

ICP Waters Report 104/2010  
Proceedings of the 26th meeting of the ICP Waters  
Programme Task Force in Helsinki, Finland,  
October 4 – 6, 2010



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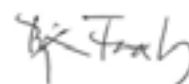
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Abstract Proceedings of presentations of national activities to the 26 <sup>th</sup> meeting of the ICP Waters Programme Task Force in Helsinki, Finland, October 4 – 6, 2010.
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CONVENTION ON LONG-RANGE  
TRANSBOUNDARY AIR POLLUTION

INTERNATIONAL COOPERATIVE PROGRAMME ON  
ASSESSMENT AND MONITORING EFFECTS OF AIR  
POLLUTION ON RIVERS AND LAKES

Proceedings of the 26<sup>th</sup> meeting of the ICP Waters  
Programme Task Force in Helsinki, Finland,  
October 4 – 6, 2010

Prepared at the ICP Waters Programme Centre  
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## Preface

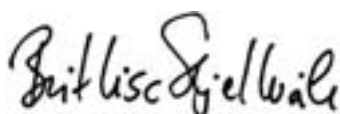
The international cooperative programme on assessment and monitoring of air pollution on rivers and lakes (ICP Waters) was established under the Executive Body of the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP) in July 1985. Since then ICP Waters has been an important contributor to document the effects of implementing the Protocols under the Convention. Numerous assessments, workshops, reports and publications covering the effects of long-range transported air pollution have been published over the years.

The ICP Waters Programme Centre is hosted by the Norwegian Institute for Water Research (NIVA), while the Norwegian Climate and Pollution Agency (Klif) leads the programme. The Programme Centre's work is supported financially by Klif.

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. More than 20 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 ICP site network is geographically extensive and includes long-term data series (more than 20 years) for many sites. The programme yearly conducts chemical and biological intercalibrations.

At the annual Programme Task Force, national ongoing activities in many countries are presented. This report presents national contributions from the 26th Task Force meeting of the ICP Waters programme, held in Helsinki, Finland, October 4 - 6, 2009.



*Brit Lisa Skjelkvåle*  
ICP Waters Programme Centre

Oslo, December 2010

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## 1. Introduction

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

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

The national contributions on ongoing activities that were presented during the ICP-Waters Task Force meeting in Helsinki, Finland in October 2010 are grouped thematically;

### 2) Water chemistry – trends and status of S and N

- The volcanic eruption under the ice at Eyafjellajökull April 2010; effects on water chemistry of rivers and lakes in Norway, *Brit Lisa Skjelkvåle, Programme centre*
- Acidifying deposition in Southern Switzerland. Assessment of trends 1998-2007, *Sandra Steingruber, Switzerland*
- Report of National ICP Waters activities in Latvia, 2009/2010 *Iveta Dubakova, Latvia*

### 3) Biological response

- Recovery of acidified lakes in Finland and subsequent responses of perch and roach populations, *Martti Rask, Finland*
- Biodiversity of benthic invertebrates - effects of air pollution and climate change, *Arne Fjellheim, Programme subcentre*

### 4) Heavy metals and POPs

- Time trends of trace metals in Swedish streams, *Brian Huser, Jens Fölster, Sweden*

### 5) Dynamic modelling/Critical Loads

- Project proposal: Calculation of nitrogen critical loads in rivers, *Brian Huser, Anne Christine Le Gall, France*

### 6) ICP Waters and EU-directives (WFD Water framework Directive, NEC National Ceiling Emission Directive)

- Guidance on Chemical Monitoring of Sediments and Biota under the WFD, *Jaakko Mannio, Finland*

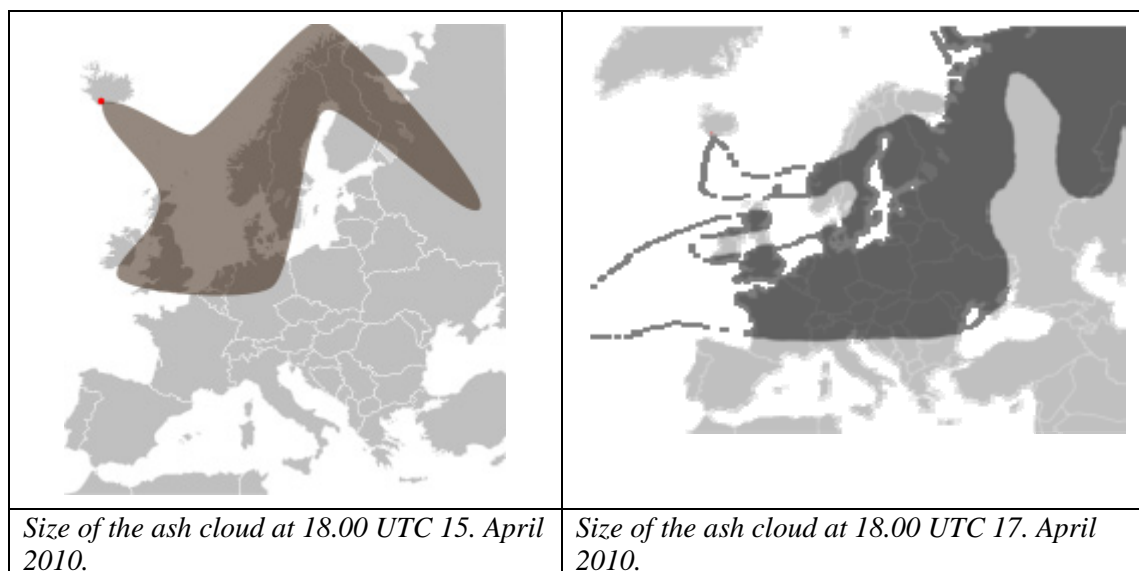
## 2. The volcanic eruption under the ice at Eyafjallajökull April 2010; effects on water chemistry of rivers and lakes in Norway

*Brit Lisa Skjelkvåle, Rolf Høgberget, Liv Bente Skancke, Atle Hindar*

*Norwegian Institute for Water Research  
Norway*

On 14 April 2010 a volcanic eruption started under the ice of Eyjafjallajökull in Iceland. In the evening on the same day, the airspace over northern Norway was closed due to the ash cloud from the eruption. The following day flights in Great Britain and Ireland were canceled when the British and Irish aviation authorities closed the airspace. The ash cloud had reached an altitude of 17 km. The main economic effect of the volcanic eruption was that it paralyzed air transport in most of Europe for nearly a week.

Questions about possible harmful effects of the ash cloud on human health and nature arose soon after the onset of the eruption. Media and the public were concerned and the authorities were pressed to quickly give statements about the possible effects.



*Figures from London Volcanic Ash Advisory Centre*

At NIVA, we decided to do two things;

- we made a short risk assessment about what we could expect of effects on freshwater quality
- we increased the intensity of monitoring at two stations in southern Norway which are part of the Norwegian national acid rain monitoring network (operated by NIVA under the auspices of the Norwegian Climate and Pollution Agency KLIF).

### **Risk assessment**

The risk assessment concluded quite clearly that the risk of water-chemical effects in Norway from the volcanic eruption on Iceland was small in the short term, but that it could have effects in the longer term (Table 1).

Sulphur, particles, fluoride and metals are among the main components that could affect water quality and water chemistry. The following text is from the risk assessment we published 20 April 2010 on our web site [www.niva.no](http://www.niva.no).

### ***Sulphur dioxide***

Sulphur dioxide (SO<sub>2</sub>) is a gas that can cause acid precipitation. The volcanic eruption is part of the planet's natural sulphur cycle, even though human-caused emissions now considerably outpace nature's own. The sulphur that is emitted from the volcanic eruption on Iceland will contribute to added acid precipitation in Norway, which in turn will affect the water chemistry of watercourses.

Most of the fallout will come in contact with the ground and thus will pass through the soil before reaching lakes and watercourses. This pertains also to sulphur components from volcanic eruptions. The key issue here is what happens when the sulphur comes in contact with the soil. Most will be quickly oxidised into sulphate, which largely will be absorbed by soil particles. Eventually as more and more sulphate is deposited the soil's capacity to bind the compound will be diminished and an increasing amount will leach out with run-off water. Sulphate is a negatively-charged ion that is always accompanied by an equal amount of positively-charged ions. In barren and poor soils, which are characteristic of large areas of Norway, most of these positive ions will be acidic (H<sup>+</sup>) or toxic aluminium ions. These cause acidic lakes, fish death and other forms of biological damage in lakes and streams.

### ***Mounting acidification as time passes***

The thickness and quality of a soil influences the length of time required for sulphate fallout to cause acidification of runoff. NIVA has previously conducted several large-scale research experiments (RAIN project 1983 – 1992, HUMEX 1988-1998) involving artificial application of sulphuric acid to determine these delay times. In these trials we watered whole headwater catchments with sulphuric acid solutions. The acidification of the runoff water occurred gradually over about 5 years. Small impacts were caused by acidic water that came in direct contact with open water surfaces.

### ***More acid with snowmelts***

Large fallouts of sulphuric acid on snow can cause acid episodes during snowmelts. This is probably because some of the melted snow bypasses the soil, running more or less directly from patches of snow into lakes and streams. In parts of southern Norway that receive high amounts of acid precipitation, such acid periods in the spring are rather common, and unfortunately they coincide with the time when trout and salmon are most vulnerable. It's quite conceivable that higher altitude and acid prone areas of western and middle Norway will receive sufficiently large sulphur inputs from the volcanic ash such that snowmelt in June and July will significantly impact surface waters.

### ***Particles***

Most of the ash consists of volcanic glass, which is not immediately water soluble. Its major components are Si- and Al-oxides with a lesser portion of other oxides. By itself the ash is unlikely to change water chemistry. The problem with the ash is its sharp edges and thus in theory it can harm and irritate the gills of fish and be detrimental to other aquatic organisms. The issue for Norway is whether sufficient ash will fall to have such an impact. Measurements of particle density (turbidity) combined with analyses of size and shape of volcanic particles in collected water samples will be indicative. The duration of the fallout of ash and the speed by which the particles are sedimented will also affect anticipated consequences.

As regards the aquaculture industry, many of the facilities for young fish already have systems for particle removal as part of their ordinary water treatment systems. These will probably filter out any ash before it reaches the fish.



**Fluoride**

Fluoride concentrations in Norwegian surface waters are by nature quite low. In a national study of lakes in 1995 fluoride concentrations were determined in 1,000 of the country's lakes. Among these, 75% had concentrations below 75 µg/L, whereas the norm for drinking water in Norway is 1,500 µg/L.

Fluoride fallout from the volcanic ash is unlikely to reach proportions that would have a negative effect on water in Norway.

**Heavy metals (Pb, Cd and Hg)**

Although some heavy metals can be expected in volcanic discharges, deposition in Norway is not expected to have significant or measurable effects on Norwegian lakes and rivers, regardless the eruptions are small or large.

*This table shows expected effects on water chemistry and biology in three different scenarios for sulphur, particles, fluoride and heavy metals.*

Component	Short-lasting eruption of Eyafjallajökull	Long-lasting eruption of Eyafjallajökull	Eruption of Katla
<b>Sulphur</b>	Little or no effect, but a risk of episodic acidification in special circumstances	Effect on water chemistry in areas that are vulnerable to acidification and that are already acidic	Fish death in areas that are vulnerable to acidification and that are already acidic
<b>Particles</b>	Little or no effects	Little or no effects	Little or no effects (?)
<b>Fluoride</b>	No effect	No effect	No effect
<b>Heavy metals</b>	No effect	No effect	No effect

**Increased intensity of monitoring at two stations in southern Norway**

To monitor the effects of the fallout from volcanic eruption, we increased the sampling frequency at the small streams at Birkenes (Aust-Agder) and Øygardsbekken (Rogaland), both of which are strongly acidified and located in areas that already receive large amounts of long-range transported pollutants. We assumed that any effect would be evident in a small catchment that was already heavily loaded with sulfur deposition, and where critical loads are exceeded.

In the week after the start of the eruption, we collected two additional water chemistry samples in addition to the normal monitoring programme that collects one sample per week; Birkenes was sampled 19, 21, 23, and 26 April and 3 May) and Øygardsbekken (18, 21, 23, and 25 April and 2 May).

In addition to this, we installed two loggers that measured pH and temperature every hour. These were installed on 20 April 2010 at Birkenes and 22 April 2010 at Øygardsbekken.



Map showing location of the two sites in southern Norway

### Results and conclusions

Neither sulfate or pH or any other measured chemical parameter showed any sign of response to the deposition from the volcanic eruption, neither in the short term (days) or in the long term (months) (Figure 1 and 2). It is therefore also unlikely that the eruption has resulted in a negative biological effect on the short term.

When we have all the results from the 2010-monitoring activities it will be possible to test if the effects from the fallout from the eruption can be seen in water chemistry or biota on a regional scale in Norwegian rivers and lakes. NILU (Norwegian Institute for Air Research) will calculate how much additional sulfur deposition was caused by the volcanic eruption.

### Recommendation for further monitoring / contingency

The uncertainties related to the effects of the eruption on Norwegian nature and the great demand for information in the media about the possible effects of the eruption suggest the need for possible emergency preparedness measures.

Routine results from the monitoring network in the Norwegian acid rain monitoring programme give good information about changes in freshwater quality caused by such incidents. This is because the data has high quality (long data series, many parameters) and because some of the monitoring sites are small and have fast responses. Documentation of a particular incident, however, presupposes that the disaster affects the parameters analysed in the monitoring programme.

During an incident, there may be a need for more intensive monitoring and investigation of other parameters. There is also a need for more rapid reporting of results than that is routine for the current monitoring programme. Automatic logging equipment can be used to monitor changes in water chemistry online, which can be a very useful tool in such situations

