonid density have only been identified at one site, which has shown the largest change in ANC on the Network. Here, the density of brown trout has expanded significantly as pH and alkalinity has increased and labile aluminium concentration has declined.

With the exception of salmonids, biological observations are wholly consistent with a regional biological recovery signal. In the case of epilithic diatom communities, where most species have maintained a viable presence when sites were in their most acidified state, the response to increasing pH or alkalinity appears to be immediate. At some sites acid sensitive aquatic macrophytes species have been detected within a year of a theoretical alkalinity threshold being reached, suggesting these plants have maintained a non-vegetative presence, possibly in the form of seeds. In most cases, however, proportional changes have been very gradual. As historical data are not available it is difficult to determine the extent to which ecosystem structure is returning along the path followed during acidification, and how extensive the current gap is with pre-acidification status. It is likely that re-establishment of species which were lost to sites, or even regions, during acidification, may take longer to re-colonise. Biological recovery may also be hampered by the sporadically disruptive effects of acidic episodes, particularly at times of high precipitation, and by competitive exclusion by dominant acid tolerant species which are not adversely affected directly by falling acidity.

In summary therefore, lakes and streams on the AWMN appear to have responded rapidly to the emission control induced decline in  $xSO_4$  deposition. ANC has declined in proportion to the rate of decline in  $xSO_4$  with the dominant effect observed in a region stretching from south-east England to south-east northern Ireland and central Scotland. An increase in organic acids and climatic variability may have partly masked responses in conventional measures of acidity status, i.e. pH and alkalinity. Gradual biological changes are apparent within the region where sites show a significant increase in ANC and are generally consistent with recovery responses. Analysis also demonstrates the sensitivity of these systems to variability in climate and provides some indication of the likely response to progressive climate change.

## 7. ANC-RECOVERY

# What is the chemical threshold values for natural reproduction during recovery from acidification?

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### ANC-RECOVERY

What is the chemical threshold values for natural reproduction during recovery from acidification?

NIVA & NINA (Norwegian Institute for Nature Research)

Project leader: B.O. Rosseland, NIVA

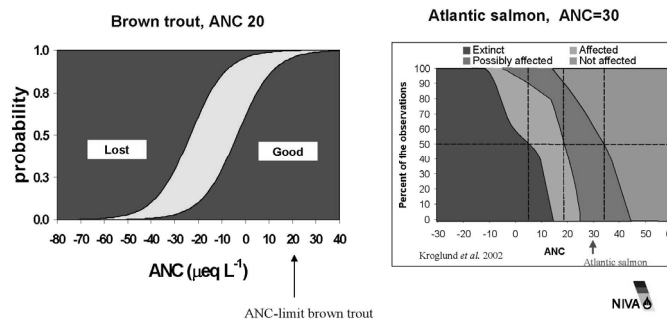
Financed: Norwegian Research Council, NIVA and NINA

#### Main goal:

Find the relation between an increased ANC and time at re-establishment of natural reproduction in fish populations – find  $ANC_{limit}$  for recovery

### Established ANC and fish levels

- Based on lake and river water chemistry and biological “endpoints” from the past, one have established:

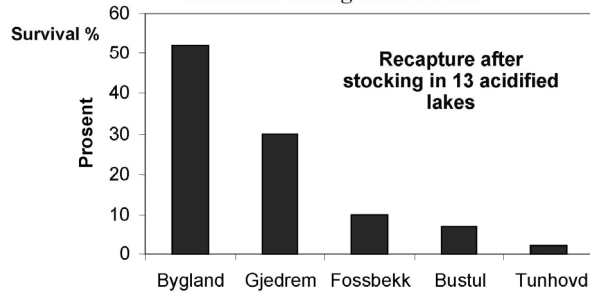


### Project strategy

- Gillnetfishing in three lakes with “historical records in Acid Rain Research in Norway”
  - Lake Saudlandsvatn, Farsund, SN.1976 - 2003
  - Lake Tveitvatn, River Tovdal, SN.1975 - 2003
  - Lake Langtjern, SE. N., 1966-2003
- Reproduction studies
  - Control of egg survival of natural spawned eggs
    - Lake Saudlandsvatn
    - Lake Langtjern
  - At site fertilization and control of egg survival until alevin stage
    - Lake Langtjern
- Ecotoxicological experiments in autumn and spring (Spawning and hatching periode)

## Experimental fish

ReFish-project (1987-1995) demonstrated strain differences in tolerance among brown trout



•ANC-Recovery project used the Bygland strain as an experimental strain in Lake Saudlandsvatn and Lake Tveitvatn  
 ⇒ maximum tolerance to acid water

•The Nordmarka-strain was used at Lake Langtjern



## Main areas for experiments Saudlandsvatn, Farsund, S. Norway

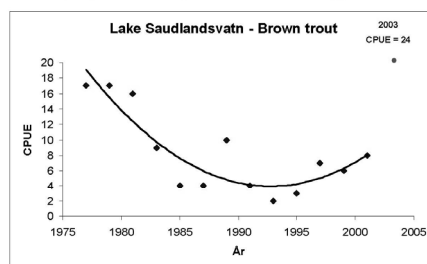


Surface area, km<sup>2</sup> 0,16



## Lake Saudlandsvatn

- Started sampling in 1976 when the fish population was decreasing



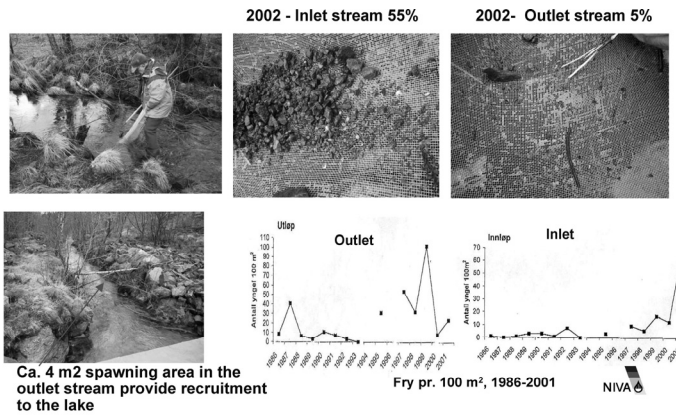
- Standard gillnet fishing
- SNSF-series
- Nordic-series

