

**FINAL REPORT 4/1999**

March 1996 - March 1999

Measuring and modelling  
the dynamic response of  
remote mountain lake ecosystems  
to environmental change:

A programme of **Mo**untain **La**ke **Re**search

**MOLAR**

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<b>Main Office</b>	<b>Regional Office, Sørlandet</b>	<b>Regional Office, Østlandet</b>	<b>Regional Office, Vestlandet</b>	<b>Akvaplan-NIVA A/S</b>
P.O. Box 173, Kjelsås N-0411 Oslo Norway Phone (47) 22 18 51 00 Telefax (47) 22 18 52 00	Televeien 1 N-4890 Grimstad Norway Phone (47) 37 29 50 55 Telefax (47) 37 04 45 13	Sandvikaveien 41 N-2312 Ottestad Norway Phone (47) 62 57 64 00 Telefax (47) 62 57 66 53	Nordnesboder 5 N-5005 Bergen Norway Phone (47) 55 30 22 50 Telefax (47) 55 30 22 51	Søndre Tollbugate 3 N-9000 Tromsø Norway Phone (47) 77 68 52 80 Telefax (47) 77 68 05 09

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**Abstract**

MOLAR (Measuring and modelling the dynamic response of remote mountain lake ecosystems to environmental change: A programme of Mountain Lake Research – MOLAR) is an extensive European co-operative research project with 23 partners. It is funded within the European Commission Framework Programme IV: Environment and Climate with assistance from INCO. It is co-ordinated by the Environmental Change Research Centre (ECRC) at University College London (UCL) and the Norwegian Institute for Water Research (NIVA). The project has four major strands also called Work Packages, and the final results from each of the Work Packages (WP) are reported here. Appendix A shows the publications from the total project activities, and Appendix B separate reports from all partners

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Bente M. Wathne  
Project manager

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Merete Johannessen Ulstein  
Research Director

**ENVIRONMENT & CLIMATE RESEARCH PROGRAMME (1994-1998)**  
**FINAL SUMMARY REPORT**  
**MOLAR Report 4/1999**

**March 1996 - March 1999**

**Contract no.: ENV4-CT95-0007 / IC20-CT96-0021**

**Measuring and modelling the dynamic response of  
remote mountain lake ecosystems to environmental  
change:**

**A programme of Mountain Lake Research -  
MOLAR**

**MOLAR co-operative partners:**

01	University College London, UK ( <i>administrative coordinator</i> )	(UCL)
02	University of Helsinki, SF	(UHEL)
03	University of Edinburgh, UK	(UED)
04	Norwegian Institute for Water Research, N ( <i>scientific coordinator</i> )	(NIVA)
05	Universität Innsbruck, Institut für Zoologie und Limnologie A	(UIBK)
06	Austrian Academy of Sciences, Limnological Institute, A	(ILIMNOL)
07	Universidad de Barcelona, ES	(UBCN.DE)
08	Universidad de Granada, ES	(UGR-ES)
09	University of Bordeaux (URA CNRS), Arcachon, F	(CNRS)
10	Consejo Superior De Investigaciones Cientificas, Barcelona, ES	(CSIC)
11	University of Bergen, Botanical Institute, N	(UIB-BI)
12	University of Bergen, Institute of Zoology, N	(UIB-ZI)
13	CNR-Istituto Italiano di Idrobiologia, Pallanza, I	(CNR-III)
14	University of Liverpool, UK	(ULIV)
15	Institute for Environmental Science and Technology, Dubendorf, CH	(EAWAG)
16	University of Zurich, CH	(UZurich)
17	Charles University, Prag, Czech Republic	(FSCU)
18	Hydrobiological Institute, Ceske Budejovice, Czech Republic	(HBI-ASCR)
19	Institute of Zoology, Bratislava, Slovak Republic	(IZ-SAS)
20	Polish Academy of Sciences, Institute of Freshwater Biology, Kracow, PL	(IFB-PAS)
21	National Institute of Biology, Ljubljana, Slovenia	(NIB)
22	Kola Science Centre, Apatite, Russia.	(INEP)
23	Laboratorio Studi Ambientali, Sezione Aria e Acqua, Ticino, CH	(LSA)

## Preface

MOLAR is an extensive European research project with 23 co-operative partners. It is funded within the European Commission Framework Programme IV: Environment and Climate with assistance from INCO. MOLAR builds on the success of the EU funded AL:PE projects.

MOLAR was launched March 1st 1996, and the first project meeting was held two weeks later in Prague, Czech Republic. Annual project meetings have been held in Barcelona, Spain in March 1997, in Bled, Slovenia in March 1998 and in Arcachon, France in February 1999.

For wide spread information MOLAR has a home page on Internet (<http://prfdec.natur.cuni.cz/hydrobiology/molar/welcome/htm>).

The Final Report summarises the activities during the project period March 1<sup>st</sup> 1996 to March 1<sup>st</sup> 1999. Convenors for the four different parts (Work Packages) of the project have been responsible for reporting the results within each part.

Oslo, 16. August 2000.

*Bente M. Wathne and Bjørn Olav Rosseland*

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# Contents

<b>1. EXECUTIVE SUMMARY</b>	<b>6</b>
1.1 Background and general objectives	6
1.2 Mountain lake ecosystem response to acid deposition	6
1.3 Measuring and modelling major element and pollutant fluxes in mountain lakes and their impact on fish	10
1.4 Climate variability and ecosystem dynamics at remote alpine and arctic lakes	11
1.5 Integrating activities	12
1.6 Acknowledgements	12
<b>2. INTRODUCTION</b>	<b>13</b>
<b>3. GENERAL OBJECTIVES</b>	<b>14</b>
<b>4. SPECIFIC OBJECTIVES AND TASKS</b>	<b>15</b>
4.1 MOLAR Work Package 1 (WP1)	17
4.2 MOLAR Work Package 2 (WP2)	18
4.3 MOLAR Work Package 3 (WP3)	18
4.4 MOLAR Work Package 4 (WP 4)	19
<b>5. MAIN RESULTS AND CONCLUSIONS</b>	<b>21</b>
5.1 MOLAR Work Package 1 (WP1)	21
5.1.1 Atmospheric Deposition - on site measurements of sulphur and nitrogen	21
5.1.2 Seasonal variability of Water chemistry	23
5.1.3 Seasonal variability of benthic fauna	28
5.1.4 Test hypothesis: histological and physiological attributes of fish indicate early acid stress	32
5.1.5 Test hypothesis: microbial activity in pelagic food web increases with acidification intensity	35
5.1.6 Evaluate applicability of various critical load models to mountain lake ecosystems, and develop a linked chemical-biological model for scenario assessment	40
5.1.7 Application of static critical loads models to high mountain lakes, and assessment of their applicability for critical load and linked chemical-biological modelling	41
5.2 MOLAR Work Package 2 (WP2)	52
5.2.1 Spheroidal carbonaceous particles, SCP	57
5.2.2 Radionuclides	59
5.2.3 Persistent organic pollutants in air, water, sediments and fish	60
5.2.4 Metals in precipitation, lake water, sediments and fish	61

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<b>5.3 MOLAR Work Package 3 (WP3)</b>	<b>64</b>
5.3.1 Introduction	64
5.3.2 Sites selected	64
5.3.3 Objectives and results	65
5.3.4 Conclusions	67
<b>5.4 MOLAR Work Package 4 (WP 4)</b>	<b>67</b>
5.4.1 Specific objectives	67
<b>6. REFERENCES</b>	<b>70</b>
<b>Appendix A</b>	<b>74</b>
<b>Appendix B</b>	<b>83</b>

# 1. Executive Summary

## 1.1 Background and general objectives

MOLAR is an extensive European co-operative research project with 23 partners. It is funded within the European Commission Framework Programme IV: Environment and Climate with assistance from INCO (ENV4-CT95-0007/IC20-CT96-0021.) It is co-ordinated by research groups in London and Oslo.

The arctic and alpine regions of Europe represent the most remote and least disturbed environments in this part of the world, yet they are threatened by acid deposition, toxic air pollutants and by climate change. The remote lakes that occur throughout these regions are especially vulnerable for a number of related reasons; a) most have little ability to neutralise acidity; b) their catchments have little soil and vegetation to prevent pollutants from reaching surface waters; c) toxic trace metals and trace organics accumulate in the food chain more easily in soft water d) some pollutants (e.g. volatile organics, mercury) accumulate progressively in cold regions; e) future climatic warming in Europe is predicted to be greatest in arctic-alpine regions. Because of this sensitivity, remote mountain lakes are not only vulnerable to environmental change, they are also excellent sensors of change and their sensitivity and high quality sediment records can be used to infer the speed, direction and biological impact of changing air quality and climate. Through the three EU Research projects AL:PE, AL:PE 2 and MOLAR, 24 lakes have been studied, many over several years. This MOLAR FINAL report summarises the results, emphasising on MOLAR activities.

The overall scientific evaluation and combination of the results are still under development, but in the following the main conclusions from each specific topic will be presented.

## 1.2 Mountain lake ecosystem response to acid deposition

### *Atmospheric Deposition – on site measurements of sulphur and nitrogen:*

Deposition and deposition chemistry have been measured at several sites throughout Europe. Values show a more marked yearly variation if compared with concentrations, mainly due to the different amounts of precipitation. The chemistry of atmospheric deposition collected in sites which are representative of remote areas in the whole of Europe, shows that the solutes present may be marine, terrigenous, and deriving from fuel-burning emissions and intensive stock-breeding. The acidity of the depositions depends on the contributions from each component, especially the terrigenous one and that deriving from anthropogenic emissions. The results show marked variability in acidity of deposition the different areas of Europe. The most impacted areas are found in central Europe (Tatra Mountains) and in some stations in the Alps. But even in areas like Scandinavia which is less affected by long-range transported air pollution, a gradient is clear from the southernmost station, Møsvatn, to Kårvatn, situated in the central part of Norway, the latter being less impacted than the southern one. Seasonal variations emerged as having great importance in determining the chemical composition of the water and linking. During winter, most of the deposition is in form of snow, so all the ionic load, including pollutants, is released in a very short space of time during snowmelt.

### *Seasonal variability of Water chemistry:*

All MOLAR lakes have been sampled for water chemistry, including major ions and nutrients. The ion concentrations have quite a wide range of variation, from very diluted to highly buffered waters. The majority of sites however, consists of sites that are acidic and sensitive to acidification with calcium concentrations below 100  $\mu\text{eq l}^{-1}$ . Of the total 23 lakes, 8 lakes have pH between 4.9 and 6.0. La Caldera (southern Spain), Jezero v Ledvici (Slovenia) and Hagelsee (Switzerland), included primarily

for their geographic location, are outliers with much higher pH and mean calcium concentrations than other MOLAR sites.

Sulphate values for the main control site, Øvre Neådalsvatn, in Norway, are very low, and represent the expected background concentration ( $< 15 \mu\text{eq l}^{-1}$ ) for this compound. Similar low values also occur in Cimera (Central Spain), and the Pyrenean sites, Etang d'Aube and L. Redo, whilst high values occur at most other sites, reflecting their geographical location in areas of high sulphur deposition and their catchment geology. As in the case of sulphate, nitrate values at the control lake Øvre Neådalsvatn represent background concentrations ( $< 5 \mu\text{eq l}^{-1}$ ), but also northernmost lakes in Norway, Finland and Russia and Cimera in Central Spain show low values. All other sites show concentrations above background, with the highest values in the Tatra Mountain lakes.

The most important event affecting water chemistry of these lakes is the snow melt, which in all the lakes causes a more or less sharp decrease in alkalinity, pH, calcium and major ion concentrations. The lake chemistry is largely determined by four factors: (1) atmospheric loads, (2) weathering processes, and (3) interaction with the vegetation in the watershed, scarce but not negligible, and (4) with the biology of the lake waters. The geological characteristics of many watersheds, made up largely of poorly soluble rocks, means that many of the considered lakes are sensitive to acidification, with some of them showing clear signs of alteration. The interaction between the vegetation cover of the watershed and the chemistry of the water is particularly important when determining nitrogen levels. In general, atmospheric nitrogen loads are high, so that nitrate is present in the water of many remote lakes in relatively high concentrations. This is particularly true with regard to the lakes in the Tatra Mountains, but also for those in the Alps. It is also striking how ammonium, which is present in significant quantities in atmospheric loads, disappears almost completely in surface waters. It is known that the uptake of ammonium from vegetation is a further source of acidity, and that the oxidation of ammonium to nitrate produces acidity.

#### ***Seasonal variability of Invertebrate fauna:***

The profundal datasets from European alpine lakes indicates homogeneity in the fauna over a latitudinal gradient. These profundal communities are, however, susceptible to anthropogenic influence, as demonstrated by historic changes in species composition in several AL:PE/MOLAR lakes. A test of environmental variables with forward selection, however, showed that only the altitude did contribute significantly to the ordination of the littoral data. This is explained by a strong contribution of zoogeographical factors that, besides environmental variables, are important explaining the distribution of freshwater biota in European mountain ranges.