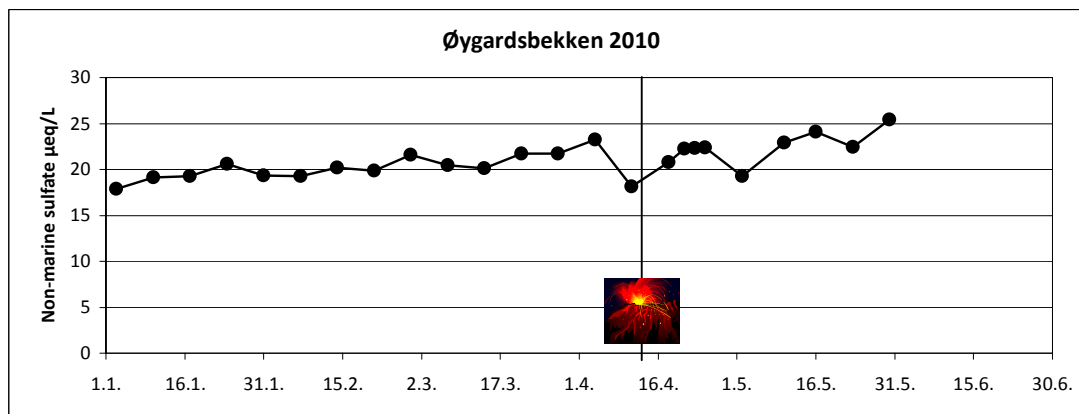
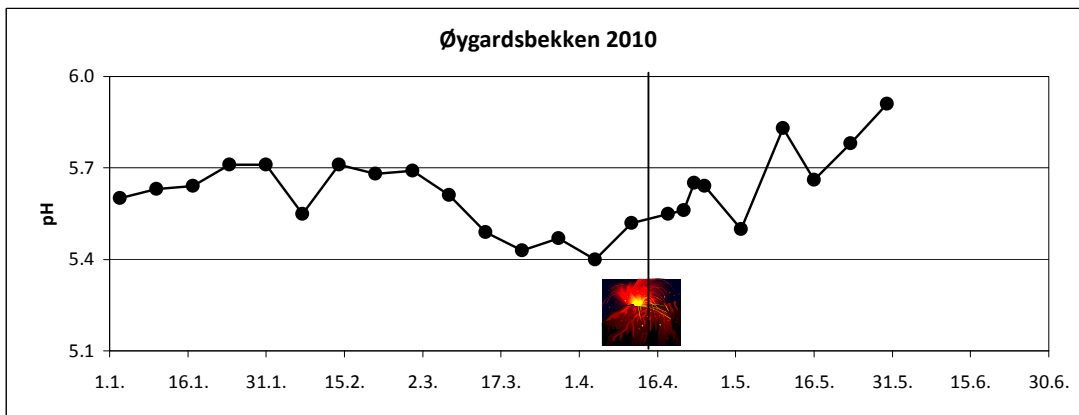
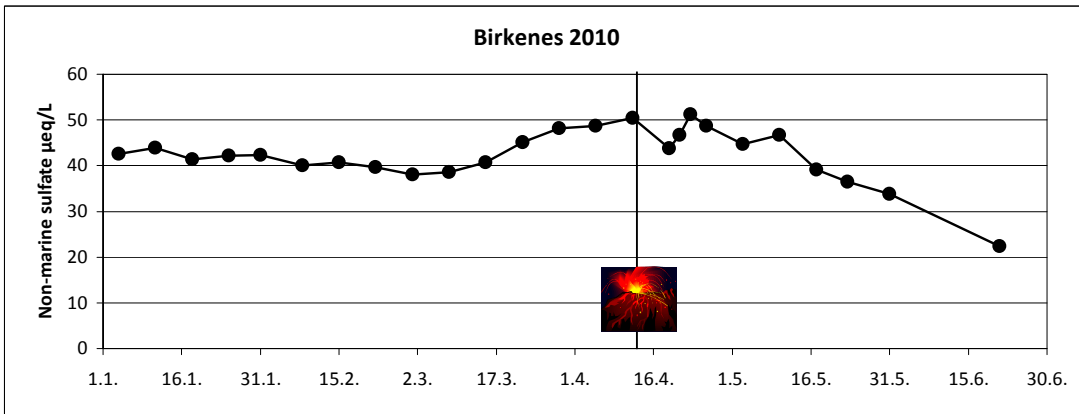
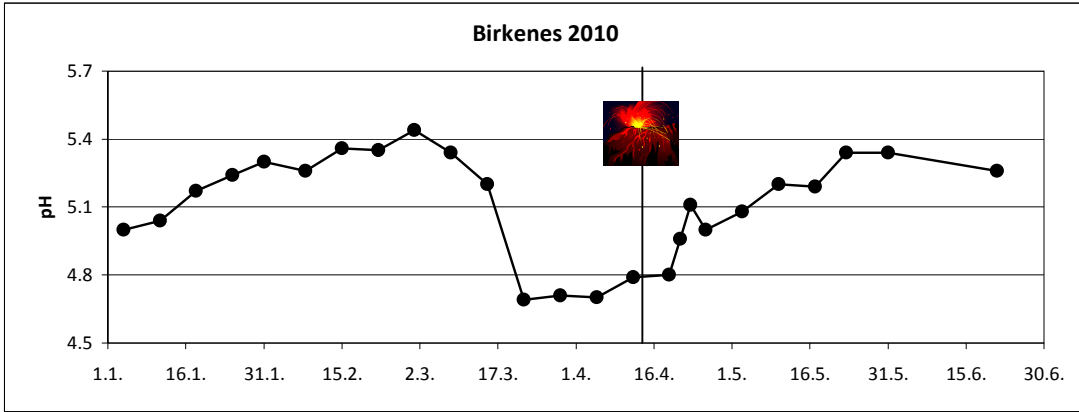


Figure 1. pH and non-marine sulphate in Birkenes and Øygardsbekken from 1.1.2010 to 1.7.2010. Time of start of the eruption is marked with a line (14 April).

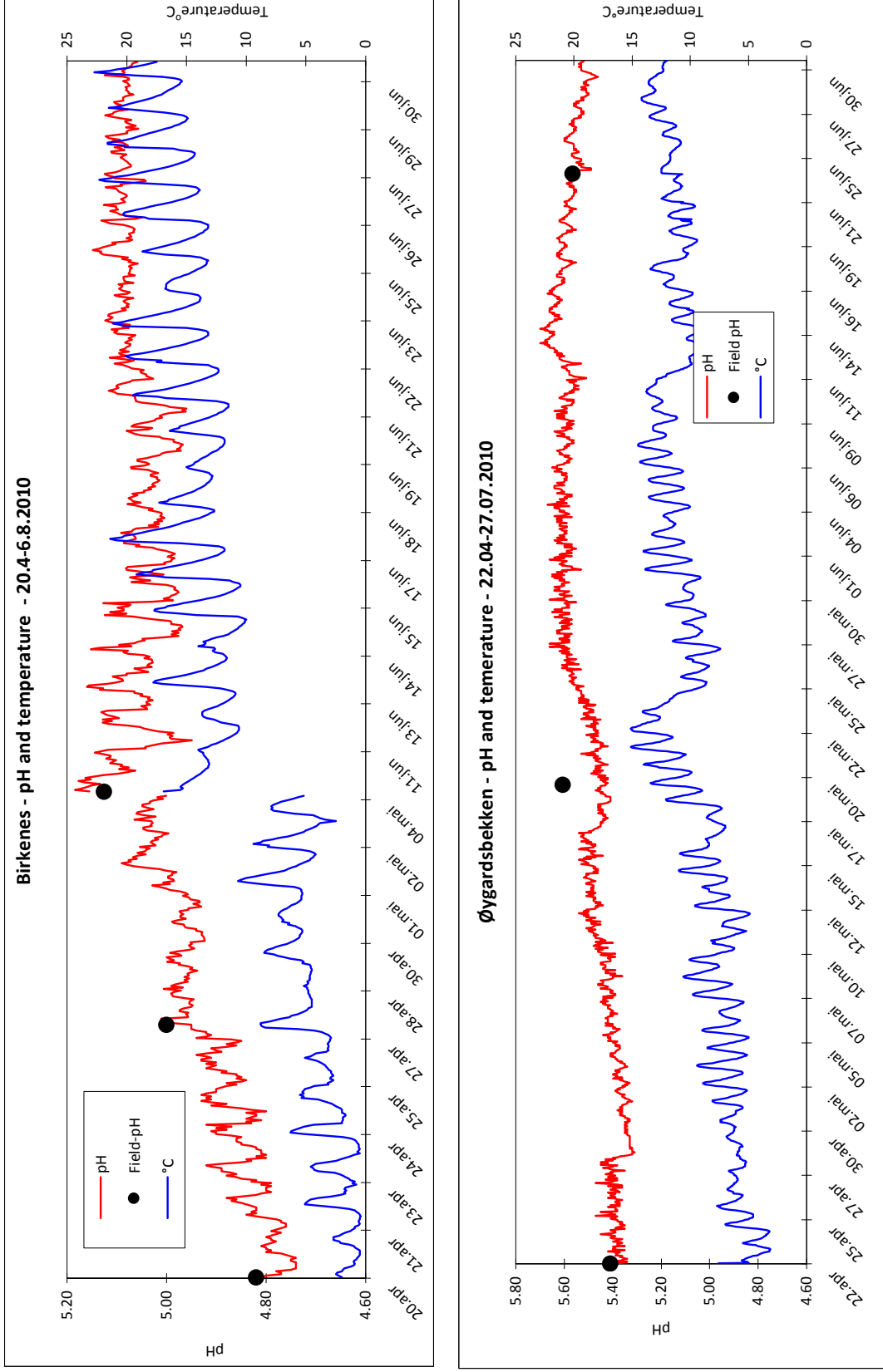


Figure 2. Data from logger at Birkenes (top) and Øygardsbekken (bottom) for the period April to August and April to July 2010. Also shown are pH is measured in the field.

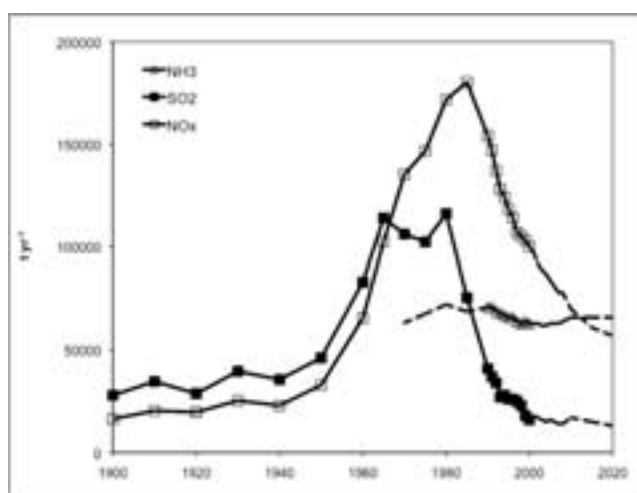
### 3. Acidifying deposition in Southern Switzerland. Assessment of the trend 1988-2007

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The sulphur dioxide and nitrogen oxides emissions in Switzerland started to increase steeply after the second world war. Sulphur dioxide reached its maximum between 1965 and 1980, while nitrogen oxides peaked around 1985. Afterwards, both sulphur and nitrogen oxides decreased continuously until 2000 (see figure A). For ammonia only a small decrease could be observed. Because of its particular meteorology the air quality in Southern Switzerland is not only influenced by the local emissions but also by transboundary air pollution originating from the Po Plain and particularly from the heavily polluted urban area of Milan. Furthermore, many high altitude soils and freshwaters of Southern Switzerland are particularly sensitive to acidification due to the dominance of base-poor rocks with low buffering capacity. As a consequence, acidifying deposition in Southern Switzerland becomes particularly relevant.



**Figure A** Annual sulphur dioxide, nitrogen oxides and ammonia emissions in Switzerland from 1900 to 2010. Dashed lines indicate estimate values.

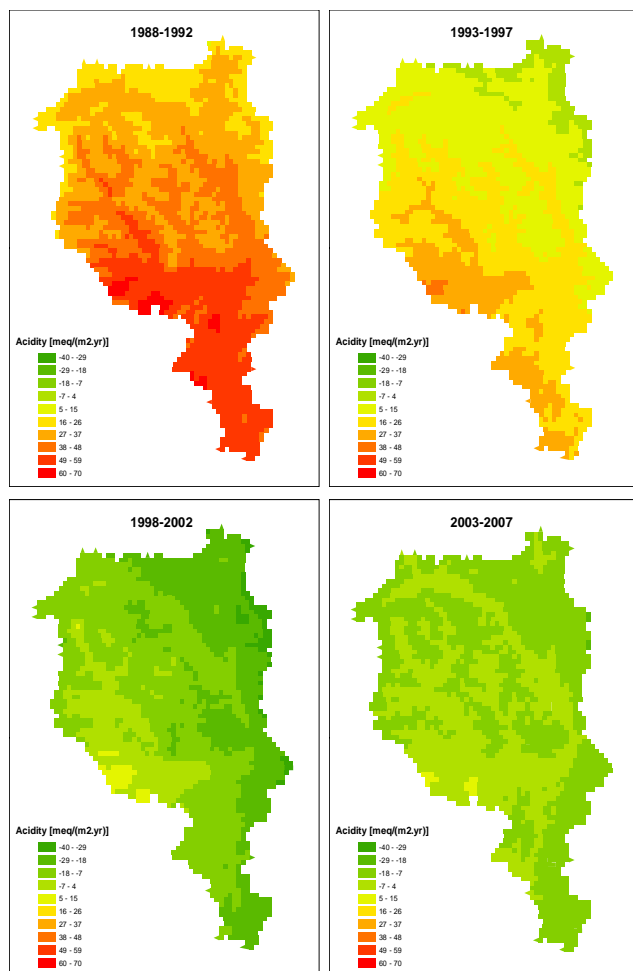
It is for this reason that rainwater quality has been studied in Southern Switzerland since the beginning of the eighties, first only at Locarno Monti and Lugano and later also at other sampling stations. Nowadays weekly precipitation is collected at 9 sampling sites distributed over the whole area of Canton Ticino. A trend analysis of the main chemical parameters in rainwater reveals that sulphate concentrations have decreased, reflecting the decrease of SO<sub>2</sub> emissions after 1980. At Locarno Monti and Lugano sulphate concentrations have decreased by around 57-66% during the last 20 years, while no significant trend could be observed for ammonium and nitrate concentrations. Concentrations of bicarbonate and base cations have increased and were particularly high during the years 1999, 2000, 2002, when precipitation was higher than usual and alkaline rain events were more frequent. As a consequence of decreased sulphate concentrations and increased concentrations of base cations, acidity of rainwater decreased and therefore pH values increased. Since the end of the eighties until the beginning of this millennium the mean annual pH values of rainwater at Locarno Monti and

Lugano increased from 4.3 to 5.0/5.3 and after 2000 the mean annual acidity became negative at most sites.

In order to analyze patterns in the data and relations between parameters, a principal component analysis has been performed with average concentrations of the main chemical parameters and with conductivity, precipitation amounts and geographic parameters over the periods of 1988-1992, 1993-1997, 1998-2002 and 2003-2007. The analysis has been extended by considering not only data from Swiss monitoring stations but also from North Italian sampling sites. The analysis has shown that most chemical parameters in rainwater correlate significantly with the geographic parameters latitude, longitude and altitude. Sulphate, nitrate and ammonium concentrations correlate with both latitude and altitude reflecting the transport of these pollutants from the urban area of Milan and from rural areas of the Po Plain towards north. Conversely, mean yearly concentrations of base cations and bicarbonate, which increase with decreasing annual precipitation (smaller dilution of alkaline rain events on an annual base), correlate with longitude because atmospheric currents causing rainfall are mostly directed from south-west to north-east. The principal component analysis also reveals that acidity correlated with latitude during the beginning of the monitored period (1988-1992), but became more and more independent of latitude and dependent of longitude after the interval of 1998-2002. This indicates that acidity was mainly determined by emissions of SO<sub>2</sub>, NO<sub>x</sub> and NH<sub>3</sub> during the first period, while alkaline rain events became more important afterwards.

The geographic distribution of chemical parameters in rainwater discussed in the principal component analysis suggested the possibility to develop a multiple regression model with the variables latitude, longitude, altitude. This can describe the geographic distribution of the concentrations of single chemical parameters in rainwater. Multiple linear regression analyses have been performed for different parameters in the periods of 1988-1992, 1993-1997, 1998-2002 and 2003-2007. For some parameters and time periods the addition of the mean annual precipitation volume as a regression variable has provided better results. In particular, parameters like base cations, bicarbonate, acidity and pH, whose annual mean concentrations are strongly influenced by sporadic alkaline rain events, are better modeled after 1993 if the amount of precipitation is also considered. The regression parameters have then been used to map concentrations of the main chemical parameters over Southern Switzerland with a resolution of 1km x 1km.

Finally, wet deposition maps for Southern Switzerland have been derived by multiplying the concentration maps of chemical parameters in rainwater by the precipitation maps (see figure B). Observations made for the concentrations of chemical parameters in rainwater do not substantially differ from those of wet deposition. In general time trends can be observed, in which sulphate deposition and acidity decrease, whereas the deposition of base cations and of bicarbonate increase. The dependency of the chemical variables on geographic parameters also did not vary over time. However, the particularly rain rich (1998-2002) and rain poor (2003-2007) years had visible consequences on deposition: wet deposition of sulphate, nitrate and ammonium were slightly higher between 1998 and 2002 compared to the immediately previous and subsequent time periods.