CPUE  
 Number of fish pr.  
 100m<sup>2</sup> gillnet area pr.  
 night

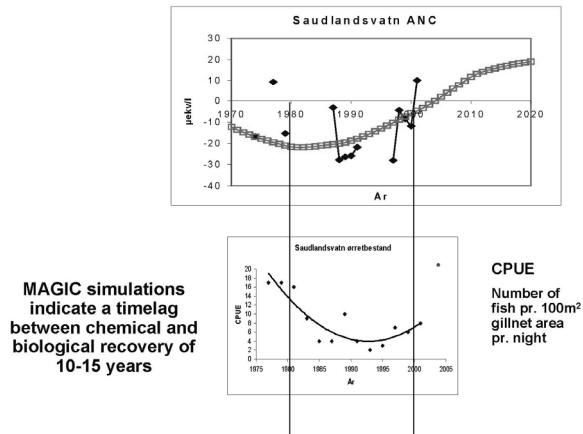


## Saudlandsvatn egg survival

- Highest mortality in the inlet stream in February 2002



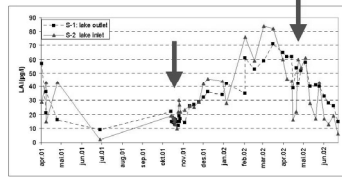
## MAGIC – CPUE - Timelag



## Ecotoxicological experiments - Saudland

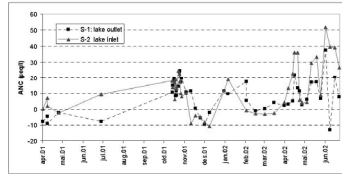


**Lake Saudlandsvann, variation in water-quality.**



Physiological recovery in October 2001

ANC 10-30



100 % mortality within a few days in April/May 2002

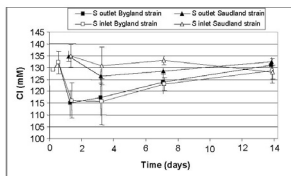
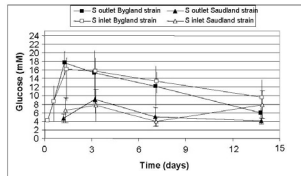
ANC 3-35



**Lake Saudlandsvann, October 2001 (spawning season).**

Water quality at lake Saudlandsvann, oct 2001, median values (n=8)

|                  | pH   | Ca   | Labile Al | ANC  | TOC |
|------------------|------|------|-----------|------|-----|
| S 1, lake outlet | 5.71 | 0.86 | 15        | 15.9 | 3.1 |
| S 2, lake inlet  | 5.60 | 0.84 | 19        | 15.6 | 3.3 |



- Nearly complete recovery in the measured parameters after two weeks
- ANC = 16, stressing but not detrimental



**Tveitvatn, Tovdal, S. Norway**

- Studied since 1975 in SNSF-project



BROWN TROUT, LAKE TVEITVATN, TOVDAL

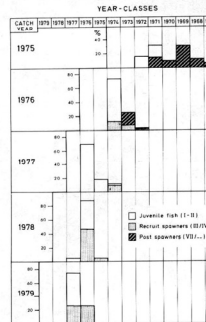
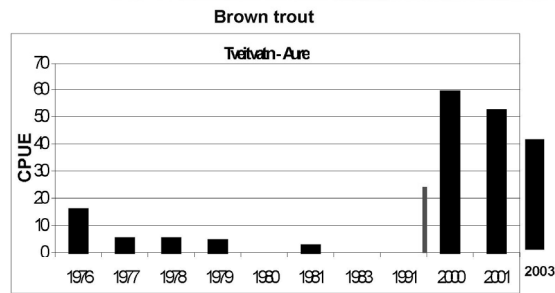


Fig. 3

From: Rosseland et al. 1980



## Tveitvatn, Tovdal, S. Norway



CPUE = Number of fish/100m<sup>2</sup> gillnet area



### Normal reproduction in Lake Tveitvatn seems to occur

- Stations for electro-fishing was established in September 2003 in the inlet stream
- Several year-classes were found



Trygve Hesthagen, NINA



60-100 fish/100m<sup>2</sup>



### Ecotoxicological experiments

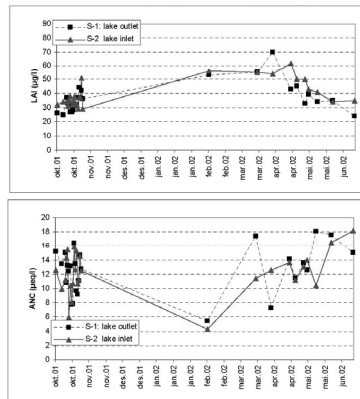


Tovdal





### Lake Tveitvatn, variation in water quality.



Survival both in October 2001 and April/May 2002 experiments.

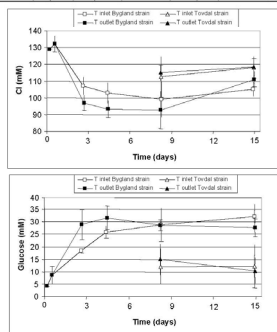
Severe physiological disturbance in Byglandsfjord strain and marked physiological disturbance in wild strain in both experiments.