A summary of the datasets from both AL:PE and MOLAR shows that the Pyrenean lake Redó and the Norwegian reference lake Øvre Neådalsvatn appeared to have the highest species richness, both with respect to total fauna, chironomids and total number of acid sensitive species. These lakes belong to areas of Europe least affected by long-range transported air pollution. The number of species increases from south to north on the Iberian Peninsula and no trend related to acidification of the lakes was evident. The diversity of most of the other lakes was generally low. Colonisation rates are low in such remote systems and this could account for the low species diversity as well as the absence of many species even though the water chemistry is suitable for their survival. Environmental factors are important in controlling the life cycle of the different taxa. The benthic freshwater fauna is highly dynamic, both with respect to seasonal variation and variations between years. Timing of the sampling is therefore important.

A negative correlation between number of species and altitude suggests that climate is an important factor regarding the distribution of freshwater invertebrates in mountain lakes. Several environmental factors are impacted by climate, of which length of ice-free season and the production of organic material in the catchments are very important. Remote freshwater ecosystems are expected to be valuable indicators of local and global temperature changes, especially since temperature changes and



corresponding effects upon the macrobenthic community is expected to be greatest in these environments.

***Fish as indicator of early acid stress:***

Test-fishing have been finalised in seven lakes, and organs from single fish were divided, and sent to different MOLAR specialist laboratories around Europe for analyses. All heavy metal analysis in kidney and liver, as well as mercury in muscle has been carried out, and isotopes of nitrogen ( $^{14}\text{N}/^{15}\text{N}$ ) and carbon ( $^{13}\text{C}/^{12}\text{C}$ ) in fish muscle have been analysed. Liver histology, blood plasma ions and liver enzyme activities have been analysed and measured and analysis of micro-organic pollutants in fish have been finalised.

When studying the ecology of remote mountain lakes and the role biotectors like fish can play as early warning of air born pollution and climate changes, a basic question is to understand how fish succeed to live in such extreme biotopes where low mineralisation is the first major stress. In fish blood (b), the main contributors of osmolarity are the Na and Cl ions. Consequently, natremia ([Na]b) and chloremia ([Cl]b) were measured and compared to reference data obtained in the same fish species living in more mineralised waters. The results show that brown trout can maintain a normal blood Na concentration ( $\geq 110 \text{ mmol}\cdot\text{L}^{-1}$ ) in waters where the mineral load is as low as  $\approx 4 \text{ mg}\cdot\text{L}^{-1}$  but that the blood Cl concentration starts to decrease below  $8\text{-}10 \text{ mg}\cdot\text{L}^{-1}$ . This [Cl]b response was not directly correlated to the concentrations of Na and Cl in the water (w) but dependent on [Ca]w. The present study demonstrates that for the brown trout, a minimal [Ca]w compatible with a sustainable life is at least  $0.38 \text{ mgCa}\cdot\text{L}^{-1}$  (the concentration in lake Aubé) and that [Cl]b can be taken as an indicator of stress in low mineralised waters. [Cl]w is the single ion which specifically stimulates the chloride cell proliferation. Together with the calcium, they play a key role in the strategy of adaptation of brown trout in low mineralised waters. When [Ca]w is higher than  $0.7 - 1.0 \text{ mgCa}\cdot\text{L}^{-1}$ , brown trout can maintain a normal chloremia even for [Cl]w as low as  $0.1 \text{ mgCl}\cdot\text{L}^{-1}$  ( $3 \mu\text{mol}\cdot\text{L}^{-1}$ , found in Gossenköllesee (Austria), a value which appears today as the lowest known water [Cl]w value compatible with fish life). Reduced plasmaion concentration in brown trout from lakes having higher [Ca]w and [Cl]w than the found threshold values, gives thus an indication of water quality stress.

***Microbial activity in pelagic food web in relation to acidification intensity:***

*Pelagic food webs 1<sup>st</sup> level* for the assessment of all components of the plankton biomass has been investigated in 12 lakes during two ice-free seasons (1996 and 1997) with some complementary data gathered in 1998. Preserved samples from all lakes were elaborated in 8 specialised labs and the database of organic carbon content in 7 components of pelagic biomass (bacteria, heterotrophic flagellates, ciliates, phytoplankton, picocyanobacteria, zooplankton small, zooplankton large) established. Species structure also was determined in several components: ciliates, phytoplankton and zooplankton. This dataset represents a unique complex survey on pelagic biota in remote lakes.

The share of microbes in pelagic food webs in lakes increases (both in the terms of biomass and activity) with increasing oligotrophication (lower P concentration). In terms of biomass, the main three components are bacteria, phytoplankton and zooplankton. Picocyanobacteria and protozoans are not significant in terms of biomass in most cases. If the acidification results in the extinction of zooplankton, the importance of microbial assemblages is more pronounced with increasing acidification. In acidified lakes with a scarce or no zooplankton, a higher total phosphorus concentration results in an increased ratio of autotrophic (phytoplankton) to heterotrophic microbial biomass. In a turbid lake (glacier inflow), the biomass was rather light limited than P limited. *Pelagic food webs 2<sup>nd</sup> level* for the assessment of primary production and exudation, bacterial production and elimination were investigated fully in 7 lakes and partly (without primary production) in two lakes.

In terms of carbon fluxes, the importance of microbial loop in pelagic food webs increases with oligotrophication. The lower primary production, the higher the EOC % (extracellular organic carbon production supply to bacteria). No direct relation to acidity was found. The extinction of zooplankton, which seems to be caused by acidification in Tatra Mts lakes, did not occur in the other lakes. With decreasing zooplankton, the importance of microbial loop increases. Primary production of phytoplankton (inorganic C assimilation, exudation to dissolved organic C pool and to bacteria) is the major carbon flux during ice-free season in most cases, but the external organic C input and its bacterial uptake is significant in some parts of the ice-free season in 3-4 lakes. The latter process could not be quantified.

#### ***Lake Acidification Models:***

A range of models, both steady-state and dynamic, have been developed in recent years as a very valuable tool to assess the response of surface waters to increasing or decreasing levels of acid deposition. Within MOLAR, the MAGIC model (Model for Acidification of Groundwater In Catchments) for trends and prognosis has been used for six lakes. MAGIC has been used to predict future trends in water chemistry given full implementation of the Oslo (1994) and Gothenburg (1999) protocols to the UN-ECE Convention on Long-range Transboundary Air Pollution. The 6 lakes are: Gossenköllesee, Estany Redó, Øvre Neådalsvatn, Lochnagar, Starolesnianske Pleso and Stavsvatn. The first three are circum-neutral and exhibit only minor acidification due to acid deposition, whereas the last 3 are acidified with high concentrations of aluminium and damage to fish and other organisms. From the model application it is clear that year-to-year variations in climatic conditions influence the surface water chemistry. Long-term change in climate can also affect future lake water quality. These model applications comprise the first step in extrapolation to entire mountain lake regions.

#### ***Critical loads and modelling:***

Critical loads for total acidity provide a measure of the sensitivity of freshwater bodies to the deposition of both acidifying sulphur and nitrogen deposition. The most simple, empirically based models, require only water chemistry data for the calculation of critical load, plus a measure of acid deposition data to calculate critical load exceedance. Two such static critical loads models have been applied to all 11 sites for which both water chemistry and acid deposition data are available; the Steady State Water chemistry model (SSWC) and the Diatom model. For SSWC model applications, two values for the critical ANC threshold ( $ANC_{crit}$ ) have been selected,  $0 \mu eq l^{-1}$ , as used in the UK, and  $20 \mu eq l^{-1}$  as used in Norway and in a previous application of the model to AL:PE sites. They indicate a wide range of acid-sensitivity in MOLAR sites. The lowest critical loads, indicating the most sensitive sites, are found at Starolesnianske Pleso in the Tatra Mountains, the two Norwegian sites (Øvre Neådalsvatn, Stavsvatn), Lago Paione Superiore in the Italian Alps, and Lochnagar, Scotland. The least acid-sensitive sites, indicated by the largest critical load values, are Jörisee and Laghetto Inferiore (Swiss Alps), and Gossenköllesee (Austrian Alps).

The critical load of three sites (Starolesnianske Pleso, Długi Staw in the Polish Tatra and Lago Paione Superiore) are exceeded using  $ANC_{crit} = 0 \mu eq l^{-1}$  in the SSWC model, while the use of  $ANC_{crit} = 20 \mu eq l^{-1}$  leads to increased exceedance at these sites plus the exceedance of critical load at an additional site, Lochnagar.

Application of the diatom model produces lower critical loads for all sites because of the greater sensitivity of the model, and while the same four sites show exceedance (Starolesnianske Pleso, Długi Staw, Lago Paione Superiore, Lochnagar), Laghetto Inferiore is also slightly exceeded.

With the FAB model (First-order Acidity Balance), it is not possible to define a single value for a critical load. In most cases of exceedance with the FAB model, either N or S deposition could be reduced in order to protect the site. Nitrogen, and not just sulphur, is therefore contributing to exceedance at all these sites. Starolesnianske Pleso is the only site where both S and N deposition are

sufficiently high to cause critical load exceedance on their own, and this is reflected by the negative ANC at the site.

None of the static models employed here can, however, indicate the likely timing of damage, which may have already occurred or which might result in several decades time. Only a dynamic model like MAGIC can predict the timing of acidification damage. With the exception of sites like Gossenköllesee and Jörisee where high weathering rates seem to provide a large buffering capacity against acidification, these high-mountain lakes do seem to be very sensitive to acid deposition. It is evident that both sulphur and nitrogen inputs contribute to critical load exceedance at all affected sites, so future reductions in S deposition across Europe resulting from the implementation of the Second Sulphur Protocol of the UNECE could mean that nitrate becomes the dominant acid anion in the future.

### **1.3 Measuring and modelling major element and pollutant fluxes in mountain lakes and their impact on fish**

One of the main goals of MOLAR has been to measure the fluxes and pathways of ions, metals, radionuclides, persistent organic pollutants and spheroidal carbonaceous particles (SCP). Conceptual models for the transport of SCPs, the deposition of radionuclides and the uptake of organic pollutants by fish have been developed. The results clearly show that high mountain lakes are remote though not pristine, and the selection of lakes has evidenced that there exists a degree of impact across Europe, for instance regarding the deposition of acids, heavy metals and organic pollutants. Since transport and redistribution of particles (SCPs), acids, metals, natural radioisotopes, anthropogenic radioisotopes and chlorinated hydrocarbons are dominated by very different meteorological, physical and chemical factors, a complex picture of impacts and responses emerges. Beside distance of source, air temperatures, altitude, geographical location, water chemistry, water renewal time, and snow melt processes play an important role. The reaction of the biota shows that chemical analysis of toxic substances can explain only part of the measured impact, and there are other environmental factors – inclusive food web structures –, which modulate the response of organisms. Although our results reflect the complex pattern of impacts, pathways and effects, there are still some open questions remaining, for instance regarding the role of hydrology and catchment characteristics.

#### ***Spheroidal carbonaceous particles, SCP:***

Samples were analysed from atmospheric deposition, sediment cores, soil cores, sediment traps and lake and stream water. A vast number of data have been collated and summarised but have yet to be fully interpreted in the light of other available data (e.g.  $^{210}\text{Pb}$ , trace metals in deposition, meteorological data etc.). It is envisaged that full data analysis will take some time but will yield a great deal of previously unknown information regarding the distributions of SCP within mountain lake ecosystems as well as information regarding deposition patterns and even possible source regions for episodes. However, a great deal of work remains if the movement of SCPs between lake and catchment and especially the level of loss to the system is to be fully understood.

#### ***Radionuclides:***

The fallout radionuclides  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$  and  $^7\text{Be}$  were measured in rainwater, soil cores, the water column and bottom sediments to validate models of transport processes through the lake/catchment system and to facilitate their use in reconstructing atmospheric fluxes of pollutants from sediment records. Although concentrations of  $^{210}\text{Pb}$  and  $^7\text{Be}$  in rainwater show large fluctuations of timescales of 2-4 weeks, mean annual values are more consistent. At sites near the Atlantic seaboard (Redo, Øvre Neådalsvatn, Lochnagar) mean annual  $^{210}\text{Pb}$  concentrations all lie in the range 66-84 Bq  $\text{kl}^{-1}$ . Significantly higher concentrations (146-173 Bq  $\text{kl}^{-1}$ ) were recorded at sites from central Europe (Gossenköllesee and Starolesnianske). This pattern reflects the global west/east increase within

landmasses due to a build of  $^{222}\text{Rn}$  concentrations in the atmosphere as the prevailing winds transport air masses over the land surface. On a local scale, variations in  $^{210}\text{Pb}$  flux are largely controlled by variations in rainfall. From these results we will be able to make improved estimates of radionuclide fluxes at most European sites, enhancing their value as tracers.

***Persistent organic pollutants:***

The sediment data show that PAH inventories in these high altitude lakes started to increase at the beginning of the century. Conversely, the increase of OC is observed in the seventies. Atmospheric deposition shows a higher content in persistent organic pollutants in wet samples. The deposition fluxes exhibit rather constant values throughout the year.

The study of fish concentrations and sediment inventories (430-2800 meters above sea level, 40-67°N) shows that lake elevation is the major variable determining the accumulation of low volatility organic compounds (OC). These compounds are also significantly correlated with annual average air temperatures. In contrast, volatile OC do not exhibit any gradient with elevation. The results obtained in the study illustrate that in temperate regions global distillation of OC involves the selective retention of the low volatility compounds at the coldest areas. This fractionation effect is responsible for the accumulation of high concentrations of potentially harmful compounds in high altitude ecosystems. In fact, for some of the DDTs and volatile PCBs, we found higher levels in fish from some high mountain lakes than in the Arctic. PAH do not show this trend with temperature.