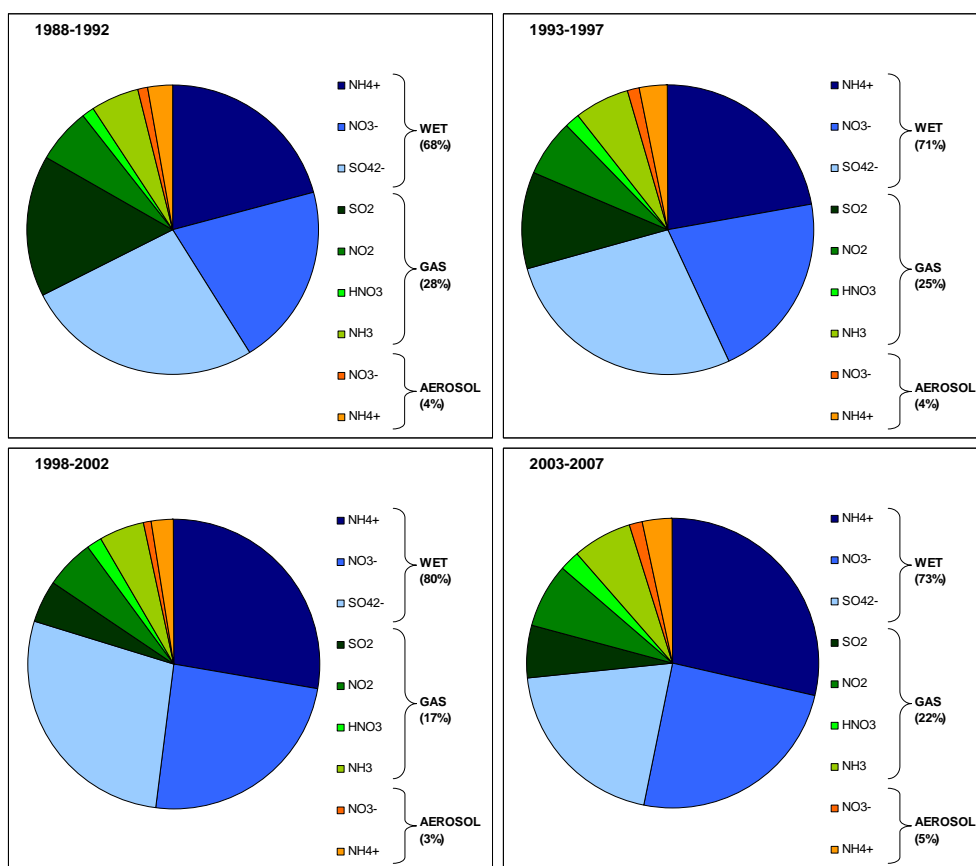


**Figure B.** Wet deposition: 1988-1992, 1993-1997, 1998-2002, 2003-2007. Deposition of acidity

In addition to wet deposition the dry deposition of gases and aerosols also contribute to the total acidifying deposition. Maps of dry deposition were prepared by Meteotest. The sum of wet and dry deposition was used to derive maps of the present load of acidity and of the total deposition of sulphur and nitrogen.

Since wet deposition mostly contributes to the total deposition of nitrogen - 70-77% - (see figure C) and to the present load of acidity - 68-80% -, the temporal trends of wet deposition are found to be similar to those of total deposition. As a consequence of reduced sulphur deposition the relative importance of sulphur compounds within the total deposition of acidifying compounds has decreased from 42% to 26% while that of nitrogen compounds has increased from 58% to 74% during the last 20 years.

**Figure C** Contribution of wet deposition and dry deposition of gases and aerosols to total acidifying load.



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## 4. Report of national ICP Waters activities in Latvia, 2008/2009

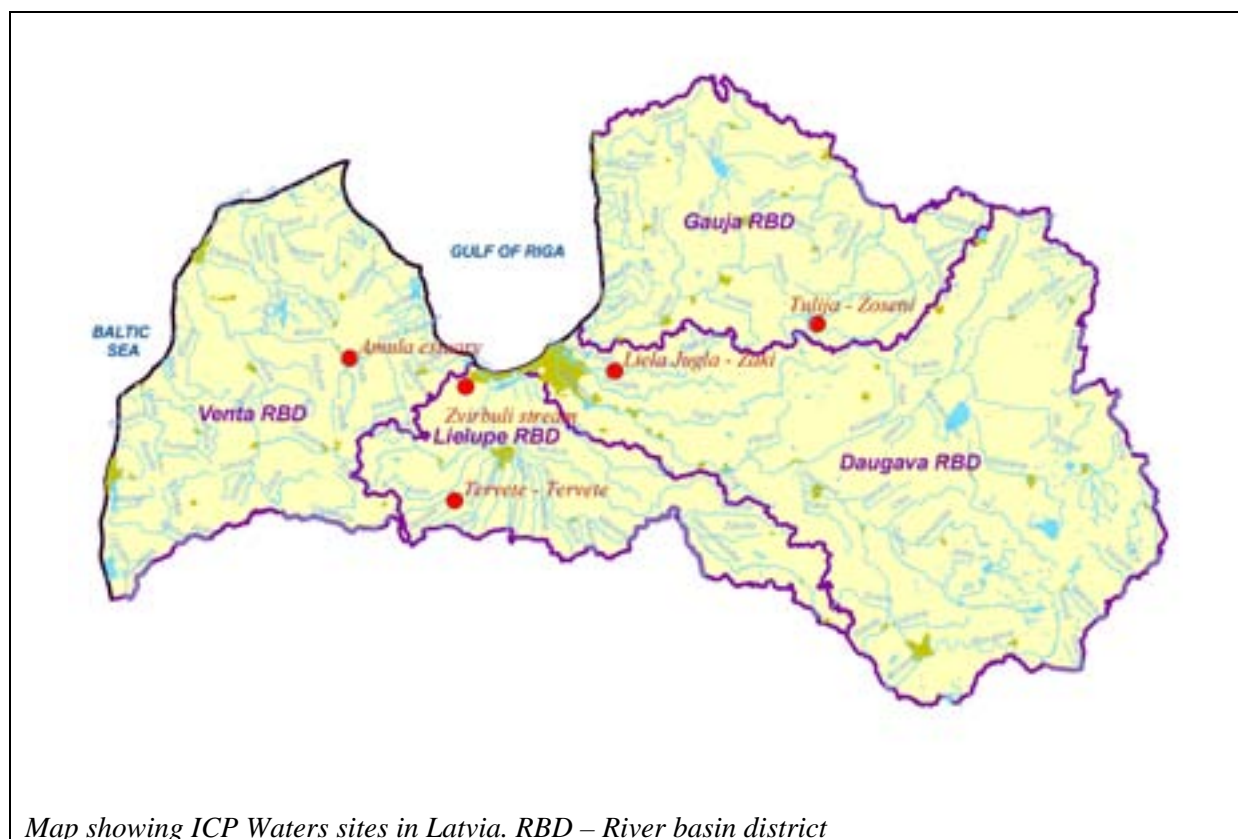
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### Major activities under the programme in 2009/2010

- In 2009/2010, ICP Waters programme covered five sites: L.Jugla-Zaki, Amula-mouth, Tulija-Zoseni, Zvirbuli stream and Tervete – upstream Tervete.



Map showing ICP Waters sites in Latvia. RBD – River basin district

- In 2009, water sampling ICP Waters sites was carried out only 4 times a year and covers the major seasons of the year due to the reduction of funding for the environment program.
- Hydrochemical and hydrobiological data for 2008 were sent to the ICP Waters programmes centre.
- The centre's laboratory participated in the hydrochemical intercomparison exercises held by NIVA (No 2309). A total of 92% of the results were within the general target accuracy of +/-20%, or the special accuracy limit for pH and conductivity. The worst results were observed for the heavy metals copper, where the concentration are rather low, and for the total organic carbon, were used cathalytic combustion method for the determination vs recommended UV/peroxodisulfate oxidation method.
- Since 2009 for water quality data has been used following approach: if concentration below the laboratory detection limit used detection limit value marked with 781 flag; if the concentration

below the quantification limit, but higher than the laboratory detection value marked with 780 flag which indicates that measurements uncertainty is high.

- Developed method for preparing water samples for the determination of inorganic labile aluminium.
- Put in the laboratory work the reference methods ISO 10695:2000 'Water quality - Determination of selected organic nitrogen and Phosphorus compounds - Gas chromatographic methods '.
- Assessment of Kemeru bog effect on the Zvirbuli stream runoff.

## Data assessment results

- *Surface water quality, the report “ Effects of Transboundary Air Pollution on Ecosystem of Latvia (LVGMA, 2008)*

The quality of surface waters mirrors the quality of the environment in a catchment under the effect of various factors. The quality of surface waters has been assessed based on observations carried out at background level in ICP IM forest streams and ICP Waters stations for the period 1998-2007. The observations allow to assess quality of waters and tendencies taking into account transboundary pollution transport and dynamics of deposition from the atmosphere in the catchment.

In the 1998-2007 period, mean pH values varied from 7.19 (Taurene stream) to 8.03 (Amula River) except for Zvirbuli stream that flows through the Kemeru bog (annual mean pH of 3.73-4.84). Annual mean pH has shown the downward tendency that testifies to acidification of surface waters at background level (fig. 1a). The tendency is statistically significant in ICP IM sites at Rucava (highly significant of  $p=0.001$ ) and Taurene (very weak of  $p=0.1$ ). Surface waters at ICP stations have become acidified compared to the years 1990-1999 while  $\text{HCO}_3^-$  data obtained for Liela Jugla and Tulija for the years 1998-2007 show the positive tendency, with the statistical significance in Tulija (very weak  $p=0.1$ ).

Sulphate concentrations were 2-3 times higher in Liela Jugla and Tervete than at other ICP stations, and 6 times as high as in Zvirbuli Stream (Fig. 1b). The higher sulphate concentrations in the former two water bodies is likely to be due to breaking up and dissolving of gypsum that enters in the composition of bedrocks. Annual mean sulphate concentrations in surface waters at ICP stations have shown the downward tendency with the statistically significant tendency in the Tulija River (very significant  $p=0.001$ ) and Taurene Stream (very weak  $p=0.1$ ). The slow decrease in sulphate concentrations occurred along with a decrease in sulphur concentrations in deposition.

At background stations, the main N sources are water-bound atmospheric nitrogen, nitrogen deposition from the atmosphere, leaching from the soil, releasing from sediments of water bodies and inflow with groundwater.

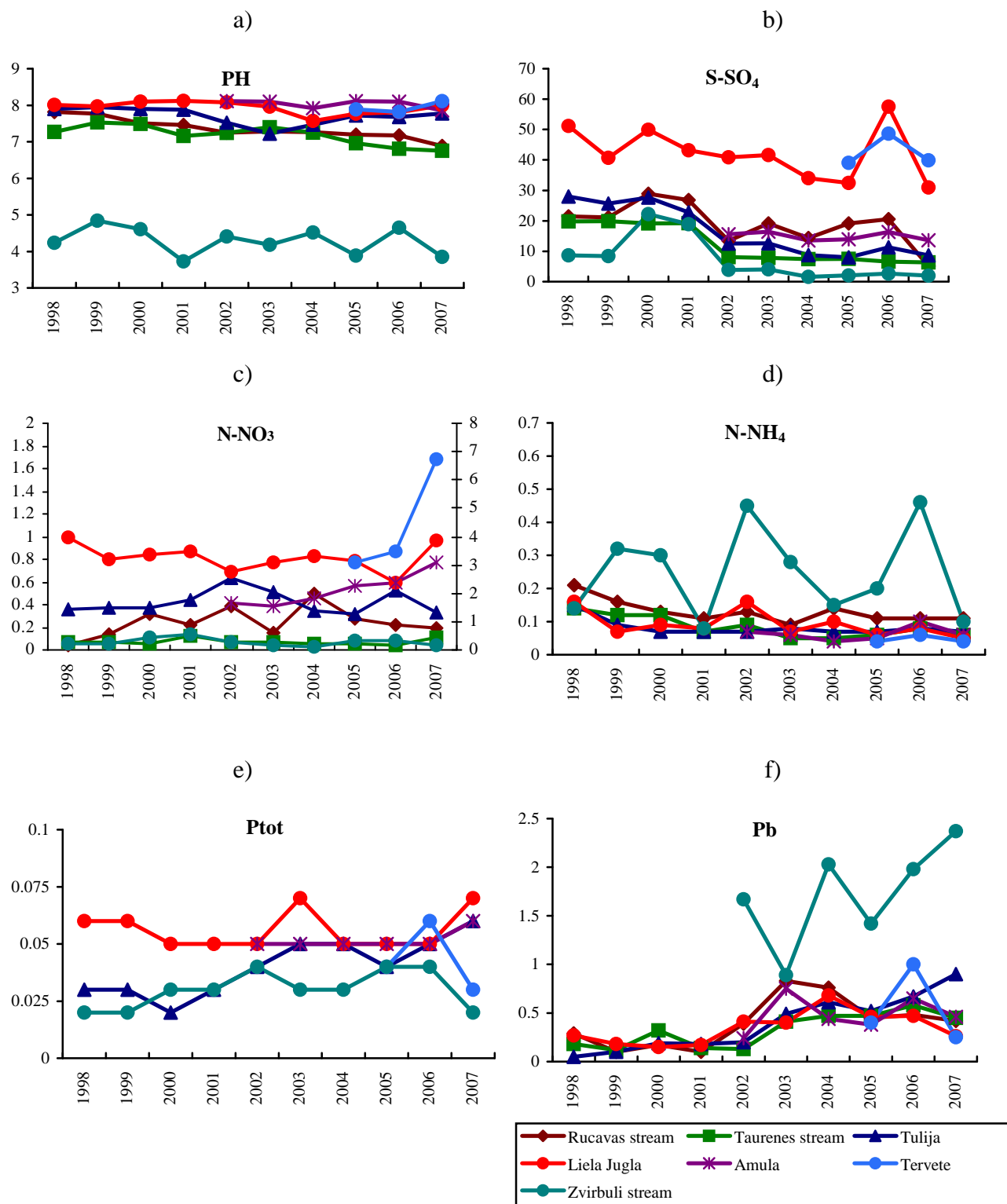
Lowest values were obtained for nitrate concentrations in Taurene and Zvirbuli streams, 0.07 mg/l on average, and in Rucava Stream, 0.25 mg/l on average. Mean nitrate values reported from the rivers Tervete, Liela Jugla and Amula ranged from 0.42 to 0.81 mg/l. In Tervete (Fig. 1c.), high annual mean concentrations of 3.07 mg/l to 6.75 mg/l may be ascribed to the anthropogenic impact on the catchment, mostly due to agricultural activities.

An elevated level of ammonium in the surface waters of ICP Rucava (annual mean values of 0.09 - 0.21 mg/l) and Zvirbuli (0.08-0.46 mg/l) Streams (Fig. 1d.) is likely to be due to the influence exposed by bogs. Other ICP stations reported  $\text{N-NH}_4^+$  annual mean values of 0.05-0.08 mg/l.

Annual mean concentrations of  $\text{N-NO}_3^-$  and  $\text{N-NH}_4^+$  showed an insignificant falling tendency or stability except for  $\text{N-NO}_3^-$  in the stream at Rucava (a bit rising tendency). The rising tendency was statistically significant (weak  $p=0.05$ ) in the stream at Taurene.

The concentration of  $\text{P}_{\text{tot}}$  was studied in surface waters of the ICP Waters stations. Judging from Fig. 1e,  $\text{P}_{\text{tot}}$  showed higher values in Liela Jugla (annual mean values of 0.047 – 0.074 mg/l) and Amula (0.048-0.058 mg/l) especially in the beginning of the period under study. The corresponding values were 0.044 mg/l in Tervete, 0.039 mg/l in Tulija and 0.03 mg/l in Zvirbuli Stream. Dynamics of

annual mean  $P_{tot}$  concentrations in Tulija (statistically significant,  $p=0.01$ ) and Zvirbuli showed the rising tendency over the whole period under study while in Liela Jugla,  $P_{tot}$  was stable.