### Lake Tveitvatn, physiology, Oct. 2001.

Water quality at lake Tveitvatn, oct. 2001. Median values, n=10

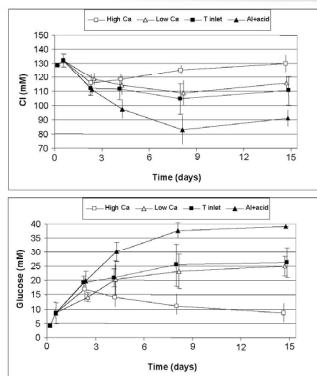
|                  | pH   | Ca   | Labile Al | ANC  | TOC |
|------------------|------|------|-----------|------|-----|
| T 1, lake inlet  | 5,31 | 0,57 | 32,5      | 12,9 | 3,6 |
| T 2, lake outlet | 5,25 | 0,54 | 34        | 11,8 | 3,6 |



ANC = 12-13  
Gradual recovery



### Lake Tveitvatn, water-quality manipulation experiment, Oct. 2001.



Water chemistry, manipulation experiment (median values, n=8-12)

|         | pH   | Ca    | Labile Al |
|---------|------|-------|-----------|
| High Ca | 6,17 | 1,03  | 6,5       |
| Low Ca  | 5,36 | 0,61  | 26        |
| T inlet | 5,31 | 0,57  | 32        |
| Acid+Al | 4,89 | 0,57* | 64,5      |



0,5 mg Ca improved water quality  
ANC = 36

30 µg LAL deteriorated the water quality, ANC = 5



## Lake Langtjern – SE Norway

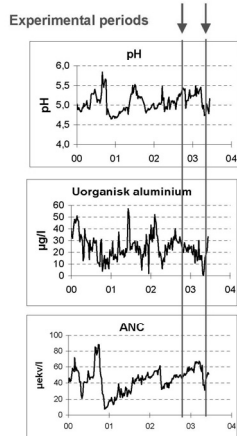


Supervised by:



NIVA

## Lake Langtjern Experimental periods



- 2001 spring – 100% mortality natural spawned and stocked egg
- 2002 spring – no spawned eggs found

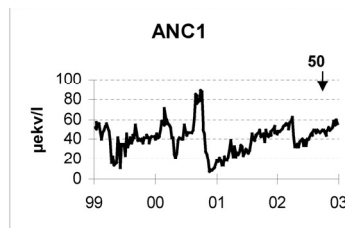
2002 autumn – no 0+ fry found by electro fishing



2003 spring ca. 20% egg survival

NIVA

## Lake Langtjern - experiments 2002/2003



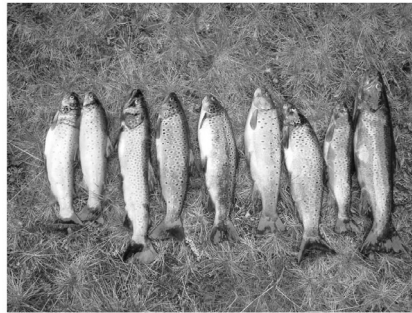
- Ecotoxicology
  - Blood chemistry
  - Gill metal accumulation
  - Mortality

Autumn 2002 - all fish died

Spring 2003 - some fish survived

NIVA

### Lake Langtjern - testfishing 2003



No recruitment despite ANC= 40-50

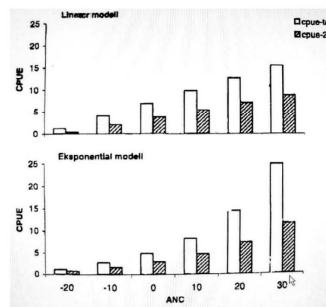
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### Parallel project - ANC and recruitment strength

Hesthagen, T., Kristensen, T. and Rosseland, B.O. (2003)

- Electrofishing in spawning areas and comparing total catch and yearclass strength of 2-year old fish by gillnet testfishing (> 30 lakes).

Increased reproduction at least up to ANC 30



NIVA

### Conclusions from the ANC-Recovery project Estimating the potential for recovery of fish populations through short-term experiments

- The water quality of a lake can be assessed by measuring the physiological response of fish.
- Capacity for ion regulation and normal values for other stress parameters is considered as indicative of long-term survival and potential for reproduction.
- The tests must be carried out at ecologically relevant times of the year in the relevant water quality.
- At site water quality manipulations can find critical levels of e.g. pH, Ca, LAI, which is target water quality for that specific site.

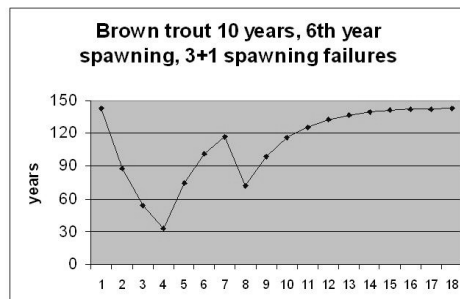
NIVA

## 8. What is a “recovered” and “helthy fish population”?

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 Norway

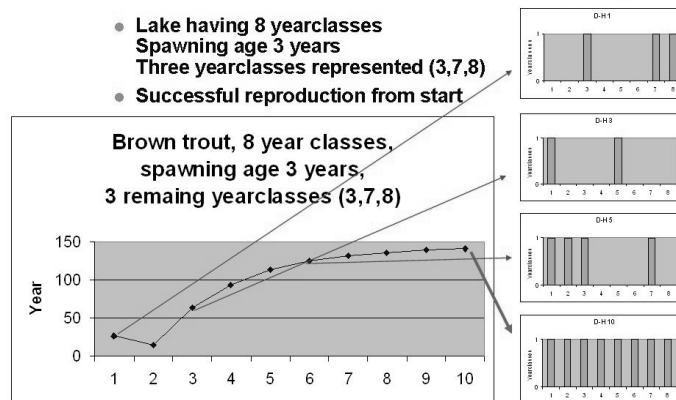
### FIB model Healthy-damaged-healthy

- Lake having 10 yearclasses  
 Spawning age 6th year



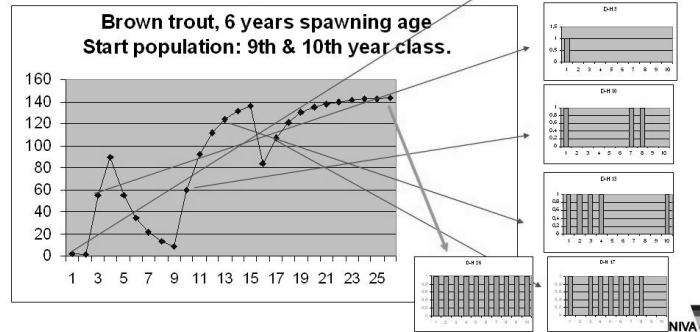
### FIB Model Damaged - Healthy

- Lake having 8 yearclasses  
 Spawning age 3 years  
 Three yearclasses represented (3,7,8)
- Successful reproduction from start