A correlation between levels of lake sediment PAH, hydroxy PAH in fish and antioxidant compounds in fish has been found in the high altitude lakes considered in this study. This is the first case of a correlation identified between markers of environmental stress and a lake pollutant. This was in a lake which for years have been considered as the best reference lake for pristine environments in Europe (Øvre Neådalsvatn)!

***Metals:***

A comparison of lakes and sites shows a large variation in metal concentration both in lakes and in atmospheric deposition. Trace metal concentrations and their speciation (both filtered and unfiltered samples), have been determined in water column samples from Gossenköllesee, Redo and Øvre Neådalsvatn. Initial results suggest that these trace metals are mainly in the soluble phase.

A total of more than 140 fish from the seven MOLAR lakes have been analysed for trace metals in different organs; mercury (Hg) in muscle, and metals in kidney and liver (Cd, Pb, Cu, and Zn, as well as Se, Cs and As). The levels confirmed results from AL:PE 2 lakes, where the brown trout in 80% of the lakes had liver values of Cd that exceeded the recommended level for consumption given by the authority in Germany and the Netherlands.

In all lakes, except in Arresjøen, the Hg concentrations in fish were low, and lower than values generally observed in boreal areas in Scandinavia. Mercury is the only heavy metal that shows biomagnification through the food chain. At Spitsbergen, Arresjøen contain a population of Arctic char that eat other fish (carnivorous) and become very old (more than 30 years of age), which lead to both bioaccumulation and biomagnification. The oldest fish in Arresjøen contained mercury levels exceeding the guidelines for fish consumption.

## **1.4 Climate variability and ecosystem dynamics at remote alpine and arctic lakes**

The relationships between short-term variations in weather patterns (from automatic weather stations) and water column behaviour and between longer-term climate trends (from 200 year long instrumental records) and proxy climate records from dated sediment cores have been explored. Air, water

temperatures and ice-cover can be modelled with good skill at remote mountain lakes, using data transferred from lowland meteorological stations. Fine resolution analysis of cores from the remote mountain lakes show coherent variations over the last 200 years that are probably related to climate influences. Core records can be compared with instrumental climate records, although the accuracy of the comparison depends on sediment accumulation rates and the accuracy of sediment dating. A decadal resolution is possible in most cases. Climate impact on mountain lakes is registered most clearly in the sediment by changes in organic matter, changes in diatom phytoplankton and changes in chironomid assemblage composition. Currently available lake models need substantial modification, especially with respect to ice behaviour, if they are to be used to predict accurately the impact of future climate change on mountain lakes.

## **1.5 Integrating activities**

A programme of integrating activities ensured the standardisation and harmonisation of field and laboratory methods, the reporting of data, centralised storage, retrieval and analysis of data, and the presentation and dissemination of results. Standardised protocols developed within the precursor AL:PE project were amended and/or extended within MOLAR to account for new determinations and/or improvements in available methods. A series of workshops was held at the beginning of the project and detailed manuals were produced and distributed to all participating groups, as well as put on the MOLAR web page. Protocols and laboratory performance have been reviewed at regular workshops throughout the project.

The primary biological, chemical, and physical data from the various study sites in the AL:PE and MOLAR projects are stored on a centralised database developed at the University of Bergen. It includes, in a consistent and structured way, all the available geographical, climatic, catchment environmental, lake chemical, lake physical, lake biological, and sediment chemical and biological data. The database will be ultimately transferred to NIVA where it will be developed and maintained in conjunction with the AL:PE/MOLAR laboratories and centres and where it will be available for use in follow-up projects. The protocols and results of the project have been published in the international scientific literature.

An international conference on remote mountain lake ecosystems has been organised under the auspices of the MOLAR Steering Group led by the University of Innsbruck, Austria, and will take place in Innsbruck in September 2000.

A Web page for the MOLAR project has been developed at Charles University Prague.  
<http://prfdec.natur.cuni.cz/hydrobiology/molar/welcome.html>.

## **1.6 Acknowledgements**

The MOLAR co-ordinators and investigators wish to acknowledge and thank all colleagues who have collected and analysed samples or contributed in any other way to the success of the programme. MOLAR has primarily been funded by the European Commission Framework Programme IV: Environment and Climate with assistance from INCO (ENV4-CT95-0007/IC20-CT96-0021.), with additional fundings from National Research Councils and Institutes. Particular gratitude is expressed to Dr H. Barth of the European Commission DGXII for his continued encouragement and support for MOLAR.

## 2. Introduction

MOLAR (Measuring and modelling the dynamic response of remote mountain lake ecosystems to environmental change: A programme of Mountain Lake Research - MOLAR) is an extensive European co-operative research project with 23 partners. It is funded within the European Commission Framework Programme IV: Environment and Climate with assistance from INCO. It is co-ordinated by the Environmental Change Research Centre (ECRC) at University College London and the Norwegian Institute for Water Research (NIVA). MOLAR was launched March 1st 1996, and the first project meeting was held two weeks later in Prague, Czech Republic. Annual project meetings have been held in Barcelona, Spain in March 1997, in Bled, Slovenia in March 1998 and in Arcachon, France in February 1999.

A Steering Group of senior scientists from laboratories engaged in the key areas of MOLAR was established when the project was launched. The Steering Group is responsible for harmonisation of administrative and scientific co-ordination, and an important tool for optimal administration of the total MOLAR project. The Steering Group Representatives are:

Rick Batterbee, UCL, UK  
Simon Patrick, UCL, UK  
Bente M. Wathne, NIVA, Norway  
Bjørn Olav Rosseland, NIVA, Norway  
Gunnar G. Raddum, UiB(ZI), Norway  
John Birks, UiB(BI), Norway  
Roland Psenner, UIBK, Austria  
Rosario Mosello, CNR III, Italy  
Vera Straškrabová, HBI-ASCR, Czech Republic  
Jan Fott, FSCU, Czech Republic  
Joan Grimalt, CSIC, Spain  
Jordi Catalan, FBG, Spain

MOLAR has four major strands also called Work Packages (WP), and the final results for each of the Work Packages are reported here. Convenors for the four different Work Packages have been responsible for reporting of the results within each part.

### 3. GENERAL OBJECTIVES

MOLAR is an extensive European co-operative research project originally established with 22 partners. After voluntary participation from a third Swiss group (participant no. 23) it was extended and has been working with 23 partners.

MOLAR is funded by the European Commission Framework Programme IV: Environment and Climate with assistance from INCO. It is co-ordinated by the Environmental Change Research Centre (ECRC) at University College London (UCL) and the Norwegian Institute for Water Research (NIVA). A Steering Group of senior scientists from laboratories engaged in the key areas of MOLAR was established when the project was launched. The Steering Group is responsible for harmonisation of administrative and scientific co-ordination, and an important tool for optimal administration of the total MOLAR project.

The arctic and alpine regions of Europe represent the most remote and least disturbed environments in Europe, yet they are threatened by acid deposition, toxic air pollutants and by climate change. The remote lakes that occur throughout these regions are especially vulnerable for a number of related reasons:

- many mountain lakes have little ability to neutralise acidity because of their low base status, and acid deposition often increases with altitude;
- nitrate levels are often higher in mountain lakes because their catchments have little soil and vegetation to take up nitrogen deposition;
- toxic trace metals and trace organics accumulate in the food chain more easily in soft water than hard water lakes, and some pollutants (e.g. mercury, volatile organics) accumulate progressively in cold regions;
- the productivity and ecological dynamics of mountain lakes is strongly controlled by climatic influence on the length of the ice-free season and the period of thermal stratification, yet climatic warming in Europe is predicted to be greatest in arctic-alpine regions.

Because of this sensitivity, remote mountain lakes are not only vulnerable to environmental change, they are also excellent sensors of change, and their sensitivity and high quality sediment records can be used to infer the speed, direction and biological impact of changing air quality and climate. The MOLAR project builds on the success of the EU funded AL:PE (Acidification of Remote Mountain Lakes: Palaeolimnology and Ecology) and AL:PE 2 (Remote Mountain Lakes as Indicators of Air Pollution and Climate Change) projects, which represented the first comprehensive study of remote mountain lakes at an European level (Wathne *et al.* 1995, 1997).

This project has **four overall objectives**, each corresponding to a major strand, also called Work Package in the proposal:

- to measure and model the dynamic responses of remote mountain lake ecosystems to acid (sulphur plus nitrogen) deposition;

- to quantify and model pollutant (trace metals, trace organics) fluxes and pathways in remote mountain lakes and their uptake by fish;
- to measure and model the temporal responses of remote mountain lake ecosystems to climate variability on seasonal, inter-annual and decadal time-scales.
- To continue the development of a high quality environmental database on remote mountain lake ecosystems in Europe and to disseminate results widely to enhance public awareness, environmental education and environmental decision making.

The main deliverables of this project will be the development of predictive models for acidity, pollutant flux and climate variability that can be used in scenario assessment studies, especially those scenarios associated with present and forthcoming UN-ECE protocols and General Circulation Model (GCM) predictions for Europe. A desirable future objective would be the linking of these models to evaluate the interaction between acidity, trace pollutant, climate and the consequences for the biota. However this must inevitably wait until a later phase of the research. In addition to model development, much of the field and laboratory work proposed is innovative for studies of such remote sites, especially:

- the focus on the seasonal dynamics of the lake system;
- the emphasis on nitrogen deposition and its biological impact;
- the study of microbial food webs in relation to acidity;
- the on-site collection and measurement of atmospheric pollutants;
- the use of radio-tracers to validate pollutant transport models;
- the study of trace metals (especially mercury) and trace organic uptake by fish;
- the on-site monitoring of climate conditions and their relationship to water column behaviour;
- the development of a methodology to infer climate trends from the high resolution analysis of recent sediments.

These objectives were unachievable before the AL:PE project started because of the almost complete lack of information on remote arctic and alpine lakes. It has now been possible to carry out such work because of the knowledge gained about individual sites from the AL:PE and AL:PE 2 projects with respect particularly to accessibility, morphometry, chemistry, biology, sediment accumulation rate and pollution status.

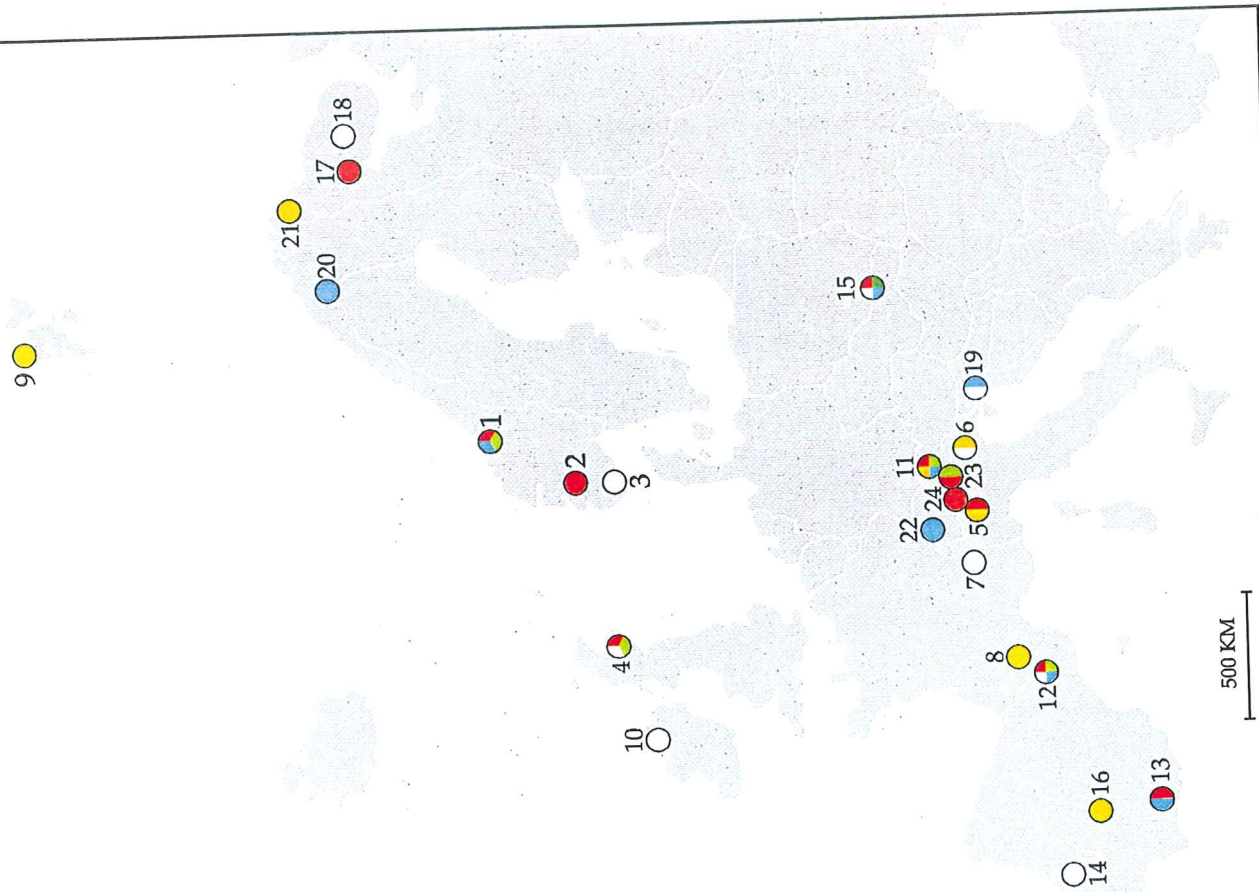
## 4. SPECIFIC OBJECTIVES AND TASKS

The four work packages of the MOLAR project concentrate on a selected number of key sites (**Figure 1**) covering Europe from the Svalbard Island (West Spitzbergen Island) to the South of Spain. Although many of the activities within each package are specific to that package, some activities (e.g. fieldwork, basic water chemistry), are common to two or more packages.