**Fig.1** Annual mean concentrations (mg/l, Pb-  $\mu\text{g/l}$ ) at ICP Waters and ICP IM stations ( $N\text{-NO}_3$  concentration Tervete is given on second y axis)

For heavy metals in surface waters, analysis has been mostly dedicated to lead and cadmium. Over the whole period under study, mean Pb concentrations varied from 0.33 (Taurene Stream) to 0.55  $\mu\text{g/l}$

(Tervete) except for Zvirbuli Stream where a mean concentration of 1.73 µg/l was 3 times higher than the limit value (Fig.1f).

With the downward tendency in Pb deposition from the atmosphere, annual mean concentrations of Pb in the surface waters of the ICP stations showed the upward tendency with the statistically significant tendency in Tulija (very significant of  $p=0.001$ ) and Taurene Stream (weak  $p=0.05$ ).

- **First results of total aluminium in the ICP Waters and ICP Integrated monitoring sites**

Aluminum enters the surface water in a natural way with the partial dissolution of clays and aluminosilicates, as well as a result of emissions of individual plants with precipitation. The content of aluminum in surface waters varies greatly depending on the degree of acidification of soils. In some acidic waters, its concentration can reach several grams per liters.

Monthly concentrations of total aluminium at the rivers and stream ICP Waters and small forest streams ICP IM sites in 2008 ranged from 0.69 µg/l

to 725.81 µg/l. Highest level of total aluminium has been observed at all measurement sites during the April-May, period of maximum water discharges (Fig.2). Monthly concentrations of total aluminium in soil water ICP IM sites in 2008 were significantly higher and reached 92.66-3881.24 µg/l. Highest level of total aluminium has been observed at 0-10cm, -20cm and -40 cm soil horizons in August-September.

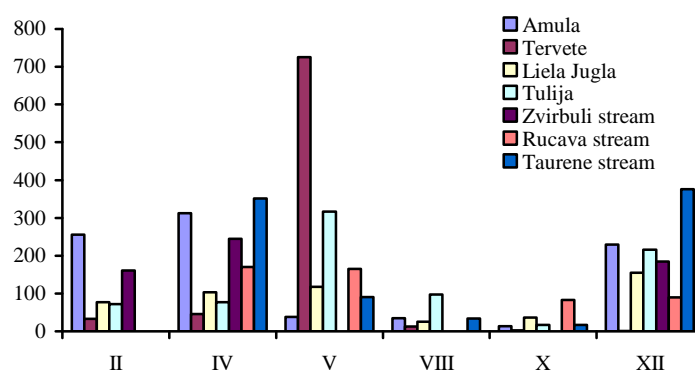


Fig.2 Monthly total aluminium concentrations at the ICP Waters and ICP IM sites, 2008.

### Future activities

- participation in hydrochemical and hydrobiological ICP Waters intercomparison events as well in new POP's intercomparison exercise under the EMEP/AMAP/CAMP/HELCOM programmes;
- participation in the work of the ICP Programme Centre to revise the ICP Waters Manual;
- 2009 data reporting to the ICP Waters data base;
- new analytical equipment: 3 gas chromatography system chlororganic pesticides and polychlorinated biphenyls, volatile aromatic hydrocarbons (BTEX) and petroleum products, determination of environmental samples, automated cold vapor atomic fluorescence spectrometer for mercury determination, inductively coupled plasma optical emission spectrometer ICP-OES determination of metal content in environmental samples, high efficiency liquid chromatography (HPLC) system of the anion composition analysis, introduce in the laboratory work. Equipments will be received under the support of European Regional Development Fund (ERDF).
- start determination of inorganic labile aluminium at the ICP Waters sites.
- assessment of Kemeru bog effect on the Zvirbuli stream hydrochemical regime.

## 5. Recovery of acidified lakes in Finland and subsequent responses of perch and roach populations

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### Introduction

The multidisciplinary Finnish Acidification Research Programme (HAPRO) in 1985-1990 revealed that a considerable number of small headwater lakes (lake area  $\geq 0.01$  km<sup>2</sup>) in Finland were suffering from acidification and damage to fish populations. In connection with HAPRO, the lake status survey in 1987 estimated the number of acidic (Gran alkalinity  $\leq 0$   $\mu\text{eq l}^{-1}$ ) lakes to be 4900 (Forsius *et al.* 1990). Correspondingly, a fish status survey in 1985-1987 reported declines and even extinction of sensitive fish species in small lakes, due to anthropogenic acidification in south and central Finland (Rask and Tuunainen 1990). The number of lakes in south and central Finland in which fish populations were affected due to acidification was estimated to be 2200-4400, and out of these 1000-2000 fish populations were estimated to be lost (Rask *et al.* 1995a). The most damaged populations were roach, and to a smaller extent European perch, the most common species in small lakes in south and central Finland. The fish status survey of Finnish lakes (lake area  $\geq 0.04$  km<sup>2</sup>) in connection with the Northern Europe Lake Survey in 1995 suggested that ca. 700 fish populations were lost and 1200 affected, mainly roach populations (Tammi *et al.* 2003). Both fish surveys suggested that perch was not extinct in any lakes. However, some strongly acidified lakes were found outside the coverage of the surveys that had lost their perch populations (Rask and Tuunainen 1990, Nyberg *et al.* 2010).

Sulphate deposition has been the major driving force in the anthropogenic acidification of surface waters in Finland as well as in other Nordic Countries (Skjelkvåle *et al.* 2001) and elsewhere in Europe (e.g. Prechtel *et al.* 2001, Wright *et al.* 2005). Following the general decreasing trend in S deposition in Finland since the late 1980s (e.g. Vuorenmaa 2004), the regional recovery of acid sensitive Finnish lakes, indicated by decreasing concentrations of sulphate and increase in alkalinity, was first observed in the early 1990s (Mannio and Vuorenmaa 1995). At the same time or in some cases even earlier than the measured chemical changes, the first signs of recovery in affected perch populations were recorded (Nyberg *et al.* 1995, Rask *et al.* 1995b). The recovery of lakes from acidification has been the strongest and most consistent in south Finland, where lakes have been exposed to highest S deposition load, and it is this region that has also showed strongest emission reduction responses in deposition (Vuorenmaa 2004, Vuorenmaa and Forsius 2008). Sulphur deposition in south Finland has declined by about 70% since the late 1980s (Vuorenmaa 2007).

In this report we present chemical and biological recovery trends of selected monitoring lakes susceptible to acidification from south Finland during the 25-year period 1985-2009. Water chemistry records for Lake Kattilajärvi, Lake Iso Lehmälampi and Lake Vitsjön (ICP Waters lake) are shown since the year 1987, when extensive monitoring of lake chemistry was started in connection with the national survey of lake acidification by subjectively chosen lakes from the survey lake population. For fish populations, examples of responses of perch (*Perca fluviatilis* L.) and roach (*Rutilus rutilus* L.) populations are given based on three-year interval monitoring since the year 1985 when the Finnish Acidification Research Project (HAPRO) was started.

### Material and methods

Finnish Game and Fisheries Research Institute and Finnish Environment Institute started an integrated monitoring of water chemistry and fish populations in acidified lakes in the early 1990s. Twelve lakes

were selected from common lake acidification monitoring sites, representing the four levels of fish population response to acidification (Rask *et al.* 1995a):

- (1) Perch extinct (lake n=4; pH<5; Al<sub>lab</sub> 80-280 µg l<sup>-1</sup>)
- (2) Perch affected (lake n=5; pH 4.8-5.5; Al<sub>lab</sub> 50-160 µg l<sup>-1</sup>)
- (3) Roach extinct (lake n=6; pH 5.2-6.0; Al<sub>lab</sub> 25-135 µg l<sup>-1</sup>)
- (4) Roach affected (lake n=6; pH 5.3-6.4; Al<sub>lab</sub> 5-40 µg l<sup>-1</sup>)

Fish were sampled with gill net series of eight nets in 1985-1992 and with NORDIC multimesh survey nets since 1995. For comparability, net panel area and selectivity corrections were calculated according to Tammi *et al.* (2004). The catch of each species was counted and total length and weight were measured. Results are expressed as NPUE (mean number of fish in one NORDIC survey net in one night). Age determinations of perch were done from otoliths and back-calculation of growth from opercular bones (Nyberg *et al.* 2010).

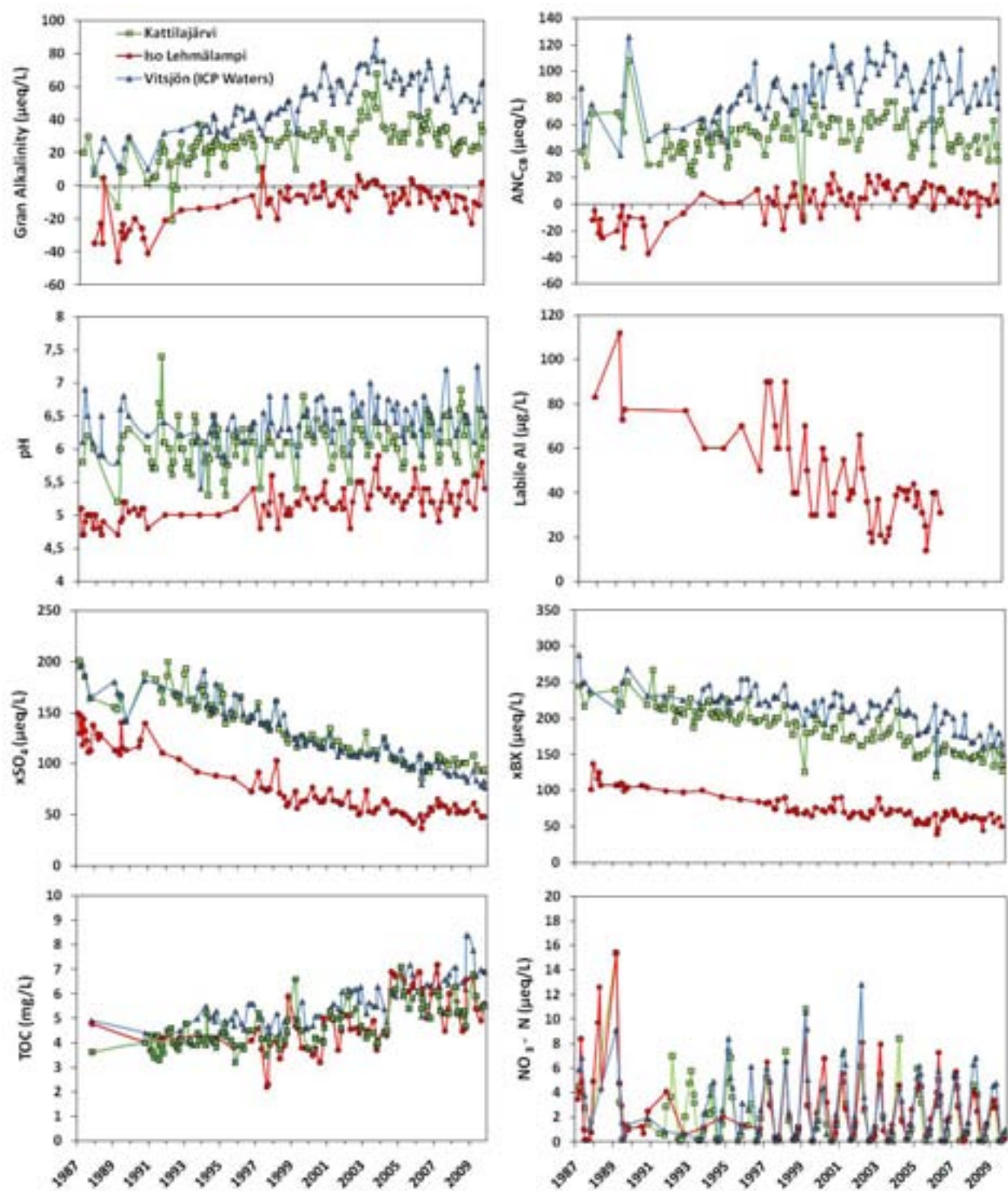
The water chemistry samples were taken from the middle of each lake, commonly one sample during the thermal winter stratification, two samples during the spring flows, one sample during thermal summer stratification and two samples during the autumn thermal overturn. The results used in this report refer to samples taken at 1 meter depth.

## Results

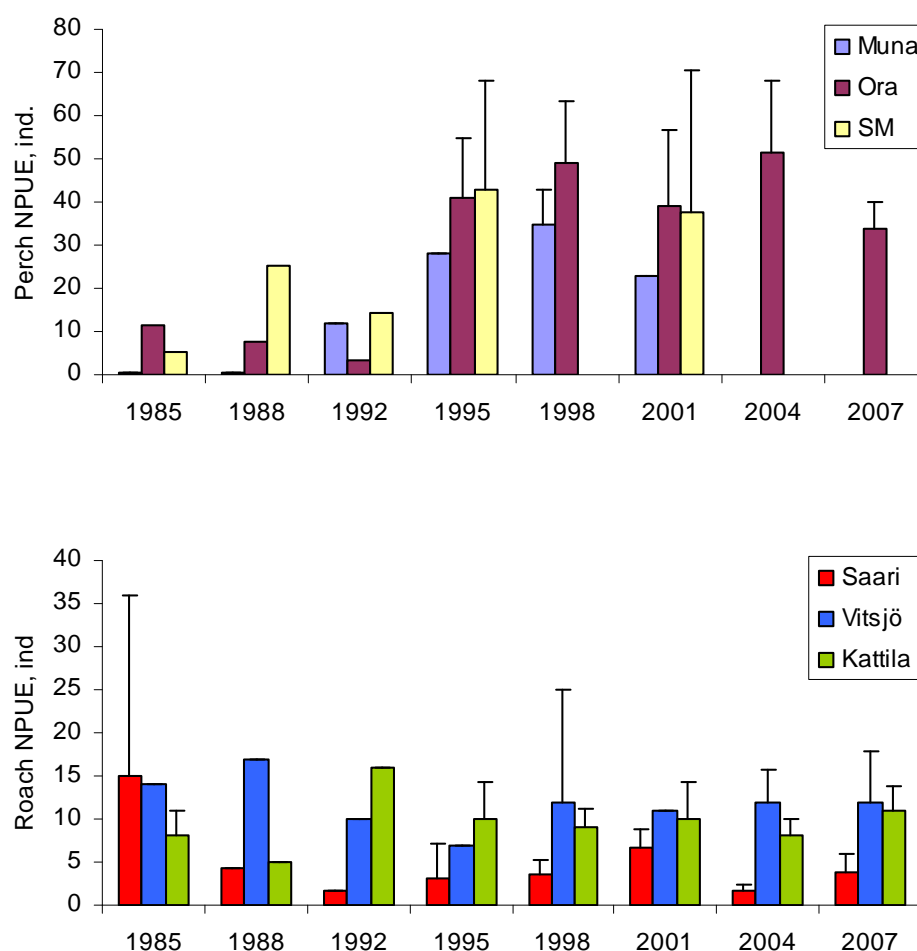
The water chemistry records showed severe or moderate acidification in all study lakes in the late 1980s and early 1990s, indicated with low alkalinity values commonly < 0 µeq l<sup>-1</sup> (Figure 1). However, improvement of water quality from severe acid conditions has taken place during the recent decade. Sulphate concentrations have decreased and pH and buffering capacity have increased from the late 1980s to date. The elevated labile aluminium concentrations in L. Iso Lehmälampi in the early 1990s (> 100 µg l<sup>-1</sup>) have decreased in the early 2000s to a level 20-40 µg l<sup>-1</sup>. There are no indications of increasing nitrate concentrations in lakes. Contrary to minerogenic acidification, organic acidity has increased, indicated by elevated TOC concentrations, during the late 2000s (Figure 1). In spite of improving water conditions, there are signs of backlash in recovery of buffering capacity in the study lakes since the year 2004, indicated by decreasing alkalinity (measured) and charge-balance ANC (calculated).