## FIB Model Damaged - Healthy

- Lake having 10 yearclasses  
Spawning age 6th year  
Two oldest yearclasses represented
- Successful reproduction from start



## Fibonacci numbers

Lake characteristics: acidified lake with total reproduction failure for 8 years

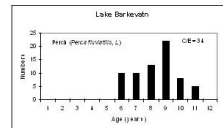
- maximum age 10.
- female spawn after 6 years,
- start with age class 9 and 10
- spawning successfully from start

R = Reproduction  
N = No reproduction

| Yearclasses | 10   | 9 | 8 | 7 | 6 | 5 | 4 | 3 | 2 | 1  | Sum |
|-------------|------|---|---|---|---|---|---|---|---|----|-----|
| 1 R         | 10,9 |   |   |   |   |   |   |   |   |    | 2   |
| 2 R         |      | 1 | 1 |   |   |   |   |   |   |    | 1   |
| 3 N         |      |   |   |   |   |   |   |   |   |    | 55  |
| 4 N         |      |   |   |   |   |   |   |   |   | 34 | 89  |
| 5 N         |      |   |   |   |   |   |   |   |   | 34 | 55  |
| 6 N         |      |   |   |   |   |   |   |   |   | 21 | 34  |
| 7 N         |      |   |   |   |   |   |   |   |   | 13 | 21  |
| 8 R         |      |   |   |   |   |   |   |   |   | 8  | 13  |
| 9 R         |      |   |   |   |   |   |   |   |   | 5  | 8   |
| 10 R        |      |   |   |   |   |   |   |   |   | 3  | 5   |
| 11 R        |      |   |   |   |   |   |   |   |   | 2  | 3   |
| 12 R        |      |   |   |   |   |   |   |   |   | 1  | 2   |
| 13 R        |      |   |   |   |   |   |   |   |   | 1  | 1   |
| 14 N        |      |   |   |   |   |   |   |   |   |    |     |
| 15 R        |      |   |   |   |   |   |   |   |   |    |     |
| 16 R        |      |   |   |   |   |   |   |   |   |    |     |
| 17 R        |      |   |   |   |   |   |   |   |   |    |     |
| 18 R        |      |   |   |   |   |   |   |   |   |    |     |
| 19 R        |      |   |   |   |   |   |   |   |   |    |     |
| 20 R        |      |   |   |   |   |   |   |   |   |    |     |
| 21 R        |      |   |   |   |   |   |   |   |   |    |     |
| 22 R        |      |   |   |   |   |   |   |   |   |    |     |
| 23 R        |      |   |   |   |   |   |   |   |   |    |     |
| 24 R        |      |   |   |   |   |   |   |   |   |    |     |
| 25 R        |      |   |   |   |   |   |   |   |   |    |     |
| 26 R        |      |   |   |   |   |   |   |   |   |    |     |

## FIB model

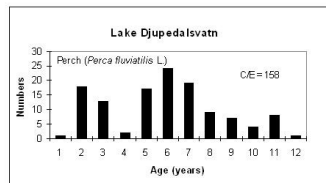
- Simulate repeated spawnings until death
  - no "resting years" like typically in the high mountain lakes
- Starting points either healthy or disturbed, or any population status



- Can easily be used to simulate
  - stocking
  - liming
  - episodic mortality

## FIB model

- Defines a typical first spawning age and maximum age for females only
- Documentation of existing year-classes by gillnet fishing (= survived into lake)
- Youngest year-class in catches normally
  - age 2 for brown trout
  - age 1 for perch



NIVA

## FIB model - "Fisk i Bedring" (Fish in recovery)

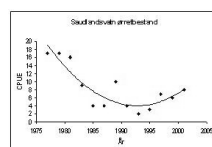
A. Bulger, B.O. Rosseland and T. Kristensen (2003)

- Defines a "healthy fish population" as being sustainable, with all expected yearclasses represented, typical for its geographical and climatic zone
- Model uses presence of in-lake- yearclasses only. Year-class strength can be simulated
- Weight the yearclasses after the Fibonacci numbers, youngest yearclasses highest value

NIVA

## How can we evaluate statements on "recovered" fish populations?

- Has there been any liming in or in areas connected to the lake or stream?
- Has there been stocking of fish in the migratory area to the lake or stream?
- Has reproduction really started?
- Few well documented cases



CPUE  
Number of  
fish pr.  
Gillnetseries  
pr. night

Saudlandsvatn, Farsund

Rosseland m.fl. 2002

NIVA

The FIB-model try to visualise the expected time for a *defined* recovery

NIVA

### What is a “recovered” and “healthy fish population”?

Bjørn Olav Rosseland, ICP-WATERS, Lugano October 8, 2003

- ICP-WATERS as well as national monitoring and action plans for liming activity, depend on a definition in areas recovering from acidification of:
  - “What is a recovered biodiversity”
  - “What is a healthy and recovered fish population”
- A criteria for good fish health status can be **re-establishment** of a fish population.
- But what does a re-established fish population mean or look like for the general public? Will it be:
  - 1) we catch fish?
  - 2) we catch a lot of fish?
  - 3) we see fish on the spawning grounds?
  - 4) we get increased Catches pr. Unit Effort (CUE in numbers or weight)?
  - 5) we find all expected year-classes represented?
- Up to now, 1-4 have dominated in the debate, especially as to when starting reductions in mitigation/liming



### FIB - model in the future

- We want to make the the model dynamic, and to build in functions for:
  - spawning age
  - “resting years”
  - oldest age
  - recruitment strength
  - links to water quality (ANC, pH, Ca, Lal, TOC)
  - Geographical/climatic/hydrological characterisations
- We believe the model can be linked to existing models like MAGIC.
- We have applied for funds from the Norwegian Research Council for 2004.