Figur 1. MOLAR sites: distribution, location and status within the MOLAR/AL:PE network.

Site nr.	Site name MOLAR/AL:PE	MOLAR WP1	MOLAR WP2	MOLAR WP3	MOLAR secondary	Other AL:PE site
1	Ø. Neðalsvatn	●	●	●		
2	Stavsvatn	●				○
3	Lille Hovvatn	●				
4.1	Lochnagar	●				○
4.2	Sandy Loch					
4.3	Loch nan Eun					○
5.1	Lago Paione Superiore	●			●	
5.2	Lago Paione Inferiore.					○
6.1	Lago Lungo				●	
6.2	Lago di Latte					
7.1	Lac Rond					○
7.2	Lac Combeynod					○
7.3	Lac Blanc					○
7.4	Lac Noir					○
8	Etang d'Aubé				●	
9	Arresjøen				●	
10	Lough Maam				●	○
11.1	Schwarzsee ob Sölden				●	
11.2	Gossenköllesee	●				○
12.1	Lago Aguiló				●	
12.2	Lago Redo	●			●	
13	La Caldera	●				○
14	Lagua Escura				●	
15.1	Starolesnianske Pleso	●				
15.2	Terianske Pleso				●	
15.3	Długi Staw	●				○
15.4	Zieloni Staw					
16	Laguna Cimera	●			●	
17	Chuna	●				○
18	Chibini					
19.1	Zgornje krško jezero				●	○
19.2	Jezero Ledvica				●	
20	Limgambergfjern				●	
21	Saanjärvi				●	
22	Hagelsee				●	
23	Jönisee	●				
24	Laghetto Inferiore	●				



All sites strictly adhere to the characteristics established for AL:PE, namely that they should be above or beyond the regional timberline, and have no evidence of human disturbance in the lake or catchment area. In other words any changes in their ecology can only be due to air pollution, climate change and natural variability.

The sites have been sampled intensively (fortnightly or monthly for physical and chemical data, 2 –4 times a year for biological data) throughout a period of 18 months to provide data for dynamic modelling, and this full sampling programme has been in operation until August /September 1998. After finishing the sampling period, sample preparation and analysis have been major topics. Site selection was based on a combination of site quality, site accessibility and availability of prior chemical and biological data. In addition to the basic requirements, criteria for site selection for WP 1 also included sensitivity to acidification, and for WP 3, minimal pollution impact. Three sites are common to all three themes: Ovre Neadalsvatn in Norway, Lago Redo in the Spanish Pyrenees and Gossenköllesee in the Austrian Alps. Four sites are used for two themes and nine for one only. Because many sites are included in more than one work package and because of the sampling frequency and the need to maintain on-site equipment, each site has a designated "site operator" responsible for the field sampling across the three scientific strands undertaken at that site. Site operators are therefore a unifying component of the overall work programme.

## **4.1 MOLAR Work Package 1 (WP1)**

### **MOUNTAIN LAKE ECOSYSTEM RESPONSE TO ACID DEPOSITION**

*Convenor: Bente M. Wathne, NIVA*

Built on the knowledge from the AL:PE and AL:PE 2 projects the main objective is to assess the impact of acid deposition on the dynamics of remote mountain lake ecosystems, and to develop models that relate acidic inputs to water chemistry, community structure and nutrient cycling. Specific objectives for WP1 are the following:

- to measure sulphur and nitrogen deposition at study sites to quantify acidifying inputs.
- to assess the seasonal variability of water chemistry at each site with respect especially to the dynamic behaviour of nitrogen, phosphorus and acidity;
- to assess the seasonal variability in populations of diatoms, zooplankton, littoral and profundal invertebrates in relation to seasonal changes in the physical and chemical environment;
- to test the hypothesis that histological and physiological analyses of fish populations can be used as early indicators of acid stress;
- to investigate whether the importance of microbial loops in the pelagic food web increases along the acidity gradient;
- to evaluate the applicability of empirical, steady-state, mass balance and dynamic critical load models to mountain lakes and to develop linked chemical-biological models for scenario assessment with respect to future EU and UNECE sulphur and nitrogen protocols.

From the AL:PE and AL:PE 2 datasets and from comparative national studies 12 primary sites sensitive to acidification were selected. The sites are located along north-south and west-east gradients in Europe (**Figure 1**). In addition four “secondary” sites were selected for a reduced sampling programme.

## **4.2 MOLAR Work Package 2 (WP2)**

### **MEASURING AND MODELLING MAJOR ELEMENT AND POLLUTANT FLUXES IN MOUNTAIN LAKES AND THEIR IMPACT ON FISH**

*Convenor: Roland Psenner, UIBK*

A need was identified for detailed studies of the deposition and transport of pollutants through high altitude catchment - lake systems that can be used to develop pollutant transfer models including interactions between pollutants, their impact on biota and their accumulation in sediments. Specific objectives for WP2 are the following:

- deposition fluxes of base cations (dust, including organic carbon and nitrogen), strong acids (S, N), trace metals, organochlorinated compounds (including PCBs) and polycyclic aromatic hydrocarbons (PAH), and spheroidal carbonaceous particles (SCPs) to high altitude lakes and catchments;
- to identify the sources (long-range, regional and local) of the various constituents of the particulate flux from the analysis of grain size, geochemistry, mineralogy, pollen, organic detritus and SCPs;
- to study the effect of atmospherically deposited dust as a neutralizing agent for acid snow and rain, as a conveyor of nutrients and as a carrier for organochlorinated compounds and PAHs;
- to investigate pathways and chemical speciation of pollutants in the lake water column;
- to investigate the effects of trace metals and organic pollutants on fish;
- to quantify the contemporary and historical depositional fluxes of the fallout radioisotope tracers  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  and SCPs to validate predictive models for pollutant transport in remote mountain lake ecosystems.

The high frequency and number of field and laboratory analyses needed in this work package required a sub-set of sites which combined remoteness with reasonable ease of access and a minimum of installations. The sites are well distributed over the study area along a low (Ovre Neadalsvatn) to high (Starolesnianske Pleso) pollution gradient (**Figure 1**).

## **4.3 MOLAR Work Package 3 (WP3)**

### **CLIMATE VARIABILITY AND ECOSYSTEM DYNAMICS AT REMOTE ALPINE AND ARCTIC LAKES**

*Convenor: Richard W. Battarbee, UCL*

The chemical and biological status of lakes is strongly related to the weather-induced physical processes acting both on the lake and its catchment, and the relative length of water column

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stratification and mixing periods is especially important. Variations in weather patterns from year to year also cause fluctuations in primary productivity, and if sustained over longer periods changes in the species composition of plant and animal populations can occur, both by direct (e.g. temperature) and indirect effects (e.g. pH). Such changes are recorded by the biogenic fraction of the lake sediment, both as amorphous organic matter and by diverse sub-fossil remains. The sediment record can then be used to evaluate both short and long-term variability in climate patterns, necessary both for the interpretation of past climates and as a baseline to assess the impact of future warming.

Specific objectives for WP3 are the following:

- to collate, harmonise and analyse appropriate long-term instrumental climate records for the regions under consideration;
- to model the relationship between climate records for mountain weather stations (at study sites) with those for lowland stations;
- to assess the physical, chemical and biological seasonal variability of non-polluted remote lakes by intensive sampling and analysis at a small number of key sites;
- to establish the relationship between the distribution of the primary biological constituents of mountain lake ecosystems that form the most important groups in sediments cores i.e. diatoms, chrysophytes, cladocerans and chironomids, and measured environmental summary variables;
- to assess underlying trends and natural variability in climate from the fine-detail analysis of the uppermost sediment of study sites;
- to compare the sediment record at study sites with instrumental records of temperature and precipitation, to calibrate and validate the DYRESM and AQUASIM models and to run the models using alternative scenarios for future climate.

The lakes in this study share the same basic limnological characteristics. They are oligotrophic, typically dimictic and have a winter ice-cover and a summer thermocline. They are all situated above or beyond the regional tree-line, and they have poorly vegetated catchments. Most of the sites were included in the AL:PE programme, and are those identified in that study to be least influenced by acid deposition. With the inclusion in the EU of Finland and Austria, and the participation of Slovenia and Switzerland, additional appropriate sites have been identified in these countries, all of which have been the subject of prior study. The sites are shown in **Figure 1**.

## **4.4 MOLAR Work Package 4 (WP 4)**

### **INTEGRATING ACTIVITIES**

*Convenor: Simon Patrick, UCL*

The three field-based work packages described above have been linked and given coherence by a programme of integrated activities to ensure the standardisation and harmonisation of field and laboratory methods, the reporting of data, centralised storage, retrieval and analysis of data, and the presentation and dissemination of results. Specific objectives for WP4 are the following:

- Coordinate a programme of standardized and quality controlled field and analytical methods.

- Extend and further develop an integrated and harmonized database
- Ensure the optimal use of database information to facilitate the application of multivariate statistical and modelling techniques in order to provide an integrated assessment of project results.
- Further develop a multidisciplinary network of environmental scientists to coordinate research, exchange knowledge and disseminate findings from studies of remote mountain ecosystems.

Administrative coordination (including financial) has been the responsibility of UCL, and overall scientific coordination has been performed by NIVA. A Steering Group of senior scientists from institutions engaged in key areas of MOLAR has been in operation to discuss, decide and communicate the most important project issues and to ensure harmonisation of administrative and scientific coordination. With such a large project group, it is important to facilitate practical decision-making. The group consists of representatives from UCL, NIVA, UiB, CNR III, FBG, CSIC, UIBK, FSCU and HBI-ASCR.

## 5. MAIN RESULTS AND CONCLUSIONS

### 5.1 MOLAR Work Package 1 (WP1)

#### MOUNTAIN LAKE ECOSYSTEM RESPONSE TO ACID DEPOSITION

Activities within Workpackage 1 (WP1) have been concentrating on the twelve primary lakes chosen for study. The listed topics are addressed to follow the specific objectives for WP1:

1. On site measurements of sulphur and nitrogen deposition
2. Seasonal variability of water chemistry
3. Seasonal variability of biota
4. Test hypothesis: histological and physiological attributes of fish indicate early acid stress
5. Test hypothesis: microbial activity in pelagic food web increases with acidification intensity
6. Evaluate applicability of various critical load models to mountain lake ecosystems, and develop a linked chemical-biological model for scenario assessment

#### 5.1.1 Atmospheric Deposition - on site measurements of sulphur and nitrogen

Measurements of deposition have been performed at 11 of the 12 primary lakes. Some of the sampling stations were not continuously operational for the whole of the two year period (July 96-June 98), due to various problems, mainly linked to the difficulty in reaching the sites. The analytical quality of the data is generally good, as emerges from the calculation of the ion balances and from the comparison between measured and calculated conductivity. The pH values range from 4.1-4.5 in the Tatra Mountain, to 4.7-5.0 in the other sites. Sulphate and nitrate prevail among the anions in most of the stations, with the exception of Kårvatn and Lochnagar, which have a marked contribution of chloride of marine origin. The ratio between sulphate and nitrate is close to 2 in the stations in the Tatra Mountains and Spain, while it approaches 1 in the sites in the Alps, and is only 0.4 in Møsvatn (representing Stavsvatn, Norway). Alkalinity was measured in significant amounts in some stations in the Eastern (Ritten, Texel) and Central Alps (Robiei). Its deposition is mainly related to the transport of Saharan dust (Guerzoni and Chester, 1996), which happens occasionally (from 2 to 5 times each year), but with high precipitation volumes in most cases, so that they are important in determining the annual volume weighted values. Among cations, the hydrogen ion prevails in the stations with pH lower than 4.5. Ammonium and calcium are the most important ions in the other stations, with the exception of the two sites close to the sea, where the highest concentrations are of sodium. The total ion content ranges between 50  $\mu\text{eq l}^{-1}$  in Møsvatn and Jorisee (Central Alps), and 200  $\mu\text{eq l}^{-1}$  for the stations of Kårvatn (Norway) and Lochnagar (Scotland), both with a high contribution of sodium and chloride of marine origin.