New strong year-classes of perch appeared in affected populations in the mid 1990s indicating recovery of perch reproduction. Perch NPUE increased correspondingly but at the same time no clear response could be seen in the affected roach populations (Figure 2). The new dominance of young and small fish in affected perch populations caused a sudden drop in the mean weight of fish, from > 500 g to 48 and 81 g in lakes Munajärvi and Orajärvi, respectively (Figure 3). Similarly, after reintroduction of perch into fishless lakes in 2002 (Nyberg *et al.* 2010), their reproduction took place successfully and mean weight remained at levels of 50-75 g in 2007.





**Figure 1.** Long-term trends of key chemical acidification parameters in three fish monitoring lakes in south Finland (1987-2009).

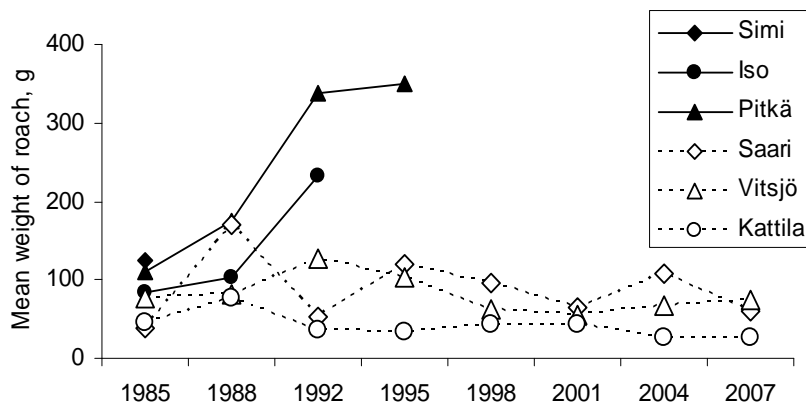
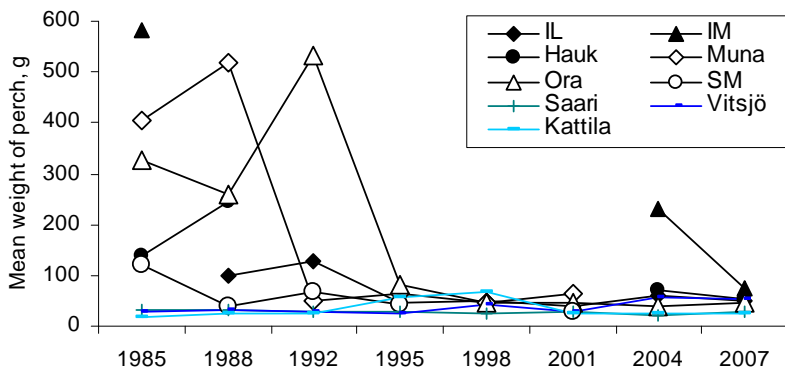


**Figure 2.** The number of perch (top) and roach (bottom) in the gillnet catches of lakes with affected populations. NPUE = mean number of fish in one NORDIC survey net in one night, Y-error bars indicate the standard deviation.

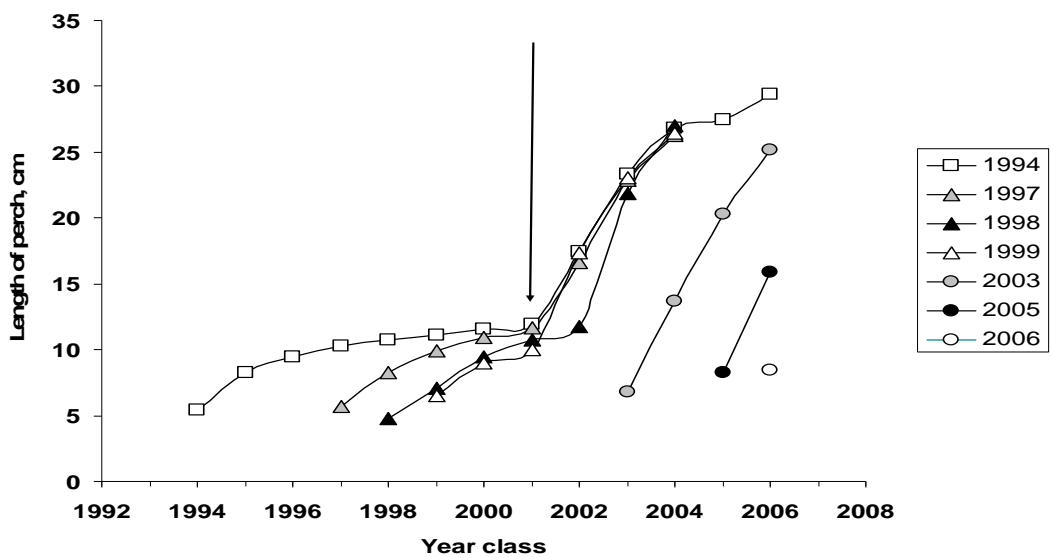
In the lakes that lost their roach populations the mean weight of roach first increased to levels of 200-350 g before the collapse of the population (Figure 3). In the lakes with affected roach populations the mean weight of roach decreased only slightly (Figure 3)

The reintroduction of perch into fishless lakes offered a good example of the density dependent growth capacity of perch. The transfer of fish from a densely populated lake to an empty one resulted in a dramatic increase of growth (Figure 4), most probably due to abundant food resources of the fishless lake (Nyberg *et al.* 2010).





**Figure 3.** Mean weight of perch (top) and roach (bottom) in lakes with lost populations (black symbols) and affected populations (white symbols). The mean weights of perch from three “roach affected” lakes are given for comparison.



**Figure 4.** Back-calculated mean length growth of perch in *L. Iso Majaslampi* where perch were reintroduced in 2002 (indicated with an arrow). New year classes born after 2002 indicate successful reproduction of perch after chemical recovery of the lake (Nyberg *et al.* 2010).

### Discussion/Conclusions

The chemical recovery of the study lakes is clearly resulting in biological recovery, the ultimate intention of emission abatement policy. Increases in pH and alkalinity, and particularly decreases in labile aluminium concentrations towards levels tolerable for acid-sensitive species are mainly responsible for this positive development (Figure 1, Tammi *et al.* 2004). Perch, which has good tolerance and adaptation ability, is responding to improved water quality conditions, and the first signs in recovery were detected in perch populations in early 1990s. Since then, the structure of most of the affected perch populations has turned normal. Successful re-establishment of disappeared perch populations also emphasizes the significant impact of the chemical recovery of the lakes. For more acid-sensitive species roach, little if any recovery of affected populations has been recorded. This may indicate that water quality is still critical for success of roach populations, and recovery in the future will depend on further reductions in acidifying emissions and consequent improvement of water conditions.

Precipitation was very high in summer and autumn 2004 and autumn 2006 particularly in south Finland, resulting in high runoff. This caused elevated leaching of humic material from the catchment, inducing higher organic acidity in the lakes, which can be important factor suppressing recovery of pH and alkalinity in acid-sensitive Finnish lakes (Vuorenmaa and Forsius 2008). Organic acid surges, together with diluted and low-buffered runoff water, may have delayed the increase of buffering capacity of lakes and slowed down the recovery from precipitation-induced acidification and – consequently – may restrict the recovery of acid sensitive fish species like roach. This highlights the importance of catchment characteristics and climatic and hydrological variability in affecting the recovery process.

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## 6. Biodiversity of benthic invertebrates – effects of air pollution and climate change

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### **Introduction**

Benthic invertebrates have species-specific tolerances with respect to freshwater pollutants. In Norway, the freshwater biota has for example been affected by acidification for many decades. Long-term monitoring has documented that the damages to the benthic invertebrate communities was severe during the 1980's and later have been declining.

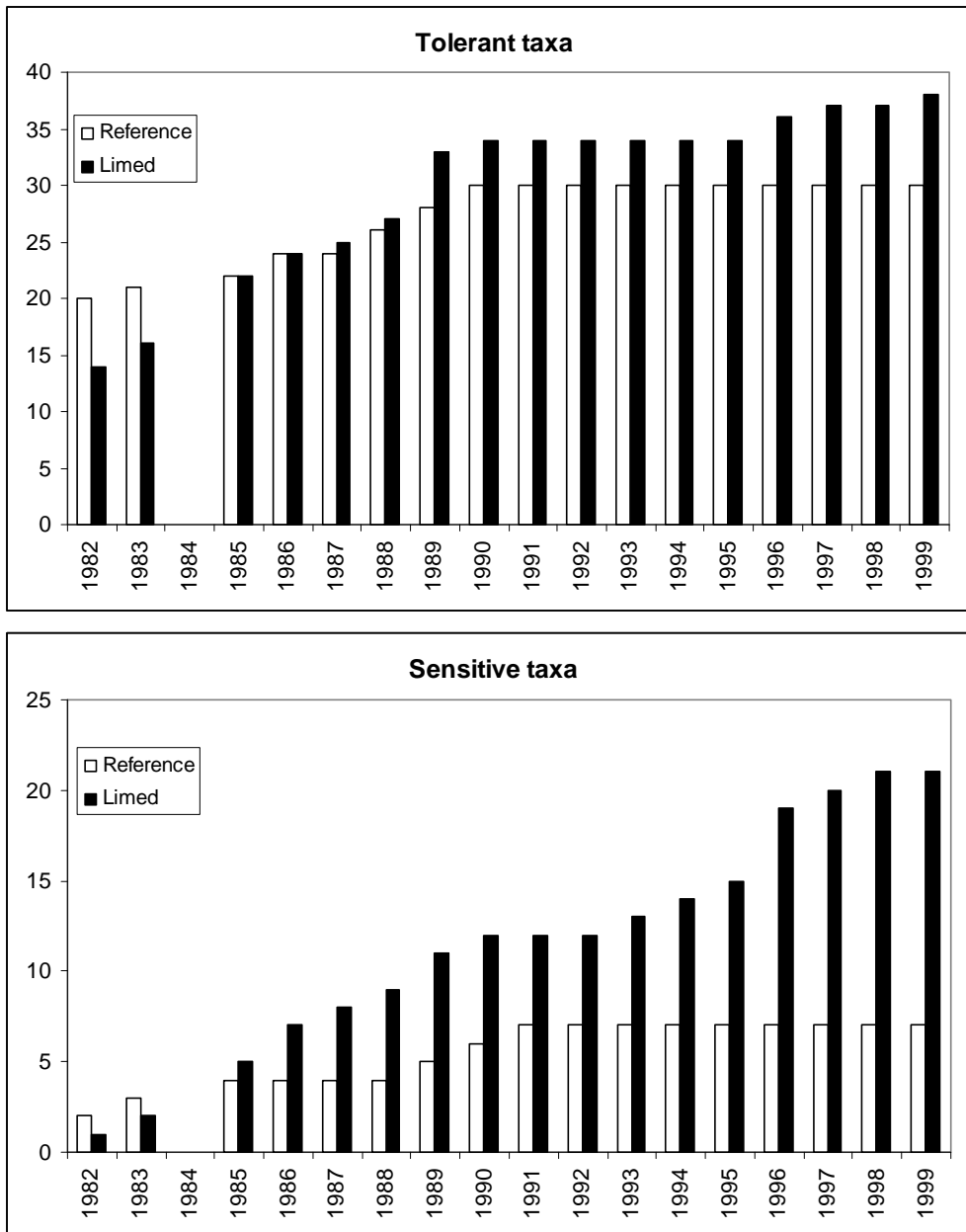
In Norway, an acidification score (metric index) was developed the 1980's in connection with monitoring of acidification (Raddum et al 1988, Fjellheim and Raddum 1990). This metric is correlated to biodiversity of sensitive species and was the first metric to be used in this field. During the latest years the effects of pollution on the invertebrate communities are measured using a wide variety of metrics. Schartau and Petrin (2010) lists more than 60 different scores designed for this purpose.

The Norwegian monitoring programme has additionally used another biodiversity metric, EPT (the number of species within the insect groups Ephemeroptera, Plecoptera and Trichoptera). These three insect orders are very useful in monitoring acidification as they are very common and that the different species within the groups represents a wide range of tolerance limits to acidic waters.

### **Effects of pollution on the ecosystem.**

A healthy ecosystem is characterised by a benthic fauna not affected by exceedance of critical limits with respect to pollution. The fauna is in a steady state, but population characteristics may vary from year to year.

Succession and biodiversity changes slowly. In polluted freshwater, the critical limits too any invertebrates are exceeded. This results in reduced biodiversity due to absence of sensitive species. When a damaged system recovers, the benthic community normally undergoes a rapid succession, mostly constituted by sensitive taxa (Figure 1).



**Figure 1.** Accumulated number of tolerant and sensitive taxa recorded in limed and unlimed sites in River Audna (after Raddum and Fjellheim, 2003).

### Conceptual models of recovery

The mechanisms of the re-establishment of a species may be divided in four different steps (Raddum and Fjellheim 2002):

- Stage 1) Critical limit is exceeded, excluding the sensitive species from the locality
- Stage 2) Dispersal of species to the watershed
- Stage 3) Dispersal of species within the watershed
- Stage 4) Natural fluctuation of the population.

These stages are illustrated in Figure 2, which gives the number of records of a moderately sensitive caddisfly in the Farsund area during 1981 – 2009. Apparently *Hydropsyche siltalai* reached stage 4 around 2004. The history of succession is species-specific. In the case of the Farsund area, the highly sensitive mayfly *Baetis rhodani* still has not reached stage 3A. The overall biodiversity is, however, considerably improved during the later years due to moderate sensitive species colonising the

localities. There is still a potential for further increase in biodiversity as highly sensitive species still have not colonised the area.

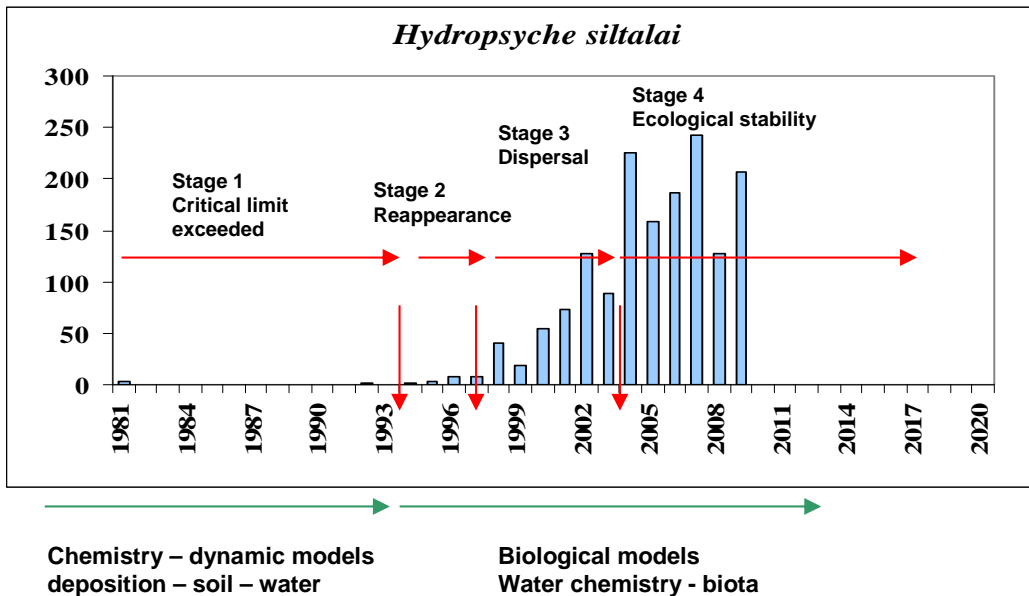


Figure 3A. The succession of the caddisfly *Hydropsyche siltalai* in the Farsund area within the frames of conceptual models of re-establishment after acidification (after Raddum and Fjellheim, 2002 and Posh et al., 2003).