# **9. European Mountain lake Ecosystems: Regionalisation, diaGnostic & socio-economic Evaluation - EMERGE Main results from Workpackage 5: Fish Ecotoxicology**

*Bjørn Olav Rosseland*  
Norwegian Institute for Water Research  
POBox 173 Kjelsås, N-0411 Oslo  
Norway

**EMERGE**

**European Mountain lake Ecosystems:  
Regionalisation, diaGnostic &  
socio-economic Evaluation**

**MAIN RESULTS FROM:**

Workpackage 5

**Fish Ecotoxicology**

**Co-ordinated by:  
Bjørn Olav Rosseland, NIVA**

ICP-WATERS Lugano, October 2003

**EMERGE**

Workpackage 5

**Fish Ecotoxicology**

Lead partners:

**3 NIVA, Norway. Bjørn Olav Rosseland (WP Coordinator), S. Rognerud**

13 Univ. Bordeaux, CNRS, Lab. D'Ecophysiol. et Ecotoxicol. France,

**J-C. Massabuau**

5 CID/CSIC, Univ. Barcelona, Spain, **J. Grimalt**

6 Univ. Innsbruck, Inst. Zoology and Limnology, Austria, **R. Hofer,**

**R. Lackner**

9 Univ. of Bergen, Inst. Zoology, Norway, **G. Raddum, Arne Fjellheim**

Co-operative partners: 1 (Pitlochry, UK), 4 Univ. Barcelona, Spain,  
17 Charles Univ. Prague, Czech Republic, 21 LFTER-NIB, Slovenia,  
23 IZ-BAS, Bulgaria,



## EMERGE

## WP 5 - Objectives

## Objective:

- Evaluate how trace pollutants accumulate in the food chain and assess the physiological response of fish to individual and combined stresses
- Examine the extent to which there are differences in contaminants between species of fish and between morphs of the same species across a gradient of pollution distribution

EMERGE WP 5  
Fish ecotoxicology

## Final Report for February 1, 2000 to January 31, 2003

Bjørn Olav Rosseland (Convenor, NIVA),  
 Jean-Charles Massabuau (CNRS),  
 Rudi Hofer (UIBK-IZL),  
 Joan Grimalt (CSIC ),  
 Sigurd Rognerud (NIVA),  
 Reinhard Lackner (UIBK-IZL),  
 Ingrid Vives (CSIC ),  
 Marc Ventura (UB-DE),  
 Evzen Stuchlik (CU-Prague),  
 Ron Harriman (UCL),  
 Peter Collen (UCL),  
 Gunnar Raddum (UiB),  
 Arne Fjellheim (UiB),  
 Teodora Trichkova (IZ-BAZ).

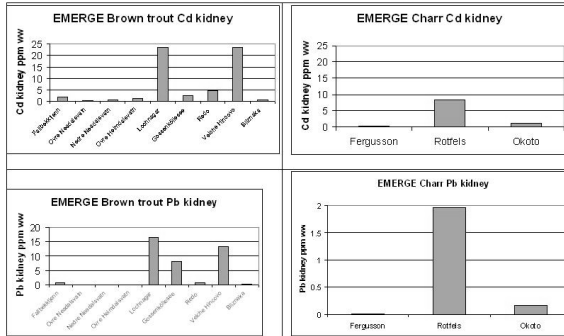
## EMERGE

## Detail training of personnel - "Accreditation of sampling"

- A workshop was held in the Spanish Pyrenees, close to Redo, in June 2000
  - Hosted by The University of Barcelona
  - Participants from Austria, Czech Republic, Spain, Norway, UK and France
  - *In-situ* training course in fish physiology and ecotoxicology applied to remote lakes
  - EMERGE MANUAL. Modified MOLAR Manual - tested and remodified (<http://www.mountain-lakes.org/methods/29.pdf>).
  - First testfishing and invertebrate sampling in Lake Redo with all participants attending



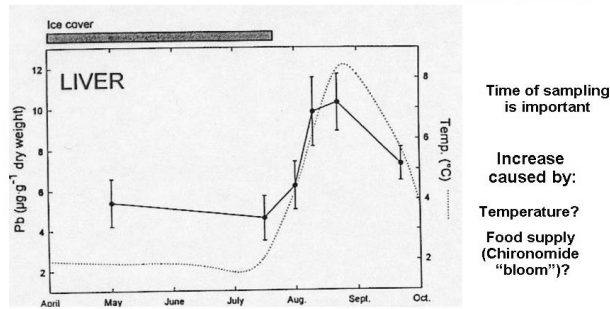
### Cd and Pb in kidney



### Bioavailability of Pb Annual variations

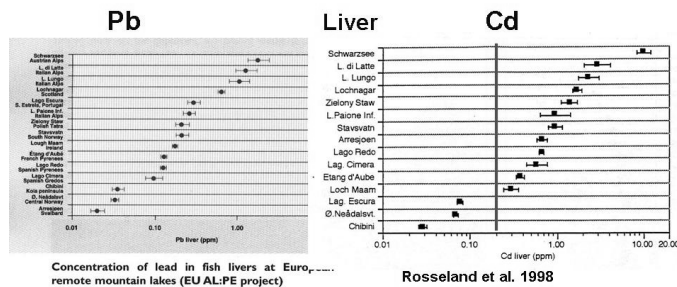


After: Köck and Hofer 1998



### Examples from 4 EU-projects in Alpine and Arctic lakes

- AL:PE, AL:PE 2, MOLAR & EMERGE
- AL:PE 2 – Screening whether heavy metals could be of any problem in fish populations



**Sampling techniques are well defined in EMERGE**

**EMERGE**



- Protocols are followed to define the handling stress ;
  - Maximum period in gillnet
  - Time from catch by fly/lure to storage/sampling
  - Max time in keep net
  - Time of processing following MANUAL
- Severe handling stress can influence results and interpretation of stress level
- So far, we have no indications of such effect in our datasets that will change the overall conclusion

**Our stress data are linked to environmental conditions!**

**Test fishing - EMERGE 2000 & 2001**

**EMERGE**

- **Spain: Lake Redo**
  - June: partners: (whole group)
  - November: partners 4, 13, 5
- **Austria: Lake Gossenköllesee and Rotfels**
  - August 2000, partner 6
  - June 2001
- **Bulgaria: Bubreka, Okoto and Bliznaka**
  - September 2000: partners 6, 23
- **Slovakia, Tatra, Velke Hincovo Pleso**
  - September 2000, Partners: 17, 5
  - September 2001
- **Norway: Fallbekktjenn, Ø, Neådalsvatn and N. Neådalsvatn (+ Øvre Heimdalsvatn)**
  - August 2000, Partners 3, 9
  - September 2001; Partners: 3, 9, 6
- **Scotland: Loch Nagar**
  - June 2001, Partners 1,3
- **Greenland: Lake Ferguson, Lake Helena**
  - August 2001: partners 3, 9, 12