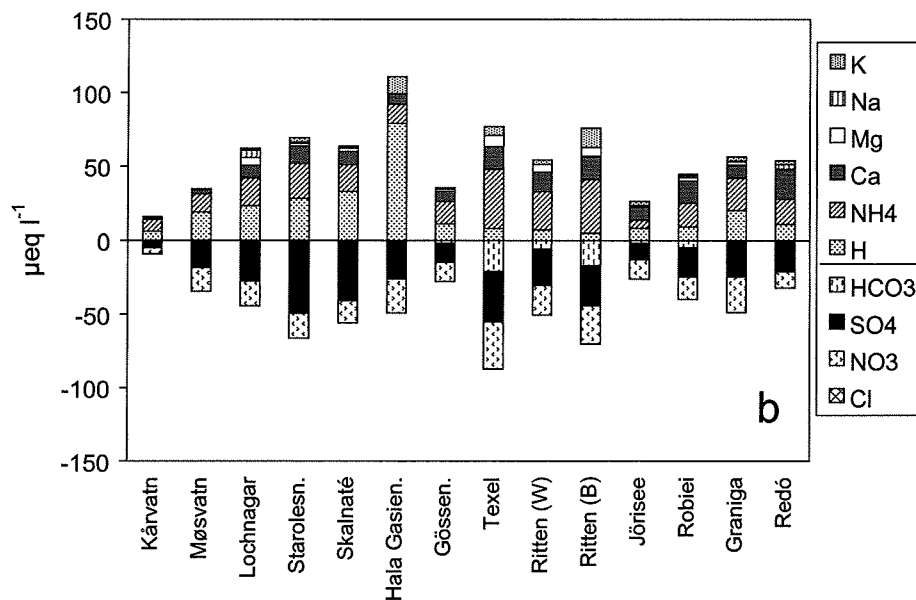
The comparability of the data improves if they are corrected for seasalt, assuming that all chloride is of marine origin and that the ratio with the other ions ( $\text{Na}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{SO}_4^-$ ) is the same as in seawater. Results (**Figure 2**) show that the lowest ion concentrations was then found in Kårvatn (25  $\mu\text{eq l}^{-1}$ ), while the correction does not substantially affect the concentrations of sulphate and the sulphate/nitrate ratio.

Deposition values show a more marked yearly variation if compared with concentrations, mainly due to the different amounts of precipitation. Some of the stations were not operational for the whole two year period, so that the amount of precipitation measured refers only to fractions of the year. For these reasons the wet deposition of ions is in **Figure 3** where the depositions are shown without the marine contribution. The deposition of acidity (hydrogen ion flux) is very high in the Polish station of Hala

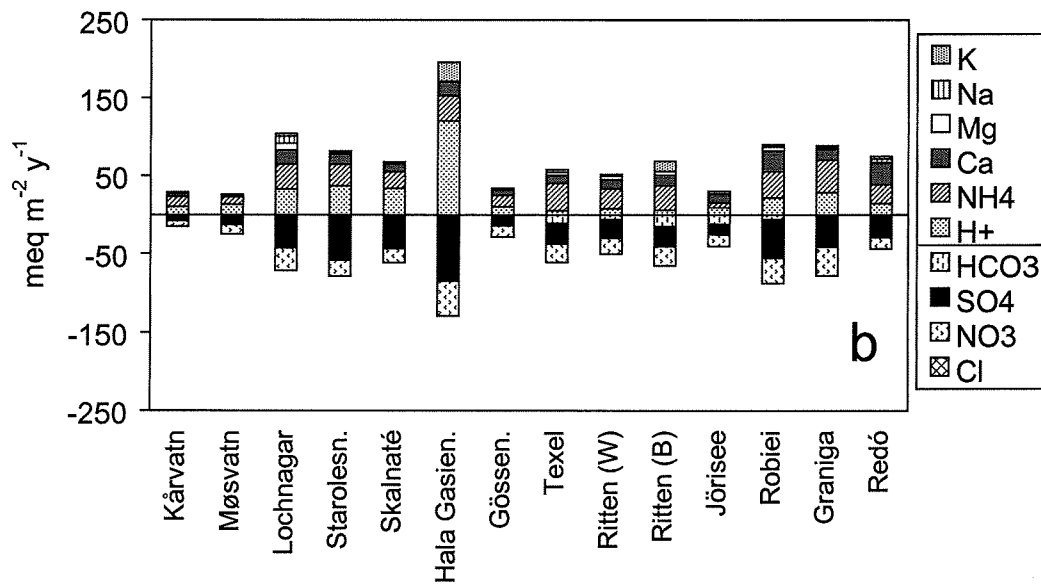
Gasienicowa, where the highest depositions of sulphate and nitrate are also measured. The stations in the Alps show wide variability, from relatively high deposition ( $20\text{-}30 \text{ meq m}^{-2} \text{ y}^{-1}$  for the sites of Graniga and Robiei in the Western Alps at altitudes between 1100-1900 m a.s.l) to the lowest values of  $9\text{-}10 \text{ meq m}^{-2} \text{ y}^{-1}$  for the stations of Gössenkollesee and Jörisee, both located at about 2500 m a.s.l. The load of hydrogen ion is also low in the Alpine station of Ritten (1780 m a.s.l.), in the Eastern Southern Alps. In these stations the ammonium load is high compared with the hydrogen ion load, and the oxidation of ammonium to nitrate may be a further source of acidity. The situation is better in the case of the northernmost stations of Kårvatn and Møsvatn, where both hydrogen and ammonium loads are low.

The chemistry of atmospheric deposition collected in sites which are representative of remote areas in the whole of Europe, shows that the solutes present may be marine, terrigenous, and deriving from fuel-burning emissions and intensive stock-breeding. The acidity of the depositions depends on the different importance in percentage terms of each component, especially the terrigenous one and that deriving from anthropogenic emissions. The results show marked variability in the different areas of Europe, with the worst situation in central Europe and in some Alpine stations. But even in areas like Scandinavia, for example, a gradient is clear from the southernmost station, Møsvatn, to Kårvatn, situated in the central part of Norway, which is less affected by long-range transported air pollution. Seasonal variations emerged as having great importance, both in the chemical composition and in the volume of water, and it must be borne in mind that, during winter, most of the deposition is in form of snow, so all the ionic load, including pollutants, is released in a very short space of time, during snowmelt, causing marked pulses in the chemistry of rivers and lakes. The relative importance of episodic events as opposed to phenomena which develop continuously in the ecosystem, is a major question requiring particular study methods.

A full description of the results is given in Mosello *et al.* 1999.



**Figure 2.** Ion balance for the mean annual concentration of atmospheric deposition before (above) and after (below) sea-salt correction. After: Mosello *et al.* 1999.



**Figure 3.** Deposition of ions from atmospheric deposition before (above) and after (below) sea-salt correction. After: Mosello *et al.* 1999.

### 5.1.2 Seasonal variability of Water chemistry

All 12 lakes have been sampled for water chemistry. Results from deposition and lake water chemistry for 1996, 1997 and 1998 are stored by CNR and NIVA and after QA sent to the MOLAR database at UIB. Intercalibration exercises have been carried out both by CNR and NIVA.

The mean concentrations for surface water in the MOLAR lakes are shown in **Table 1**, where the number of samplings performed in each site is also indicated. The ion concentrations have quite a wide range of variation ( $88\text{--}3360 \mu\text{eq l}^{-1}$ ), from very diluted to highly buffered waters. The corresponding range of variation of conductivity is  $6\text{--}148 \mu\text{S cm}^{-1}$  at  $25 \text{ }^\circ\text{C}$ . The pH values are in the range  $4.9\text{--}6.0$  in 8 of the 23 lakes, while three lakes (La Caldera, Hagelsee and Jezero v Ledvici) show values higher than 7.5. Alkalinity is very high for Jezero v Ledvici and Hagelsee ( $1303$  and  $1167 \mu\text{eq l}^{-1}$ ), ranges between  $118\text{--}343 \mu\text{eq l}^{-1}$  for lakes Jörisee, Saanajärvi and La Caldera, and is lower than  $50$  and  $20 \mu\text{eq l}^{-1}$  in 15 and 7 lakes, respectively. Sulphate ranges from  $11$  to  $252 \mu\text{eq l}^{-1}$ ; the highest values show that atmospheric deposition cannot be considered as the only source of sulphate, but in some cases (e.g. Hagelsee, Jezero v Ledvici, Schwarzsee ob Sölden) there is also a sulphate contribution deriving from watershed weathering. Nitrate concentrations are very low (below  $10 \mu\text{eq l}^{-1}$ ) in the northernmost lakes in Norway (Øvre Neådalsvatn, Stavsvatn, Limgambergtjern and Arresjøen), Finland (Saanajärvi), Russia (z. Chuna) and Spain (Laguna Cimera). The highest values ( $36\text{--}42 \mu\text{eq l}^{-1}$ ) are found in the lakes in the Tatra Mountains (N. Terianske and Dlugi Staw). The lakes in the Alps show values between  $15\text{--}26 \mu\text{eq l}^{-1}$ , with the lowest value for Hagelsee ( $12 \mu\text{eq l}^{-1}$ ). Nitrate concentration is also relatively low (below  $12 \mu\text{eq l}^{-1}$ ) in the lakes in Spain (Redó, Cimera and La Caldera).

The most important event affecting water chemistry is the snow melt, which in all the lakes causes a more or less sharp decrease in alkalinity, pH, calcium and major ion concentrations **Figure 4** and



**Figure 5** show these variations in the Norwegian lake Øvre Neådalsvatn, the lakes Paione Superiore and Gossenköllesee in the Alps, and Redó, in the Pyrenees. The first three lakes clearly show the effects of the snowmelt, while in the case of Redó there are no variations, although they have been observed in years with a higher sampling frequency (Catalan, 1992).

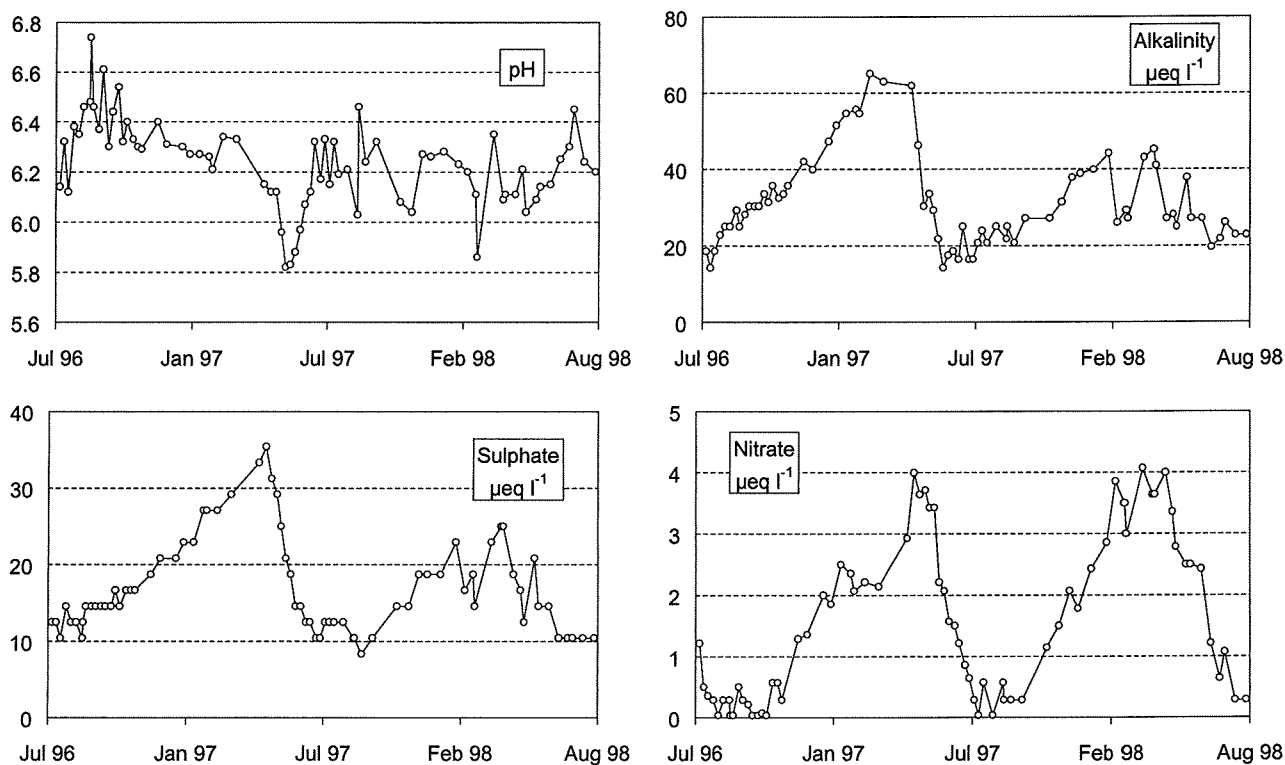
The chemistry of these lakes is largely determined by three factors: (1) atmospheric loads, (2) weathering processes, and (3) interaction with the vegetation in the watershed, scarce but not negligible, and with the biology of the lake waters. The geological characteristics of many watersheds, made up largely of poorly soluble rocks, means that many of the considered lakes are sensitive to acidification, with some of them showing clear signs of alteration. The interaction between the vegetation cover of the watershed and the chemistry of the water is particularly important when determining nitrogen levels. In general, atmospheric nitrogen loads are high, so that nitrate is present in the water of many remote lakes in relatively high concentrations. This is particularly true with regard to the lakes in the Tatra Mountains, but also for those in the Alps. It is also striking how ammonium, which is present in significant quantities in atmospheric loads, disappears almost completely in surface waters. It is known that the uptake of ammonium from vegetation is a further source of acidity, and that the oxidation of ammonium to nitrate produces acidity. For this reason, pH is not the best indicator of the real acidifying capacity of atmospheric deposition; more detailed studies are, however, required.