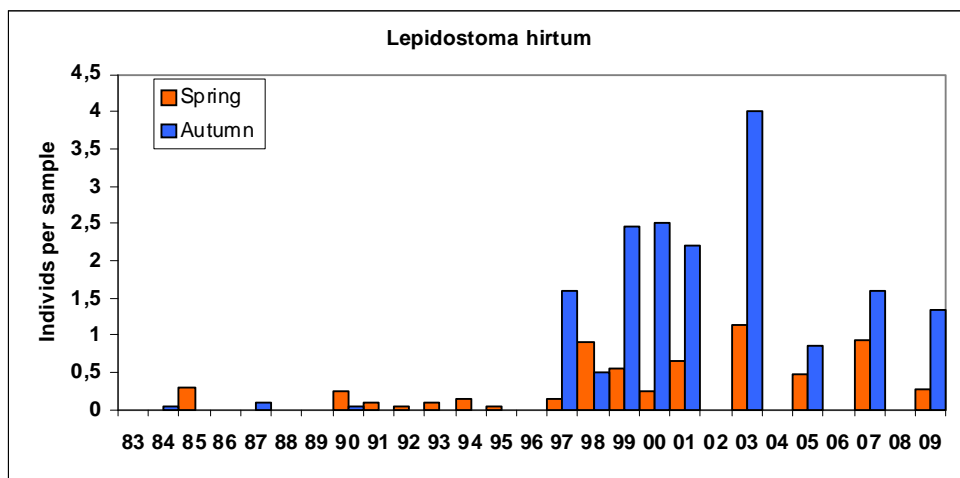


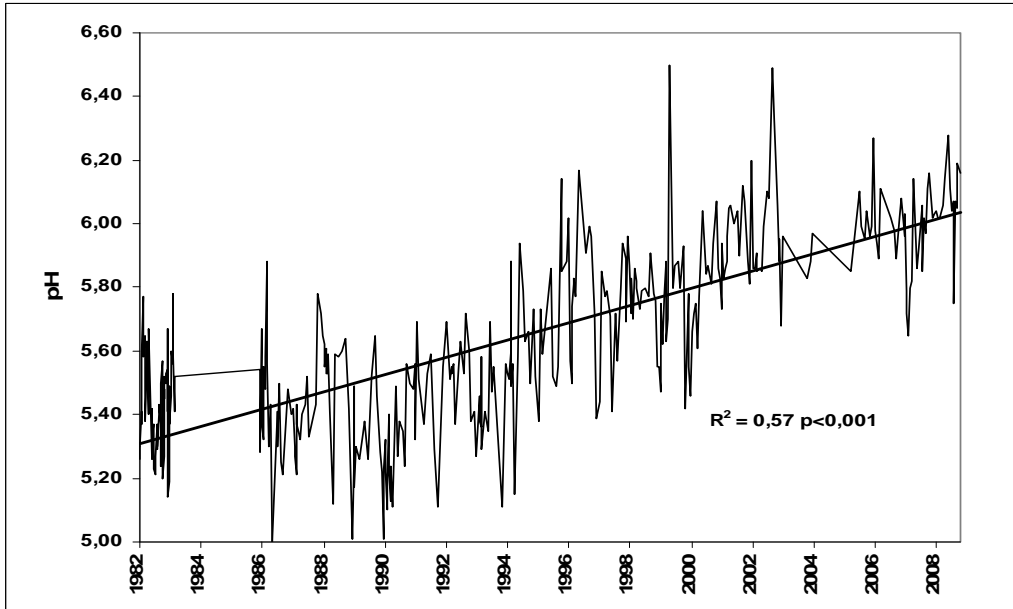
Figure 3B. The number of *Lepidostoma hirtum* per sample in the Nausta watershed. Sampling after 2001 bi-annually.

Another example may be illustrated by the case of the caddisfly *Lepidostoma hirtum* in the Nausta watershed (Figure 3B).

The population of *L. hirtum* in Nausta remained in stage 2 until 1996. After 1997, a population increase was observed and the species, has probably reached stage 4.

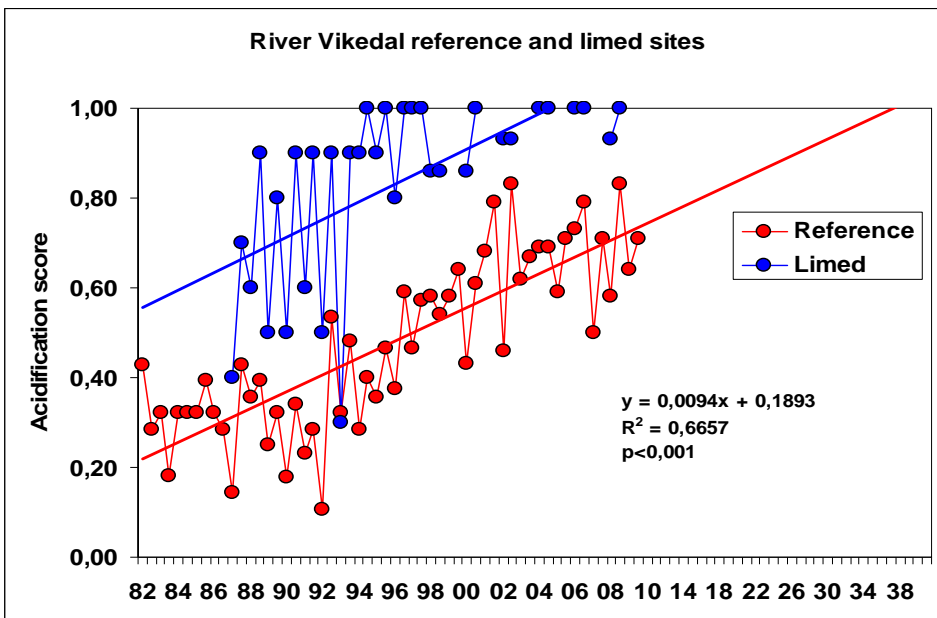
### River Vikedal – an example of recovery of biodiversity in a formerly strongly acidified river

The upper part of River Vikedal, which is unlimed, has been monitored since 1982. Due to reduced amount of pollutants in the precipitation the pH in this part of the river has recovered considerably (Figure 4). This is especially evident for the last two decades.



**Figure 4.** pH in the River Vikedal (main river – unlimed section) during 1982 to 2009.

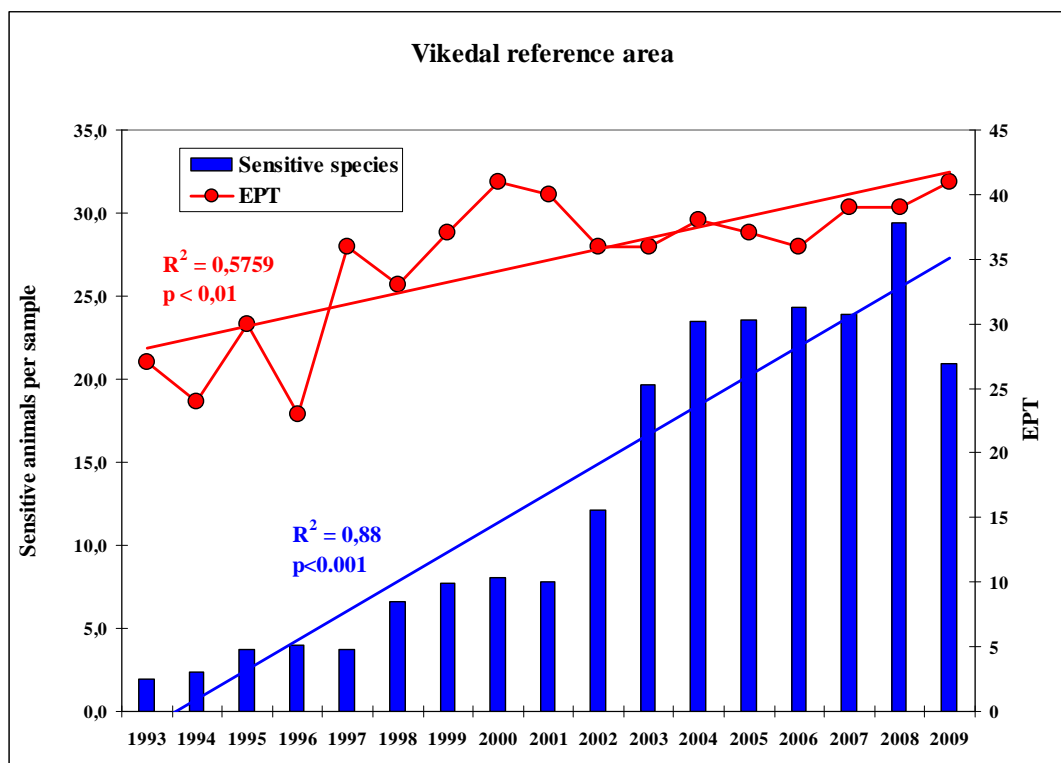
Regular monitoring of benthic invertebrates has been performed bi-annually both in the limed (since 1987) and upper, unlimed section of the watershed. The results show that the acidification score improved significantly (Figure 5).



**Figure 5.** Mean acidification scores in the limed and unlimed River Vikedal during 1982 to 2009. The regression shows that the unlimed section is not yet recovered. Recovery endpoint depends on the future nature of succession.

This acidification score is reflected by a considerable proportion of sensitive animals colonising the less acidified sites, resulting in increased biodiversity. This is illustrated in Figure 6, which shows

significant increases in both EPT diversity and an increase in the number of acid-sensitive animals in this part of the watershed. These results demonstrate that besides the qualitative response there is also a strong quantitative response in the benthic community.

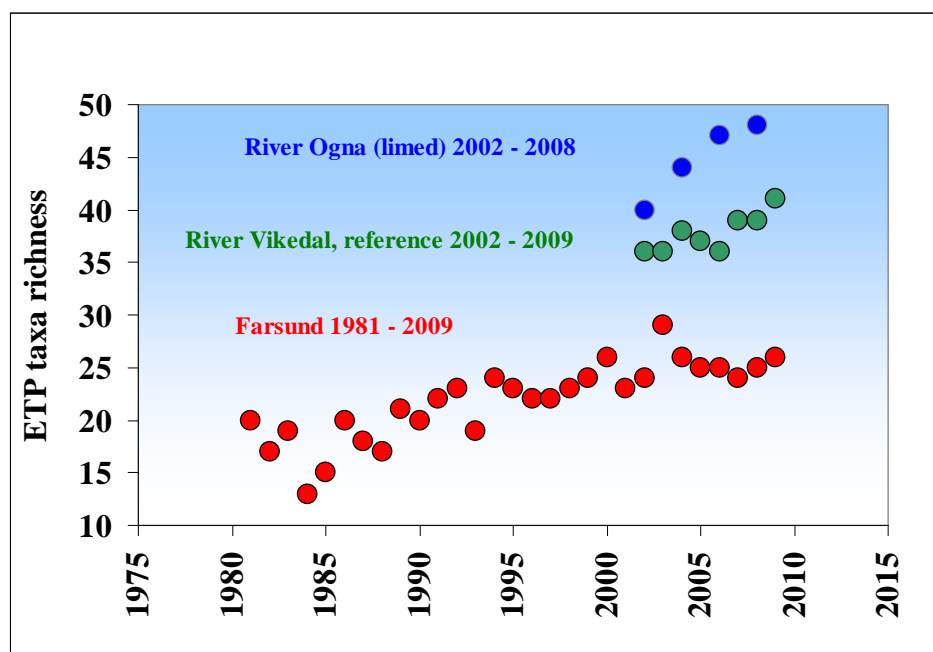


**Figure 6.** EPT index in the unlimed River Vikedal during 1993 to 2009. The figure also presents mean number of acid-sensitive benthic animals per sample.



### Is it possible to predict the endpoint of biological recovery?

Data from three watersheds, Farsund, Vikedal and Oгна demonstrates differences in biological diversity (Figure 7). The reason for this is partly differences in acidification, and in the case of Farsund, differences in catchment size and complexity.



*Figure 7. ETP species richness in three south-western Norwegian watersheds.*

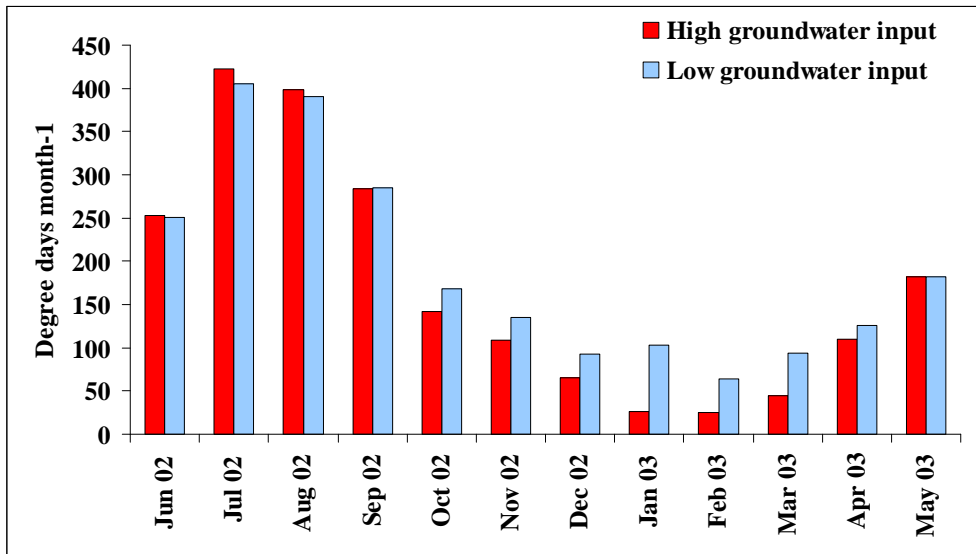
River Oгна is monitored every two years, while the other two are monitored each year. River Oгна, which has the same size as River Vikedal, is a more complex watershed. Some parts of the catchment are well buffered. The monitoring data from Oгна show that the diversity of EPT-species is still increasing. The same is true for River Vikedal. We expect that the diversity of River Vikedal gradually will be more like River Oгна. Our own data demonstrates that it is difficult to predict an endpoint of recovery. There are several reasons for this. Generally it is difficult to find natural reference areas, as large areas are affected by the pollution. Additionally, acid “setbacks” are still occurring (acidic episodes, sea salt storms etc.). Due to the dynamic nature of the invertebrate community, biodiversity is not an exact number of species. There will always be succession processes going on, changing the number of species over time.

### Climate change – effects on the freshwater fauna

Climate change is a relatively new issue in the science of freshwater biology. A search in literature bases shows that the number of papers dealing with climate change and freshwater has increased by 600 times per year during the last 50 years. Most of the information has been given during the last 20 years. A reason for this is formerly low awareness of the problem. Another is that the technology of recording water temperature has improved considerably during this period.

Effects of temperature change on benthic invertebrates may either be direct, induced by physiological response to the changed environment or indirect, for example as a consequence of changes in the flora or fauna. In the following I will give an example of how changed temperature may influence freshwater animals.

The example is taken from a case-study in the regulated River Aurland (Fjellheim and Raddum 2008). Due to transfer of water to the power station, a section of the river got a considerable reduced discharge. One locality of this stretch receives considerable amounts of groundwater. This water is warmer than the surface-water during winter (Figure 8).