Fallbekktjenn, Norway

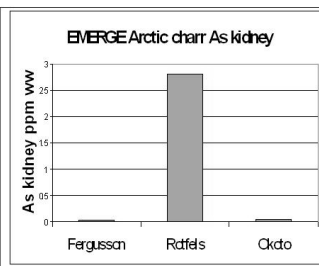
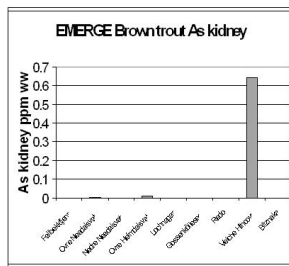


Øvre Neådalsvatn, Norway



Lake Ferguson, Greenland

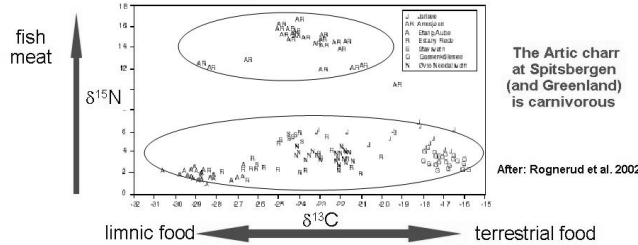
**Arsene (As) in salmonidae**



### Biomagnification of Mercury $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$

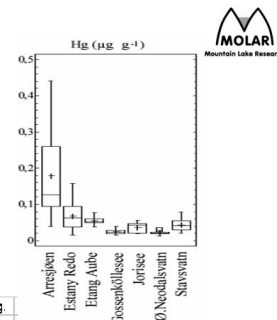


- Food chain analyses (stable isotopes of C and N)
- Determined how the fish was contaminated through the food web *i.e.* the origin of the contaminants



### High Hg levels at Spitsbergen could not be explained by water chemistry

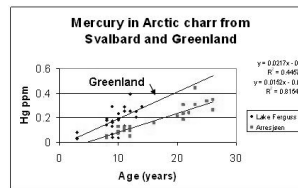
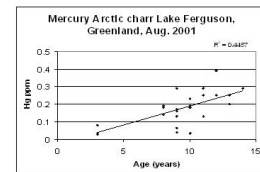
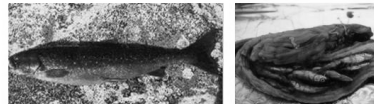
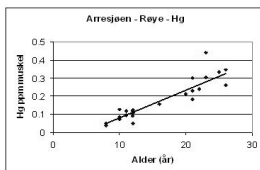
After: Rognerud et al. 2002



Tabell 1. Lake characteristics, water quality and surface sediment flux of Hg.

| Lake           | Altitude<br>m | Air temp.<br>C | Lake area<br>ha | Max depth<br>m | Catchment<br>km <sup>2</sup> | Alkalinity<br>µeq/l | pH  | DOC<br>mg/l | Surf. Hg flux<br>µg/cm <sup>2</sup> /year |
|----------------|---------------|----------------|-----------------|----------------|------------------------------|---------------------|-----|-------------|---|
| Arresjøen      | 20            | 0.1            | 35              | 32             | 3                            | 24                  | 5.8 | 0.43        | 0.0004                                    |
| Estang d'Alube | 2031          | 3.5            | 8.6             | 45             | 0.77                         | 22                  | 6.3 | 0.9         |   |
| Estang Rødo    | 2240          | 3.5            | 24              | 73             | 1.55                         | 41                  | 6.3 | 0.76        | 0.0026                                    |
| Gossenkillesee | 2417          | 0.85           | 1.7             | 10             | 0.2                          | 85                  | 6.8 | 0.45        | 0.0017                                    |
| Jorisee        | 2519          | 0.32           | 5               | 21             | 1.1                          | 109                 | 6.8 | 0.68        |   |
| Ø Neodalsvatn  | 728           | 2.2            | 50              | 18             | 16                           | 26                  | 6.2 | 0.73        | 0.0008                                    |
| Stavsvatn      | 1053          | 0.6            | 40              | 17             | 243                          | 21                  | 6   | 0.73        | 0.0012                                    |

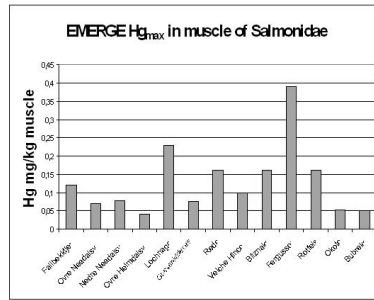
### Mercury in Arctic charr from Svalbard and Greenland



Hg accumulation is higher in Arctic charr from Greenland compared to Svalbard

After: Rosseland et al. 2003

## EMERGE - Hg<sub>max</sub> in European lakes

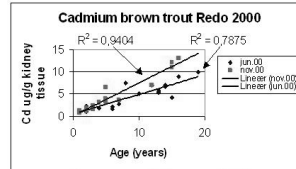
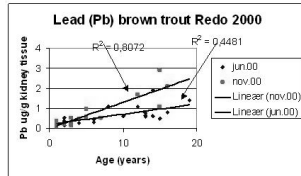


Highest Hg in:  
Lake Ferguson,  
Greenland  
and  
Lochnagar, Scotland

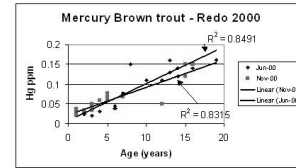
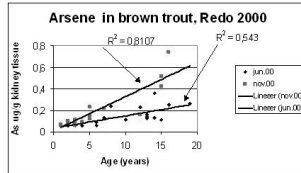
After: Rosseland et al. 2003