A full description of the results is given in Mosello *et al.* 1999.

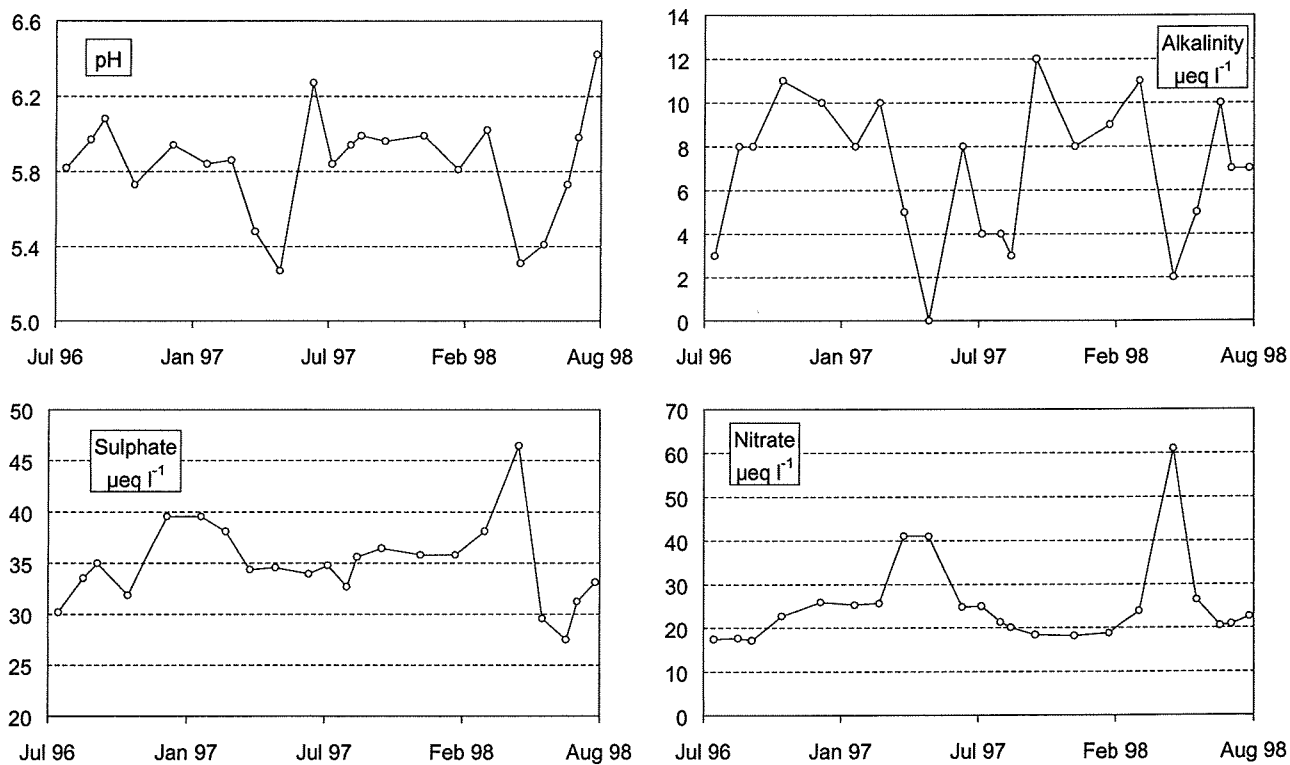
Table 1. The mean concentrations for surface water in the MOLAR lakes. After: Mosello *et al.* 1999. ( $\mu\text{eq l}^{-1}$ ).

Lake name	n° data	pH	H <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	Ca <sup>++</sup>	Mg <sup>++</sup>	Na <sup>+</sup>	K <sup>+</sup>	Alk	SO <sub>4</sub> <sup>=</sup>	NO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Cations	Anions	Ions	Meas. cond.	Calc. cond.
Ovre Neadalsvatn	93	6,22	1	0	32	14	44	4	32	17	2	47	94	98	193	11,5	11,9
Stavsvatn	15	5,93	1	2	44	10	21	5	19	35	7	17	82	78	160	10,4	10,5
Lochnagar	71	5,32	5	1	40	41	93	6	8	55	19	80	186	162	348	22,0	23,7
Lago Paione Superiore	24	5,82	2	3	42	8	11	7	7	35	26	5	72	73	146	10,7	10,2
Lago Paione Inferiore	15	6,55	0	0	68	11	14	10	34	44	25	4	103	106	209	13,1	13,2
Lago di Latte	15	6,46	1	4	100	12	16	8	70	59	17	3	141	148	290	18,3	17,8
Aubé	1	5,71	2	0	24	6	13	3	6	20	8	6	48	40	88	6,1	6,2
Arresjøen	2	6,41	0	1	35	52	216	6	26	34	1	251	311	311	622	38,5	39,4
Schwarzsee ob Sölden	3	5,98	1	1	80	28	19	4	8	106	8	3	132	125	257	16,7	17,5
Gossenköllesee	38	6,76	0	1	142	18	15	5	86	58	19	3	181	166	346	19,2	20,7
Redó	23	6,41	0	1	72	7	11	1	47	27	12	7	92	94	186	11,3	11,2
La Caldera	21	8,12	0	1	241	54	14	2	343	18	12	9	311	382	693	29,3	36,3
Starolesnianske pl.	49	4,95	12	4	28	6	7	2	0	43	13	5	59	60	119	11,8	11,7
Nizne Terianske pl.	16	6,48	0	1	150	8	14	3	77	55	36	5	177	173	350	21,2	21,3
Dlugi Staw	17	5,59	5	9	92	12	14	3	42	56	42	11	135	151	286	26,5	19,7
Laguna Címera	25	6,33	1	2	17	11	13	2	31	11	4	6	46	51	97	5,7	5,7
z. Chuna	22	6,14	1	0	46	11	24	2	20	35	4	21	85	81	165	10,3	10,6
Jezero v Ledvici	34	7,69	0	5	1199	639	42	6	1303	42	20	105	1891	1470	3361	148,2	179,0
Limgambergfjern	4	5,79	2	1	56	51	122	4	12	79	0	129	236	220	456	28,2	29,9
Saanajärvi	27	7,02	0	1	145	51	51	6	175	86	3	49	256	314	569	27,5	33,2
Hagelsee	23	8,11	0	4	1225	205	21	14	1167	252	12	18	1468	1449	2917	115,0	160,4
Jörisee	28	7,03	0	1	128	27	18	9	118	56	17	3	183	193	376	17,4	21,8
Laghetto Inf.	12	6,56	0	1	64	9	12	10	34	38	16	2	96	90	187	11,6	11,7

**Øvre Neådalsvatn**

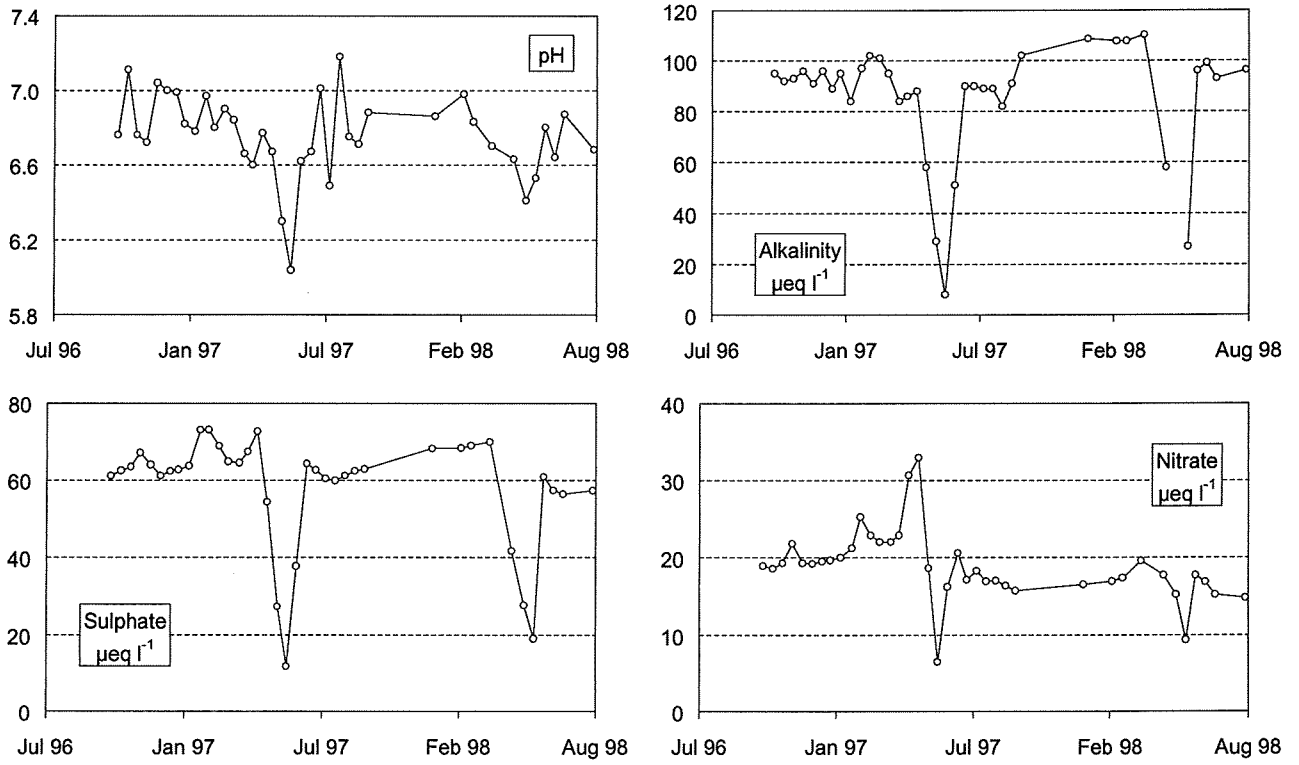


**Lago Paione Superiore**

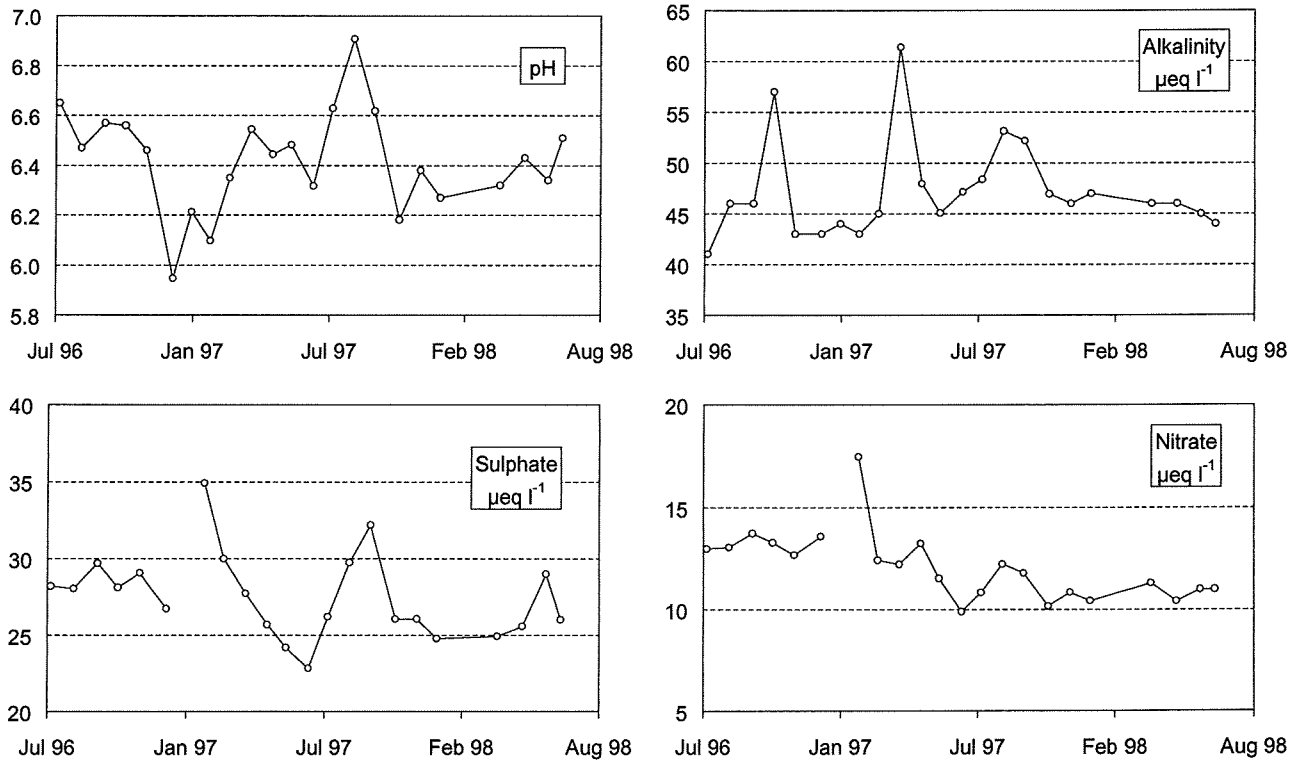


**Figure 4.** Seasonal variations of pH, alkalinity, sulphate and nitrate in lakes Øvre Neådalsvatn and Paione Superiore. After: Mosello *et al.* 1999.