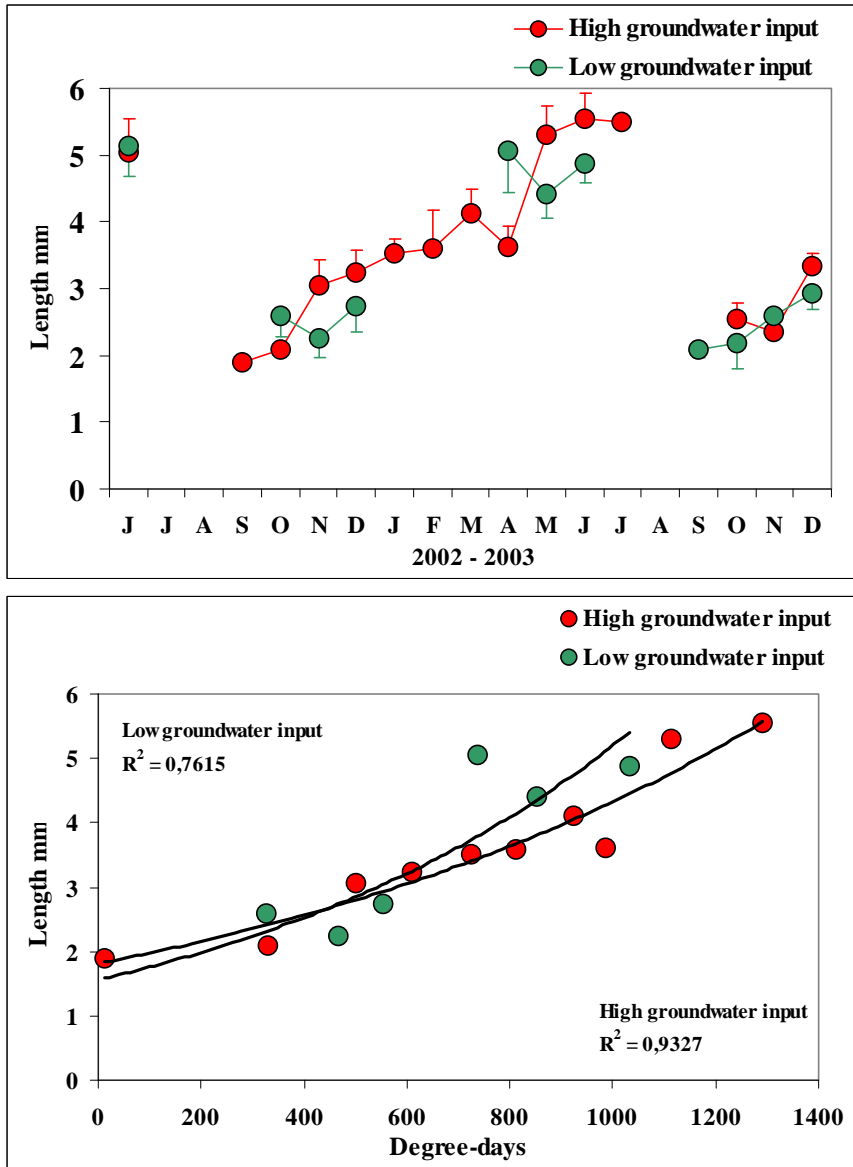


**Figure 8.** Mean accumulated degree-days at two closely situated localities in the regulated river Aurland during 2002 – 2003.

The reduced discharge amplifies the differences in temperature between the groundwater and the surface water at the station with high groundwater input. In January the mean number of degree-days in the groundwater-influenced section was four times that of the section only affected by surface-water. The differences were greatest in winter, while the summer-temperature was slightly lower due to colder groundwater compared to the surface water.

The influence of temperature on growth and life cycle of invertebrate species were studied at the two localities. As an example, the growth of the stonefly *Amphinemura sulcicollis* is shown in Figure 9. This species grew significantly faster in the area subjected to groundwater input compared to the area influenced by surface water. Other examples are given by Fjellheim and Raddum (2008) and Raddum et al.(2008).

The life-cycle studies in River Aurland showed that the growth and biological responses to changed temperature were species-specific. A summary of the responses of common EPT-taxa is given in Table 1. Generally the individual growth of a species was correlated to the water temperature. An exception was found in the caddisfly *Rhyacophila nubila* (Figure 10). This species is univoltine, but has a complex life-cycle resulting in the presence of several instars (life-stages) at the same time. The size of the instars varies through the year, indicating that temperature plays an important role in the life-cycle of this predatory caddisfly (Fjellheim 1976).



**Figure 9.** The growth of the stonefly *Amphinemura sulcicollis* in two localities subjected to different groundwater input in the regulated River Aurland, Norway (upper panel) and growth of the same species correlated to accumulated temperature (lower panel), after Fjellheim and Raddum (2008).



Figure 10. The caddisfly *Rhyacophila nubila*. Photo A. Fjellheim.

**Table 1.** Summary of the life cycle characteristics of common EPT taxa in a study of temperature effects on benthic invertebrates in two closely situated localities with different input of groundwater in the regulated River Aurland (after Fjellheim and Raddum (2008)).

Family	Species	Growth type	Life cycle length	Main growth period	Pearson correlation Mean individual size vs.	
					Low groundwater	High groundwater
Ephemeroptera	<i>Ephemerella aurivillii</i>	synchronous	univoltine	autumn	p<0,001	p<0,001
Ephemeroptera	<i>Ameletus inopinatus</i>	synchronous	univoltine	winter	p<0,001	p<0,05
Ephemeroptera	<i>Baetis rhodani</i>	asynchronous	univoltine (bivoltine)	summer	p<0,01	p<0,01
Plecoptera	<i>Amphinemura borealis</i>	synchronous	univoltine	spring	p<0,01	p<0,01
Plecoptera	<i>Amphinemura sulciollis</i>	synchronous	univoltine	winter/spring	p<0,001	p<0,05
Plecoptera	<i>Protonemura meyeri</i>	synchronous	univoltine	winter/spring	p<0,001	p<0,001
Plecoptera	<i>Leuctra fusca</i>	synchronous	univoltine	spring/summer	p<0,001	NS
Plecoptera	<i>Leuctra hippopus</i>	synchronous	univoltine	autumn	p<0,001	p<0,001
Trichoptera	<i>Apatania sp.</i>	synchronous	univoltine	winter/spring	p<0,001	p<0,05
Trichoptera	<i>Rhyacophila nubila</i>	asynchronous	univoltine?	variable	NS	NS

Invertebrates may respond to thermal changes in different ways: 1). By extinction 2). By immigration, 3). By adapting to the new situation through ecological changes within the existing population, for example through quantitative changes and changed life cycle pattern. The latter may involve changes within the length of the different life cycle stages and in extreme cases, changes in voltinism. The thermal demands of the aquatic part of the life cycle will be the accumulated temperature needed to

fulfil the egg and the larval stage. The species presented in Table 1 all managed to complete their life cycle within the annual number of degree-days measured at the two localities (2300 and 2060). Most of the species studied also managed to stay univoltine in colder regime of 1500 degree-days prior to regulation (Fjellheim and Raddum 2008). Examples of extinction were found in the two stonefly species *Nemurella pictetii* and *Leuctra nigra*, both being present in the river before the regulation (Larsen 1968). A possible explanation for the disappearance of these species may be difficulties to shift from a semivoltine mode of life in the colder temperature regime (1500 degree-days, low summer temperature) to the new temperature conditions (>2000 degree-days, higher summer temperature), probably leading to a life-cycle length between one and two years.

An example of positive response in the form of immigration was found in the mayfly *Ephemerella aurivillii*. This species was not recorded in the localities prior to regulation, while it was abundant after. The species needed more than 1500 degree-days to complete its life cycle, a condition not present before regulation (Raddum and Fjellheim 2006). The study of the invertebrates in River Aurland demonstrates the usefulness of linking life cycle data close to temperature data. The thermal demands of the different species are vital in explaining faunistic changes induced by a changed environment.

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## 7. Time trends of trace metals in Swedish streams

*Brian Huser, Jens Fölster and Stephan Köhler*

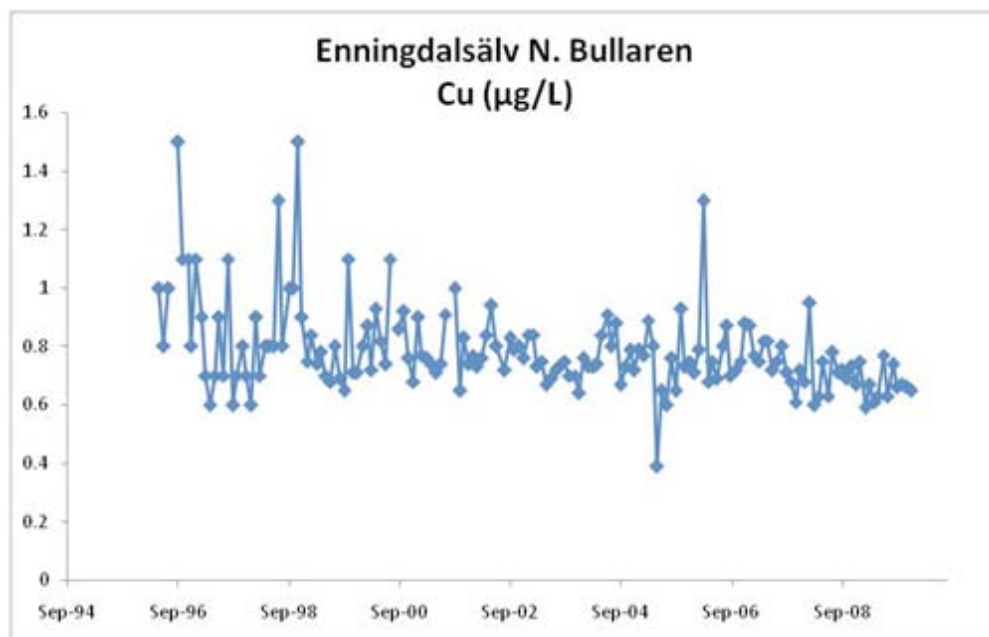
*Dep. of Aquatic Sciences and Assessment. Swedish University of Agricultural Science, Sweden*

The streams included in this study are situated throughout Sweden (Figure 1) and the data time series ranged from 1996 through 2009. Data analyzed include total concentrations of trace metals arsenic (As), copper (Cu), cobalt (Co), chromium (Cr), nickel (Ni), lead (Webster, Soranno et al.), zinc (Zn), and vanadium (V). Other parameters analyzed included Fe, pH, sulphate ( $\text{SO}_4^{2-}$ ), and total organic carbon (TOC). Only monitoring sites that were not influenced by point sources (e.g. wastewater treatment plants, mining facilities, industrial plants, etc.) were included in the analysis. From these sites, streams that had a minimum of 8 years of data (with sampling occurring monthly) were selected and included in the final group, resulting in a final data set including 139 streams (Figure 1). Since the concentrations of trace metals in those natural waters are usually low and close to the detection limits, the risk for contamination is high. In this study we excluded outliers, defined as concentrations double as high as any other observation in each time series with a filtered versus unfiltered absorbance for the sample that did not indicate elevated particulates, meaning the sample was likely contaminated. A decrease over time in number of outliers indicated that data quality has improved over time.

All parameter concentrations analyzed in the study were higher (medians) when comparing southern to northern Sweden. In contrast to depositional patterns over Europe (Harmens et al. 2008) and in particular Sweden (Ruhling and Tyler 2004), a substantial portion of the trends were positive, especially for V, As, and Pb. Other metals (Zn and Cr) generally decreased over the time period of the study, were mixed (Ni and Zn), or had very few trends (Co). Trends by region were also analyzed and some showed significant variation between the north and south of Sweden (Cu and Pb). An example of one of the long-term data series sties is shown in Figure 2. Additional results will be detailed in an upcoming publication.



**Figure 1.** All stream monitoring locations for this study with the *limes norrlandicus* boundary separating the southern and northern regions of Sweden.



*Figure 2. Long term data series for Cu (ug/L) in Enningdalsälven, 1996-2009.*

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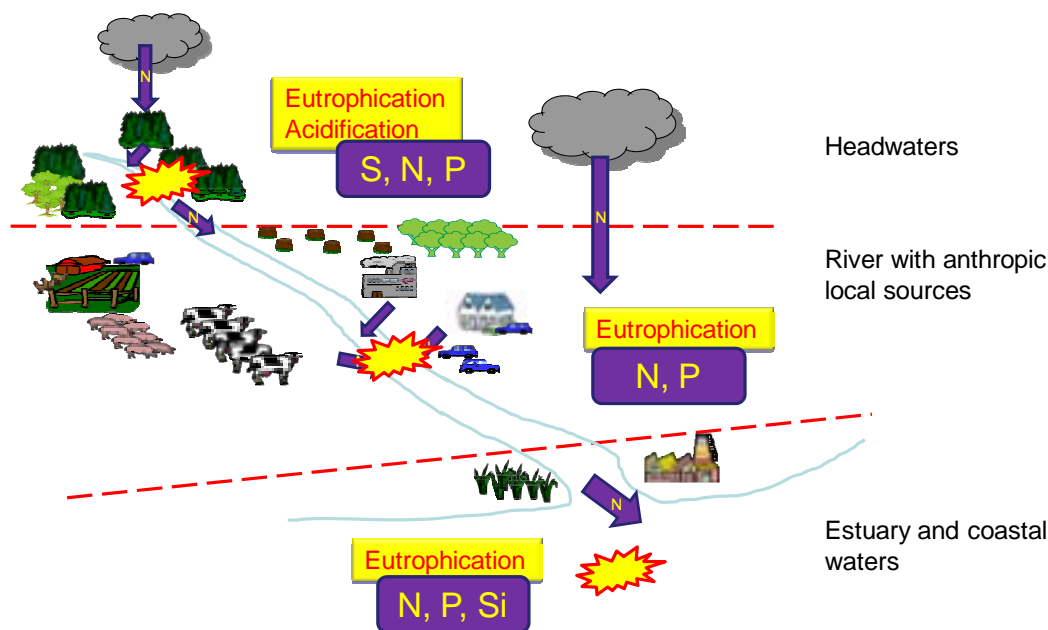
## 8. Project proposal: Calculation of nitrogen critical loads in rivers

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*INERIS France*

The overall objective of the present proposal is to develop a method for the calculation of critical loads for nutrient nitrogen in waters. With this tool, it is aimed at evaluating the relative importance of atmospheric deposition, urban, industrial and agricultural nitrogen inputs on river water quality. It is also aimed at comparing the relative impacts of nitrogen deposition on aquatic and terrestrial ecosystems. Thus, the results of the calculation may be used as a decision support for watershed environmental managers.

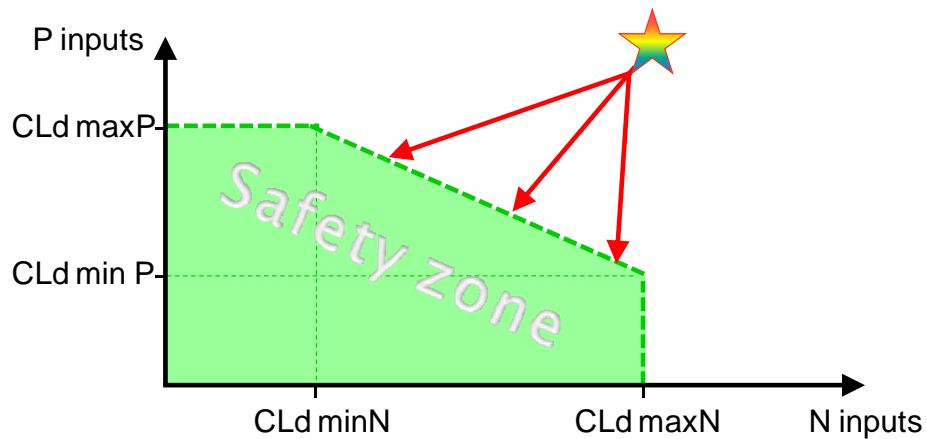
The method is to be based on existing knowledge and know-how. One major particularity of the approach is to consider the impact of pollution over the whole watershed, from source to coastal waters. The processes that will be considered are acidification and eutrophication, as both are partly caused by nitrogen. This however implies that other elements than nitrogen will be considered: Sulphur for acidification, phosphorous for eutrophication in freshwaters, and phosphorous and silica in marine waters. Sources of pollutants will be atmospheric deposition, urban, industrial and agriculture inputs. Figure 1 illustrates the major impacts and sources considered.