## EMERGE Bioaccumulation and seasonal levels Brown trout - Redo - Kidney



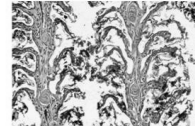
No seasonal changes in Hg



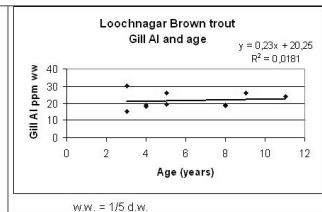
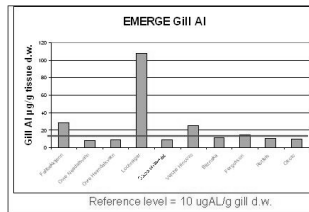
## Al deposition on fish gill

- Increased levels at three sites:

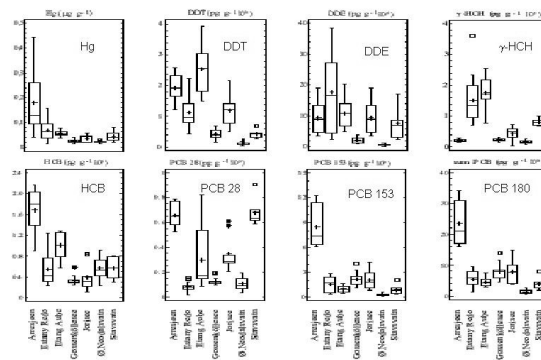
- Lochnagar, Scotland
- Fallbekktjenn, Norway
- Velche Hincovo, Slovakia



- Al do not bio-accumulate as a function of age = direct water/gill interaction



## MOLAR Hg and OC in fish muscle



### WP 5 Relevance for end-users

EMERGE

#### Polymakers and managers

##### European-scale

- Convention on Long-Range Transboundary Air Pollution (UN-ECE) ICP-WATERS evaluation of existing protocols,
- scientific support for revisions
- data used for modeling
- establish national and international manuals and protocols for comparison of environmental data

##### National scale

- fulfillment of Water Framework Directive
- fish management and selective stocking of least polluted-risk species
- food safety and health risk

##### General public

- sport fisheries
- nature conservation
- recreation and tourism



EMERGE

### WP 5 - Relevance for Water Framework Directive

#### Objective: obtain good surface water status

- ecological status - structure and function

#### Lakes: quality elements for classification

- composition, abundance and age structure of fish fauna
- concentrations of micro-pollutants
- chemical elements supporting the biological elements

#### Lakes: good status

- biological elements deviate only slightly from undisturbed conditions

#### But:

The Water Framework Directive

lack

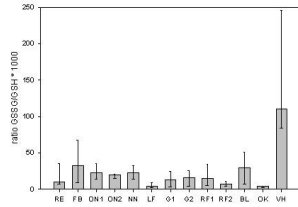
Ecotoxicological and Ecophysiological approach

AL:PE - EMERGE have proven the need for including these parameters of early warning and relevance for Nature conservation, Nature management and Safety of food

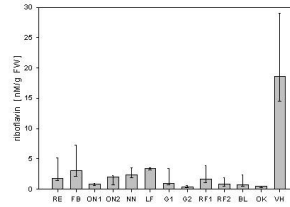
**EMERGE**

**Biomarkers for Oxidative stress**

- POPs are major sources for oxidative stress
- Breakdown of POPs releases reactive oxygen (free radicals)
- Major antioxidant is Glutathione (GSH) → Glutathione disulphide (GSSG)
- GSH/GSSG indicate oxidative stress level in fish



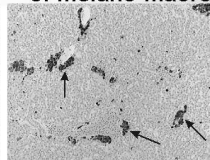
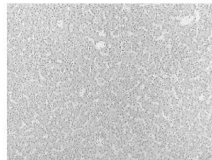
**Glutathion / glutathion disulphide**  
Oxidative stress parameter



**Riboflavin** - linked to macrophage density or activity

**EMERGE**

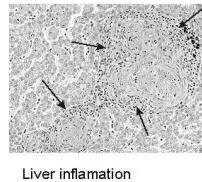
**Histological biomarkers**  
Liver inflammation and accumulation of melano-macrophages



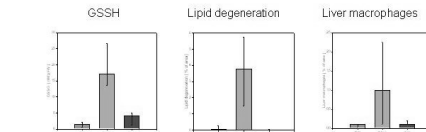
Melano macrophages



Gossenköllerses, Ø. Neädalsvatn and Redo



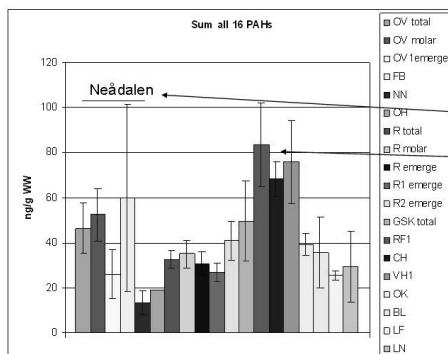
Liver inflammation



High concentration PAH breakdown products in bile from Ø. Neädalsvatn

**EMERGE**

**PAH metabolites in fish bile**



Results confirm data from MOLAR

High levels in:

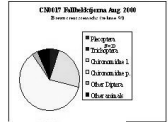
•Norway, Neädalen

•Slovakia, Tatra Mountains

•Czech Republic

•Austria

Chironomides might be the link from sediment



### PCBs, HCHs and PAH in high mountain snowpack

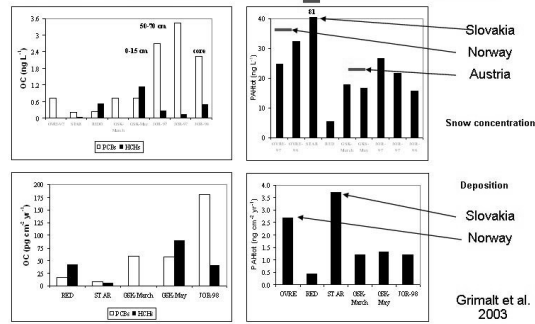
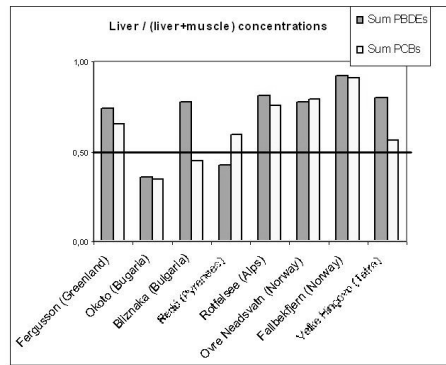