**Gossenköllesee**



**Redó**



**Figure 5.** Seasonal variations of pH, alkalinity, sulphate and nitrate in lakes Gossenköllesee and Redó. After: Mosello *et al.* 1999.

### 5.1.3 Seasonal variability of benthic fauna

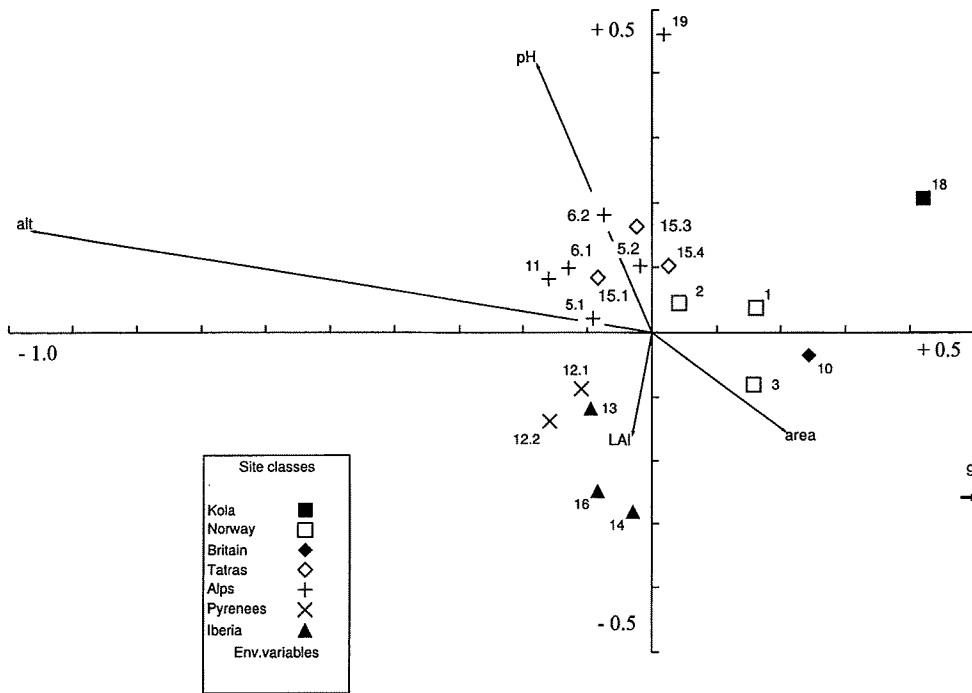
The profundal datasets from European alpine lakes indicates homogeneity in the fauna over a latitudinal gradient. This may be related to substrate homogeneity, the strong restrictions of low temperatures during most of the year and the small amount of food reaching the deepest areas of these ultraoligotrophic lakes, especially in the deepest ones. This fact is interesting because it indicates that profundal areas of remote mountain lakes, independent of their latitude and their history after glaciation, are colonized by closely related communities. These profundal communities are, however, susceptible to anthropogenic influence, as demonstrated by historic changes in species composition in several AL:PE lakes (Schnell and Raddum 1993).

A test of environmental variables with forward selection showed that only the altitude did contribute significantly to the ordination ( $p < 0.01$ ) of the littoral data. The altitude was negatively correlated with the first ordination axis ( $r = -0.93$ , weighted correlation). The ordination is presented as a site-environmental biplot in **Figure 6**. In this ordination the different regions have a tendency of grouping together. This is explained by a strong contribution of zoogeographical factors that, besides environmental variables, are important explaining the distribution of freshwater biota in European mountain ranges.

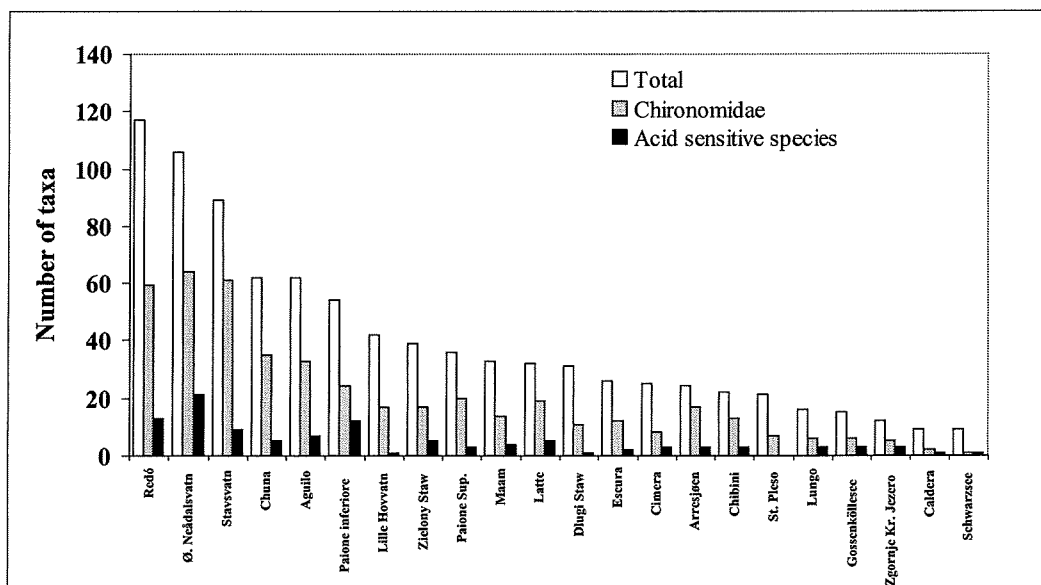
A summary of the datasets from both AL:PE and MOLAR shows that the Pyrenean Lake Redó and the Norwegian reference Lake Ovre Neadalsvatn appeared to have the highest species richness, both with respect to total fauna, chironomids and total number of acid sensitive species (**Figure 7**). These lakes belong to areas of Europe least affected by long-range transported air pollution. The number of species increases from south to north on the Iberian Peninsula and no trend related to acidification of the lakes was evident. The diversity of most of the other lakes was generally low. Compared to the rest of the fauna, many chironomid species are relatively widespread in the investigated localities. The most common species were *Heterotrissocladius marcidus* (Walker) and *Micropsectra radialis* (Goethghebuer). Colonisation rates are low in such remote systems and this could account for the low species diversity as well as the absence of many species even though the water chemistry is suitable for their survival.

The importance of altitude is demonstrated by the difference in species richness between the two adjacent lakes Paione Superiore and Paione Inferiore (**Figure 7**). Besides geological factors, climatic differences are also important in such high altitudes. Over small distances in altitude, temperature, length of the ice-free period or amount of allochthonous production in the catchment may vary considerably and seems to be of great importance to the benthic community.

Environmental factors are important in controlling the life cycle of the different taxa. The benthic freshwater fauna is highly dynamic, both with respect to seasonal variation and variations between years. Timing of the sampling is therefore important. In the MOLAR programme sampling were conducted several times during the season. Such sampling gives more information of the biodiversity as well as important data of the life cycle of different species. The relative distribution of chironomids from the profundal of two lakes, the northern lake Ovre Neadalsvatn and Lake Redó in the Pyrenees (**Figure 8**) gives an example of this. In such homogenous environments the various species have more synchronised life cycles than in heterogeneous environments like rivers and the littoral zone. This means that important species may be completely out of the system and will be missed with only one sampling date.

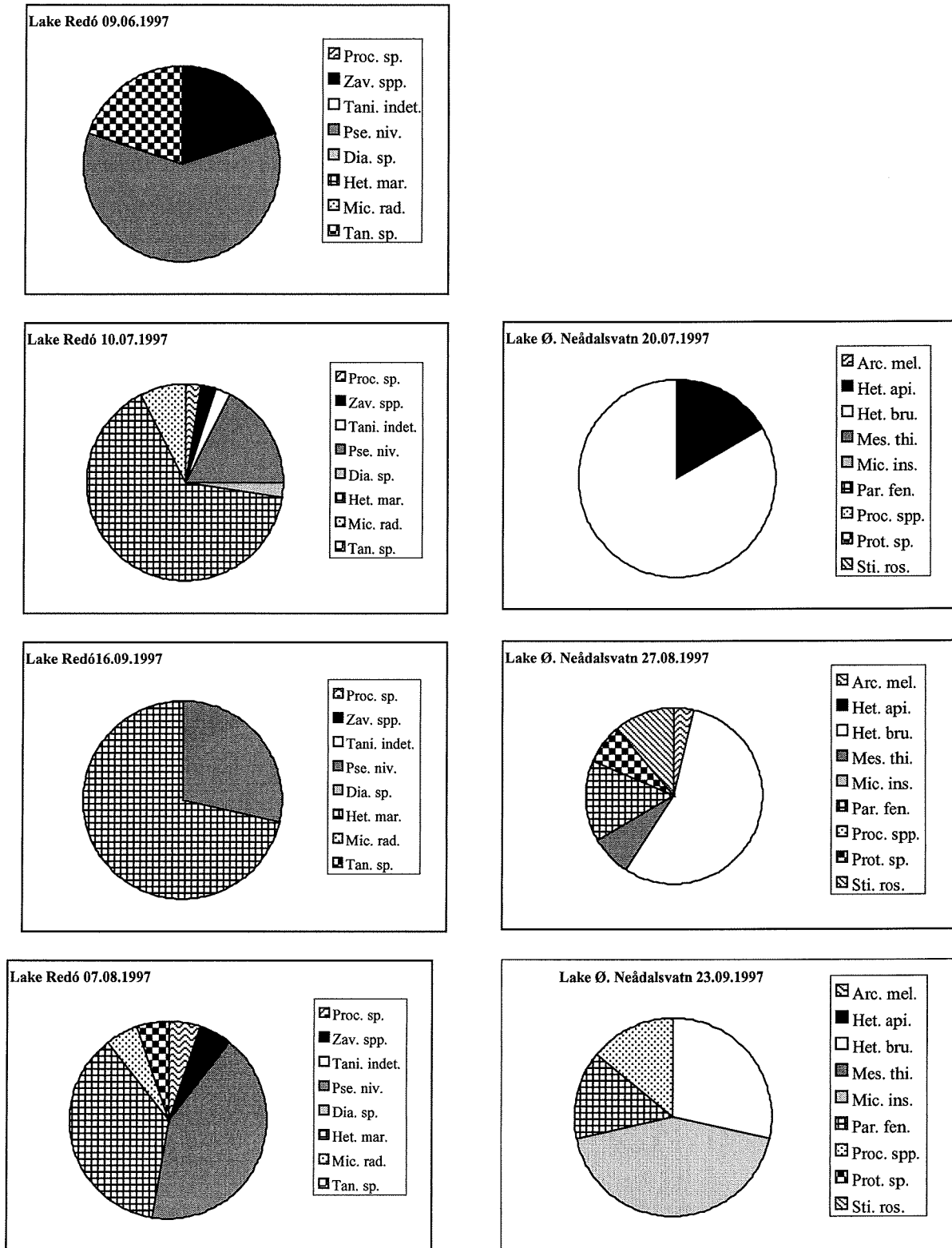


**Figure 6.** Site – environmental biplot of mountain lakes of different regions of Europe. The environmental variables 'latitude' and 'Ca' are not shown. The variable 'latitude' is positively correlated ( $r = 0.77$ ) with the first canonical axis, while the variable 'Ca' is positively correlated ( $r = 0.66$ ) with the second axis. After: Fjellheim *et al.* (In press).



**Figure 7.** An overview of the biodiversity of European remote mountain lakes, based on the AL:PE and MOLAR datasets.

An overview of the number of acid-sensitive species in AL:PE and MOLAR lakes (**Figure 7**) shows that the distribution of sensitive species is generally low in European remote mountain lakes. The Norwegian reference Lake Ovre Neadalsvatn had the highest number of sensitive invertebrates, reflecting low impact of acidification. Also the relatively clean sites in the Pyrenees hosted several sensitive species, while the fauna of more affected areas like many sites in the Alps, Tatra and South Norway were mainly composed of acid-tolerant species. A negative correlation between number of species and altitude (Fjellheim *et al.* in press) suggests that climate is an important factor regarding the distribution of freshwater invertebrates in mountain lakes. Several environmental factors are impacted by climate, of which length of ice-free season and the production of organic material in the catchments are very important. Remote freshwater ecosystems are expected to be valuable indicators of local and global temperature changes, especially since temperature changes and corresponding effects upon the macrobenthic community is expected to be greatest in these environments.



**Figure 8.** Seasonal occurrence of different taxa of chironomids in Redó and Ovre Neadalsvatn.



#### 5.1.4 Test hypothesis: histological and physiological attributes of fish indicate early acid stress

To ensure that samples were collected comparably, a MOLAR fish training workshop was arranged in Arcachon, France, in 1996, a video of the sampling procedures was made, and the sampling procedures were described in detail in the MOLAR manual. Organs from single fish were divided, and sent to different MOLAR specialist laboratories around Europe for analyses. This also included the otoliths for age determination, as a correct ageing of the individual fish is extremely important for evaluating the contamination levels.

Test-fishing and following age determination have been finalised in seven lakes as planned. All heavy metal analysis in kidney and liver, as well as mercury in muscle has been carried out, and isotopes of nitrogen ( $^{14}\text{N}/^{15}\text{N}$ ) and carbon ( $^{13}\text{C}/^{12}\text{C}$ ) in fish muscle have been analysed. Liver histology, blood plasma ions and liver enzyme activities have been analysed and measured and analysis of micro-organic pollutants in fish has been finalised.