**Figure 1:** Pollution sources and their impacts in a watershed to be considered while developing a tool to calculate nitrogen critical loads in a rivershed.

One important step of this project will be to propose critical limits for the different parts of the watershed. It is proposed that eutrophication dose-response relationships will be used. These will be functions of phosphorous, nitrogen and, in seawater, silica. One possible approach is to base these functions on nutrients ratios (Vollenweider in freshwaters, Redfield in seawater). Maximum acceptable concentrations for each individual nutrient shall as well be considered. Thus an approach similar to that followed for acidification critical loads functions can be established as illustrated by Figure 2.





**Figure 2:** Schematic presentation of a critical load function for eutrophication in riverwater. Any inputs above the dash line are above the tolerable levels for the ecosystems. The star represents an hypothetical input scenario, the arrows possible options to decrease the inputs to acceptable levels (adapted from acidification critical loads function Posch et al., 2001).

This project is being led by INERIS (France) and partly funded by ONEMA (office national de l'eau et des milieux aquatiques, France). It is expected that it may develop through international collaborations.

**Reference:**

Posch, M., De Smet, P. A. M., Hettelingh, J. P., and Downing, R. J., eds. (2001). Calculation and mapping of critical thresholds in Europe. Status report 2001, pp. 1-188. RIVM, Bilthoven, the Netherlands.

## 9. Chemical monitoring of sediment and biota under the WFD needs signals from headwaters

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### Scope and the legal background

There is an inherent and obvious difference in hydromorphology between Central European river systems and Nordic or Alpine lake districts. The Water Framework Directive (WFD) of EU is designed mostly to the first type of landscape and to local sources of pollution. This has been clearly reflected in the whole structure and scope of the WFD. During the development of monitoring objectives and principles, sediment and biota was largely "pending" until established expertise from marine conventions was consulted. On general level, links between WFD and CLRTAP objectives and monitoring has been discussed earlier within the ICP Waters (Wathne *et al.* 2009).

Environmental Quality Standards (EQS) at EU level have now been established for over 30 substances, but they are mostly limited to concentrations in the water column (Directive 2008/105/EC). Only Hg, HCB and HCBd (hexachlorobutadiene) have EQS in biota, based on protection against secondary poisoning of predators. Member States do have the possibility to establish EQS for the other substances in sediment and/or biota at national level and apply such EQS instead of the EQS for water.

Sediment and biota are important matrices for the monitoring of substances with significant potential for accumulation. In order to assess long-term impacts of anthropogenic activity and trends, Member States should take measures, subject to Article 3(3) of the EQS Directive, with the aim of ensuring that existing levels of contamination in biota and sediment will not significantly increase. This is the point where headwater lakes and other lakes with good sedimentation conditions come into the picture:

- To assess long-term changes in natural conditions and to assess the long term changes resulting from widespread anthropogenic activity.
- To assess compliance with the "no deterioration objective" (concentrations of substances are below detection limits, declining or stable and there is no obvious risk of increase) of the WFD.
- To monitor the progressive reduction in the contamination of priority substances (PS) and phasing out of Priority Hazardous Substances (PHS)

To this end, sediments are suitable for revealing past recent history of contaminants whereas biota is proper matrix to follow up the development of contamination. Both have time integrating and "smoothing" tendency, which is a cost effective aspect. This contribution focuses especially on sediments as a case study example presented in the Guidance n:o 25 of WFD on sediment and biota monitoring (EC 2010).

### Short cores - cost effective monitoring of sediments

The concept is based on short sediment core sampling (ca. 10 to 30 cm), checking the recent history of especially priority hazardous substances with high affinity to particle phase such as HCHs, HCB, HCBd, Hg, PAHs, PBDE and TBT. This is useful (background) information for the assessment purposes already in the first phase of WFD (before 2015). The method is well applicable to many of the candidate substances such as PCB, PCDD/F, HCBDD and heptachlor/-epoxide, for which the Commission is expected to propose also EQS in biota in 2011.

In the past, sediments of many polluted lakes have been dated using radiochronology. Sediment dating is very much site (and core) specific, but the general picture is possible to reveal for substances with little degradation/diagenesis in the sediment and long history in use/emissions and later in regulation (PAHs, most OCPs, metals, TBT, PBDE). This has been demonstrated widely for e.g. Pb, Hg, PCB and PCDD/F in similar studies in Boreal and Alpine European lakes as well as in North America and Arctic regions (e.g. Mannio 2001, Usenko *et al.* 2007). The accumulation conditions in (well selected) lakes are not as difficult to interpret as in marine systems.

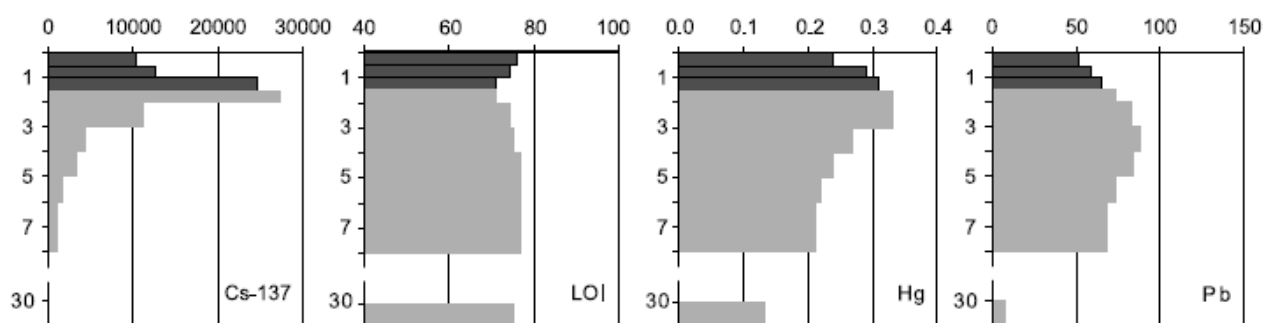


Figure 1. Trace element concentrations ( $\mu\text{g g}^{-1}$  dry weight),  $^{137}\text{Cs}$  activity ( $\text{Bq kg}^{-1}$  dw.) and organic matter (LOI, loss on ignition, %) in recent sediments of Lake Valkea-Kotinen. The dark area represents recent sedimentation after 1986, based on  $^{137}\text{Cs}$  dating. The continuous stratigraphy (0–8 cm) represents ca. 50 years. The lower reference layer (30–31 cm) represents pre-industrial background (from Mannio 2001).

Short core sediment monitoring/survey aims to look at the recent history (<30-40 yrs) of contaminants. The top of the sediment is sliced to e.g. 3-6 slices (a' 0.5-3 cm) and one reference slice from deeper sediment layers (> 20cm) depending on the sedimentation rate. With some expert judgment, local knowledge and caution, this can be done without radiochronology.

There is good knowledge on the typical sedimentation rate in Nordic lakes from tens-hundreds of lakes, sampled e.g. for Hg surveys (e.g. Munthe *et al.* 2007). The sedimentation rate in these lakes can be from 0.5-2.0 mm/yr to more than 10 mm/yr. Sedimentation is not, however, several centimeters per year. These lakes represent a very significant portion of the whole lake population in Europe.

In comparison to a grab or single sample of sediment surface, slicing the sediment reveals the relative timescale of the subsequent samples. Analysing only one top layer does not reveal any timeframe, only the present status of the sediment, at least on the first sampling occasion.

The concept works only for certain types of environment like lake deeps with relatively well known sedimentation rate and little influence of water currents. The technique is also applicable to sheltered coastal conditions at least in the Baltic Sea.

### Biota monitoring - fish

After analysing "trend" of ca. 5 slices (with 2-3 replicates and perhaps pooling), one can shift to biota (fish) monitoring to follow the exposure to, possible effects and future changes (1-3 yr frequency) of the same contaminants. In WFD Guidance perch (*P. fluviatilis*, L.) Arctic char (*Salvelinus sp.*) and brown trout (*Salmo trutta*, L.) are presently the main suggested species in Nordic countries/Alpine regions, but harmonisation is still ongoing regarding species, size, number of individuals and pooling of samples. ICP Waters Manual (draft 2010) could be one option to suggest further details in method harmonisation.

## Recommendations

Short core sediments can provide information, which is not possible to gain with other WFD matrices. Retrospective analysis of cores is invaluable information of the effectiveness of the past control policies for Priority Hazardous Substances and other strongly controlled PBT/vPvB substances (Persistent, Bioaccumulative, Toxic). Regionally coherent sediment data can be compiled for larger geographical assessments and status reports.

The strategy to combine sediment and fish monitoring is best applicable to surveillance and investigative monitoring, but should work even for impact monitoring in many River Basin Districts. Results should be made available in national data banks and utilized in both WFD and ICP Waters status reporting and in scientific assessments.

Experts of the ICP Waters community are welcomed to spread this information in their country to enhance the knowledge of cost-effective methods to monitor long-term changes of PBT substances.

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## Annex II Agenda

# Agenda for the 26<sup>th</sup> Task Force ICP Waters October 4.-6. 2010, Helsinki, Finland

### 1. Introductions

- Meeting welcome, *Laura Höijer, Research Director, Ministry of the Environment, Finland*
- Adoption of the agenda, *Berit Kvaeven, ICP Waters Chairperson*
- General information about the meeting and excursion, *Jussi Vuorenmaa, Finnish Environment Institute, Finland*
- *WFD-monitoring of lakes in Finland, Sari Mitikka, Finnish Environment Institute, Finland*
- Reports from the Executive Body, Working Group on Effects and work undertaken by the Bureau of Working Group on Effects, *NN*
- Reports from other ICPs, *ICP IM: Sirpa Kleemola, Finnish Environment Institute, Finland, Anne Christine LeGall, ICP Modelling and Mapping*

### 2. Reports from the ICP Waters Programme activities 2009/2010

- Status of the ICP Waters programme, *Brit Lisa Skjelkvåle, Programme centre*

### 3. Water chemistry

- Presentation of the draft trends-report, *Øyvind Garmo, Programme centre*
- Water chemical effects in Norway from volcanic eruptions at Iceland in April 2010, *Brit Lisa Skjelkvåle, Programme Centre*

### 4. Biological response

- Recovery of acidified lakes in Finland and subsequent responses of perch and roach populations, *Martti Rask, Finnish Game and Fisheries Research Institute, Finland*
- Biodiversity - effects of air pollution and climate change, *Arne Fjellheim, Programme subcentre*

### 5. Heavy metals and POPs

- Hg in fish, *Matti Verta, Finland*
- Short stories and long time trends of trace metals, *Brian Huser, Sweden*

### 6. Presentation of the N-report

- Nutrient enrichment effects of atmospheric N deposition on biology in oligotrophic surface waters – a review, *Heleen de Wit, Programme centre*

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## 7. Dynamic modelling / Critical Loads

- Ex post analysis – report from the ongoing work, *Jean-Paul Hetteling, CCE (Coordination Centre for Effects)*
- *Discussion on contribution from ICP Waters*
- Nitrogen critical load in watersheds – suggestion for a new project, *Anne Christine Le Gall, ICP Modelling and Mapping*

## 8. ICP Waters and EU-directives (WFD Water Framework Directive, NEC National Ceiling Emission Directive)

- Guidance on Chemical Monitoring of Sediment and Biota under the WFD, *Jaakko Mannio, Finnish Environment Institute, Finland*

## 9. Common work for all effect-oriented programmes

- (i) Targets and ex-post application
- (ii) Robustness
- (iii) Links with biodiversity
- (iv) Trends in selected monitored/modelled parameter

*Brit Lisa Skjelkvåle, Programme centre*

## 10. Revision of the programme manual

- The 2010 ICP Waters Programme Manual, *Bente Wathne, Programme centre*

## 11. Intercalibration/intercomparison

- Chemical intercomparison, *Bente Wathne, Programme centre*
- Biological intercalibration, *Arne Fjellheim, Programme subcentre*

## 12. Workplan

- Draft 2011 Workplan, *Programme centre*

## 13. Other Business

- TF meeting 2011

## 14. Adoption of the minutes

## Time schedule

### Monday 4 October

- 8.00 - 9.00 Registration  
9.00 - 12.00 Task Force meeting (*item 1-2*)  
12.00 - 13.30 Lunch  
13.30 - 18.00 Task Force meeting including coffee breaks (*item 3 – 7*)

Coffee break 10.30-11 and 15.30-16.00 **OK**

### Tuesday 5 October

- 09.00 - 12.00 Task Force meeting including coffee break (*item 8 -10*)  
12.00 - 13.00 Lunch  
13.00 – 23.00? Excursion including Task Force dinner

Coffee break 10.30-11.00

### Wednesday 7 October

- 09.00 - 12.00 Task Force meeting including coffee break (*item 11 – 15*)  
12.00 - 13.00 Lunch

Coffee break 10.30-11.00

## Documents to be presented and discussed at the meeting – can be downloaded from <http://www.icp-waters.no/>

- **ICPW 99/09:** Biological intercalibration
- **ICPW 100/10:** Proceedings from the 25th Task Force meeting
- **ICPW 101/10:** Nutrient enrichment effects of atmospheric N deposition on biology in oligotrophic surface waters – a review
- **ICP W 102/10:** Chemical intercomparison 0923
- The draft ICP Waters manual
- Draft trends report

## Information for the excursion

An excursion is planned that will include:

- By ferry to Suomenlinna, and a guided tour there, including visit to Suomenlinna Museum.
- Task Force dinner in a Myllysali banquet hall 17:30 – 23:00

## Reports and publications from the ICP-Waters Programme

All reports from the ICP Waters programme from 1987 up to present are listed below. All reports are available from the Programme Centre. Reports and recent publications are also accessible through the ICP-Waters website; <http://www.icp-waters.no/>

- 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.
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- 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.**
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- Norwegian Institute for Water Research, 1990. Data Report 1988. Programme Centre, NIVA, Oslo.
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- Proceedings for the 5th Meeting of the Programme Task Force Freiburg, Germany, October 17 -19, 1989. Prepared by the Umweltbundesamt, Berlin July 1990.
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- Norwegian Institute for Water Research, 1991. Summary of The Three Year Report 1987 – 1989. Programme Centre, NIVA, Oslo.
- Scientific papers presented at the Sixth Task Force meeting in Sweden 23 - 24 October 1990. Swedish Environmental Protection Agency, Sweden, September 1991.
- Seventh Task Force meeting of international Co-operative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes. Galway, Ireland. September 30 - October 3 1991. Proceedings.
- Johannessen, M., Skjelkvåle, B.L. and Jeffries, D. 1992. International cooperative Programme on Assessment and Monitoring of Rivers and Lakes. In: Conference Abstracts, Intern. Conference on Acidic Deposition, Glasgow 16-21, sept. 1992, p. 449. Kluwer Academic Press.
- Hovind, H. 1992. Intercalibration 9206: 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, Al and DOC. Programme Centre, NIVA, Oslo. **NIVA-Report 2784-92.**
- Norwegian Institute for Water Research, 1992. Data Report 1990. Programme Centre, NIVA, Oslo.
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- Hovind, H. 1993. Intercalibration 9307: 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, total aluminium, reactive and non-labile aluminium, TOC and COD-Mn. Programme Centre, NIVA, Oslo. **NIVA-Report 2948-93.**
- Raddum, G.G. 1993. Intercalibration of Invertebrate Fauna 9301. Programme Centre, NIVA, Oslo. **NIVA-Report SNO 2952-93.**
- Proceedings of the 9th Task Force Meeting in Oisterwijk, the Netherlands, November 1-3, 1993. Programme Centre, NIVA, Oslo.
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