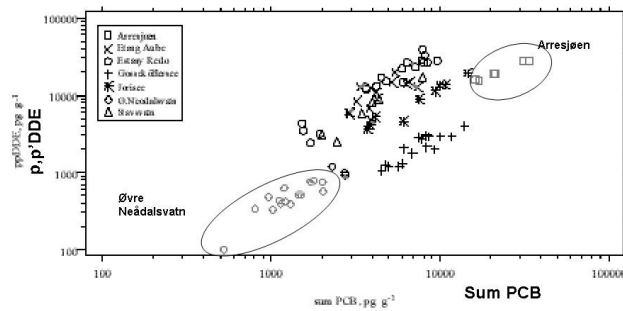
Figure 3.3.6. Concentrations and annual deposition flux of PAH tot (sum of 22 parent compounds), PCB (sum of seven congeners), and HCH (sum of  $\alpha$ - and  $\gamma$ -HCH) in snow from the study areas

### Bromated flame retardants PBDEs and PCBs

In most cases we find an enrichment in liver relative to muscle



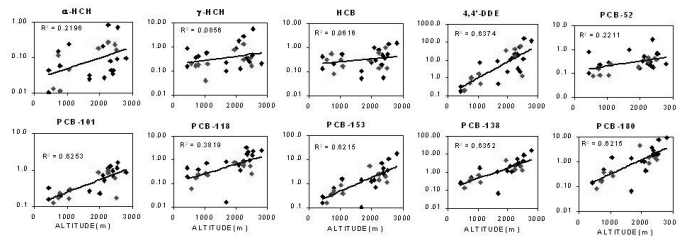
### PCBs and p,p'-DDE in fish





**Analyses of POPs in fish muscle at different elevations m.a.s.l.**

**EMERGE**

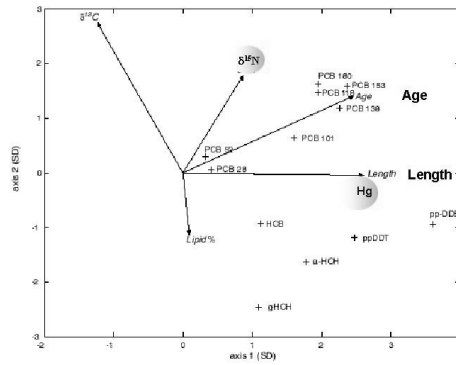


**DDTs and Higher congeners of PCB:**

- Increase with elevation and low temp.
- Bioaccumulate
- Biomagnify

Grimalt et al. 2001, 2003

**RDA analyses of Hg and OC in fish**



**Hg, DDT/DDE and PCB of higher congeners biomagnify**

After: Rognerud et al. 2002

**ICP-WATERS should include:**



## 10. Reports and publications from the ICP-Waters Programme

All reports from the ICP Waters programme from 1997 up to present are listed below. All reports are available from the Programme Centre.

Manual for Chemical and Biological Monitoring. Programme Manual. Prepared by the Programme Centre, Norwegian Institute for Water Research. NIVA, Oslo 1987.

Norwegian Institute for Water Research, 1987. Intercalibration 8701. pH, K<sub>s</sub>, SO<sub>4</sub>, Ca. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1988. Data Report 1987 and available Data from Previous Years. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1988. Intercalibration 8802. pH, K<sub>25</sub>, HCO<sub>3</sub>, NO<sub>3</sub>, SO, Cl, Ca, Mg, Na, K. Programme Centre, NIVA, Oslo.

Proceedings of the Workshop on Assessment and Monitoring of Acidification in Rivers and Lakes, Espoo, Finland, 3rd to 5th October 1988. Prepared by the Finnish Acidification Research Project, HAPRO, Ministry of Environment, October 1988.

Norwegian Institute for Water Research, 1989. Intercalibration 8903: Dissolved organic carbon and aluminium fractions. Programme Centre, NIVA, Oslo. NIVA-Report SNO 2238-89.

Note: Some reflections about the determination of pH and alkalinity. Prepared by the Programme Centre, Norwegian Institute for Water Research. Håvard Hovind, NIVA, Oslo October 1989.

Hovind, H. 1990. Intercalibration 9004: pH and alkalinity. Programme Centre, NIVA, Oslo. NIVA-Report SNO 2465-90.

Skjelkvåle, B.L. and Wright, R.F. 1990. Overview of areas sensitive to acidification: Europe. Programme Centre, NIVA, Oslo. Acid Rain Research Report 20/1990. NIVA-Report 2405-90. ISBN 82-577-1706-1.

Johannessen, M. 1990. Intercalibration in the framework of an international monitoring programme. Proceedings of the third annual Ecological Quality Assurance Workshop, Canada Centre for Inland Waters, Burlington Ontario. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1990. Data Report 1988. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1990. Data Report 1989. Programme Centre, NIVA, Oslo.

Proceedings for the 5th Meeting of the Programme Task Force Freiburg, Germany, October 17 -19, 1989. Prepared by the Umweltbundesamt, Berlin July 1990.

Hovind, H. 1991. Intercalibration 9105: pH, K<sub>25</sub>, HCO<sub>3</sub>, NO<sub>3</sub> + NO<sub>2</sub>, Cl, SO<sub>4</sub>, Ca, Mg, Na, K and TOC. Programme Centre, NIVA, Oslo. NIVA-Report 2591-91.

Norwegian Institute for Water Research, 1991. The Three Year Report. Summary and results 1987 – 1989: Results from the International Co-operative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes. Programme Centre, NIVA, Oslo.

Norwegian Institute for Water Research, 1991. Summary of The Three Year Report 1987 – 1989. Programme Centre, NIVA, Oslo.

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