##### *Physiological analysis*

When studying the ecology of remote mountain lakes and the role biotectors like fish can play as early warning of air born pollution and climate changes, a basic question is to understand how fish succeed to live in such extreme biotopes where low mineralisation is the first major stress. Taking advantage of the palette of water ionic composition observed in the Molar lakes, we studied the minimal concentration of key ions (Na, Cl, Ca, and alkalinity) compatible with fish life. The aim of the study was to gain more insights into the basic knowledge necessary to interpret secondarily contamination processes in the brown trout (*Salmo trutta* L.).

Basically, it is worthwhile noticing that fish in such situation must develop two strategies of adaptation:

- First, they must reduce the ionic leaks by decreasing their gill permeability. It was classically known from laboratory experiments that the calcium ion play a key role to solve this problem but, to our knowledge, there was no field data about values of minimum water calcium concentration compatible with fish life in these biotopes.

-Second, they must improve the efficiency of their ionic pumps at the gill level. From laboratory study, it was well known that chloride cells participate to the ionic balance between blood and water. More especially, it was shown that in brown trout a decrease of NaCl in water stimulates their proliferation in low mineralised waters. However, beside this pioneer demonstration, the *in situ* ionic concentration at which this mechanism of adaptation could occur was completely unknown as well as if it was Na, Cl or both Na and Cl that were specifically responsible of this physiological adaptation. Importantly, note that all data were obtained from fish that were at least 2-4 years old and which were either native of these lakes or stocked as 0+. All animals were caught with gill nets except a series in Lake Jorisee (Switzerland) captured by fishing rods.

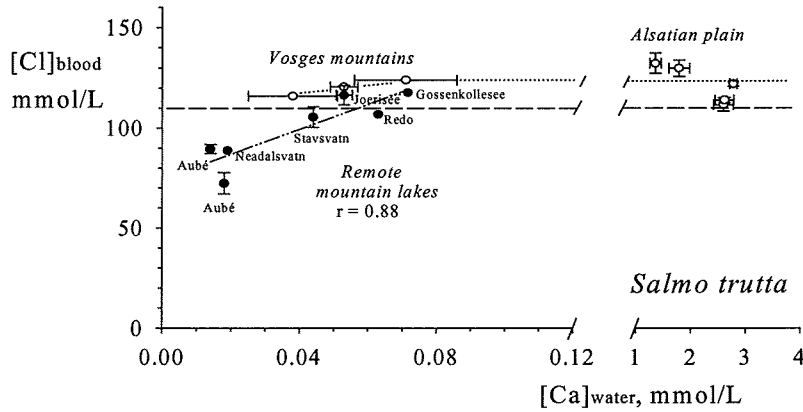
*Plasma ion analysis.* In fish blood, the main contributors of osmolarity are the Na and Cl ions. Consequently, natremia ([Na]<sub>b</sub>) and chloremia ([Cl]<sub>b</sub>) were measured and compared to reference data obtained in the same fish species living in more mineralised waters (Alsatian plain and Vosges mountains, north-eastern France). Results were analysed as a function of water chemistry data.

The results show that brown trout can maintain a normal blood Na concentration  $\geq 110 \text{ mmol}\cdot\text{L}^{-1}$  in waters where the mineral load is as low as  $\approx 4 \text{ mg}\cdot\text{L}^{-1}$  but that the blood Cl concentration starts to decrease below  $8\text{-}10 \text{ mg}\cdot\text{L}^{-1}$ . This [Cl]<sub>b</sub> response was not directly correlated to the concentrations of Na and Cl in the water but dependent on [Ca]<sub>w</sub> (**Figure 9**). When [Ca]<sub>w</sub> is higher than  $30\text{-}40 \text{ }\mu\text{mol}\cdot\text{L}^{-1}$ , brown trout can maintain a normal chloremia even for [Cl]<sub>w</sub> as low as  $3 \text{ }\mu\text{mol}\cdot\text{L}^{-1}$  (see below). This is coherent with literature data on the role of Ca in impermeabilising biological membranes but give new insights into critical limits compatible with brown trout life in remote mountain lakes and/or extremely diluted water solutions. Note that it is in lake Aubé (french Pyrénées) where [Ca]<sub>w</sub> is only  $14\text{-}15 \text{ }\mu\text{mol}\cdot\text{L}^{-1}$ , and in lake Ovre Neadalsvatn that trouts exhibited the lowest chloremia (70-75

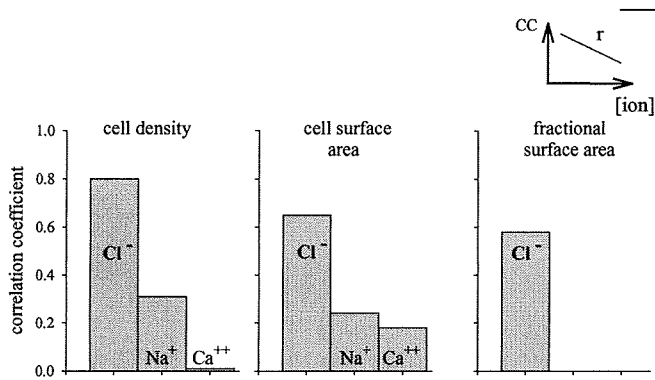
mmol·L<sup>-1</sup> for [Cl]<sub>w</sub> = 7-9 μmol·L<sup>-1</sup>). Note also, that due to our fish sampling protocol with gill nets, which obviously imposed a severe stress to all fishes, we were unable to say if the low chloremia was the result of the low calcium concentration *per se* or the result of the stress imposed by the test fishing at this low calcium concentration. Nevertheless, the present study demonstrates that for the brown trout, a minimal [Ca]<sub>w</sub> compatible with a sustainable life is at least 15 μmol·L<sup>-1</sup> (the concentration in lake Aubé) and that [Cl]<sub>b</sub> can be taken as an indicator of stress in low mineralised waters.

*Insights into the adaptation of ion pumping mechanism at the gill level.* This study was performed by analysing the fish gill anatomy by scanning microscopy. All fish gills collected in the Molar lakes were prepared in the field for the anatomical analysis in scanning microscopy. A first global analysis integrated with blood data clearly showed first that the proliferation of chloride cells (characteristic of osmoregulatory problems) in trout gill increases when the mineral load decreases. Three parameters were then specifically analysed. The cell density, the cell surface area and the fractional surface area that is the ratio of the cell surface area per unit of secondary lamellae area. The correlation coefficient between these morpho-anatomical characteristics and the water ionic composition were then calculated in an attempt to discriminate between the various ions able to stimulate the proliferation of chloride cells. The relationships were only considered to be of some adaptive value when a decrease of water ionic concentration was associated to a proliferation or an increase of cellular size of the surface aspects of the chloride cells. **Figure 10** shows that the only ion which was systematically associated to an increase of chloride cell density, surface and fractional surface was the chloride ion. Based on literature data and the present study, we consequently suggest that in these biotopes, [Cl]<sub>w</sub> is the single ion which specifically stimulates the chloride cell proliferation. Together with the calcium, they play a key role in the strategy of adaptation of brown trout in low mineralised waters. Remarkably, the largest proliferation of chloride cell was measured on the gills of brown trouts from Gossenköllesee where [Cl]<sub>w</sub> was only 3 μmol·L<sup>-1</sup> ([Ca]<sub>w</sub> ≈ 80 μmol·L<sup>-1</sup>). This value appears thus today as the lowest known water [Cl]<sub>w</sub> value compatible with fish life.

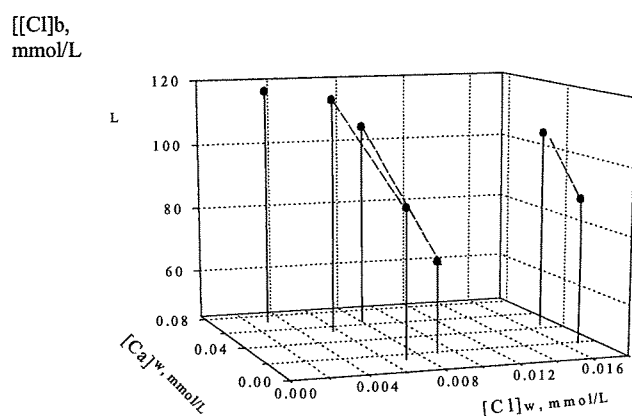
Note, in addition that although the problem arising from a low [Cl]<sub>w</sub> can be counterbalanced by a chloride cell proliferation, this physiological adaptation can not replace the deleterious effect of a low [Ca]<sub>w</sub> on the gill epithelium permeability. Indeed, **Figure 11** illustrates that at any [Cl]<sub>w</sub> ranging from 5 to 17 μmol·L<sup>-1</sup> the chloremia systematically decreased for [Ca]<sub>w</sub> ≤ 20 μmol·L<sup>-1</sup>. A high enough [Ca]<sub>w</sub>, is consequently a prerequisite to allow fish life in these extreme environments.



**Figure 9.** Relationship between blood chloride concentration ( $[Cl]_b$ ) in brown trout *Salmo trutta* and water calcium concentration in remote mountain lakes. It is only in lakes where  $[Ca]_w < 30 \mu\text{mol}\cdot\text{L}^{-1}$  that brown trout caught with gill nets can not maintain a normal  $[Cl]_b$ .



**Figure 10.** Relationship between chloride cell (CC) morphometry of brown trout and water ionic concentration in remote mountain lakes exhibiting a palette of water ionic concentrations. The relations were only considered to be of some adaptive value when a reduction of a given ion stimulated the CC proliferation (see insert). The correlation coefficient was systematically higher with  $[Cl]_w$ . It was lower or absent for all other ions.



**Figure 11.** Summary relationship between blood Cl concentration ( $[Cl]_b$ ), water Ca ( $[Ca]_w$ ) and water Cl ( $[Cl]_w$ ) concentrations. A normal  $[Cl]_b$  can be maintained only in mountain lakes where  $[Ca]_w$  is high enough (see **Figure 9**). The stimulation of chloride cell proliferation occurring at low  $[Cl]_w$  (see **Figure 10**) does not allow by itself to compensate for a low  $[Ca]_w$ .

### 5.1.5 Test hypothesis: microbial activity in pelagic food web increases with acidification intensity

For the assessment of pelagic microbial food webs and activity, a set of methods suitable for screening and measurement in hardly accessible oligotrophic lakes was prepared in the MOLAR Manual (Wathne and Hansen 1997 and Straškrabová *et al.* 1999a). A methodical training workshop was organized (České Budějovice, May 1996) before the sampling season started. During the project, intercomparison of methods for the assessment of bacteria was organized with 6 partners.

**Pelagic food webs 1<sup>st</sup> level** for the assessment of all components of the plankton biomass has been investigated in 12 lakes during two ice-free seasons (1996 and 1997) with some complementary data gathered in 1998. Preserved samples from all lakes were elaborated in 8 specialized labs and the database of organic carbon content in 7 components of pelagic biomass (bacteria, heterotrophic flagellates, ciliates, phytoplankton, picocyanobacteria, zooplankton small, zooplankton large) established. Species structure also was determined in several components: ciliates, phytoplankton and zooplankton. This dataset represents a unique complex survey on pelagic biota in remote lakes.

Numbers of autotrophic picoplankton (picocyanobacteria) were very low except of one lake. Photoinhibition in clear water lakes might be the reason. Also the numbers of heterotrophic bacterial grazers (heterotrophic flagellates and ciliates) were rather low and they reached a considerable biomass only occasionally. Most probably, a major grazing on bacteria in MOLAR lakes was accomplished by mixotrophic phytoplankton (flagellates), espec. *Dinobryon*, which was frequent in the lakes studied.

**Table 2.** Mean values of biomass (ug/l C) in pelagic food webs. Averages from all depths and from two ice-free seasons 1996 and 1997. Mean values of chemical parameters for the same period. BAC – bacteria, HNF - heterotrophic nanoflagellates, CIL - ciliates, HNF - heterotrophic nanoflagellates, CIL - ciliates, PHY - phytoplankton, ZOO – zooplankton, THMi - total heterotrophic microbial biomass, TBi - total pelagic biomass.

Lake	BAC	HNF	CIL	PHY	ZOO	THMi	Tbi	PHY/ THMi	ZOO/ PHY	THMi/ TBi	PHY+ THMi/ TBi	pH	alkali	TN	TP	TOC	TAL	RAL	
	ug/l C	ug/l C	ug/l C	ug/l C	ug/l C	ug/l C	ug/l C	ratio	ratio	%	%		ueq/l	ug/l	ug/l	mg/l	ug/l	ug/l	
Ovre Neadalsvatn	10.56	0.76	0.33	10.92	7.25	11.65	29.8	0.94	0.66	39	75	6.2	32	65	1	0.8	na	10	
Stavsvatn	18.47	1.85	0.16	46.65	42.7	20.48	110	2.27	0.92	19	61	5.9	18	181	1.5	1.6	na	85	
Lochnagar	26.49	1.85	0.07	10.84	29.26	28.41	68.5	0.38	2.7	41	57	5.3	7.5	304	3	1.5	85	30	
L. Paione	21.84	5.23	2.21	11.96	51.32	29.27	92.6	0.41	4.29	32	45	5.8	7.5	>365	2.5	na	na	na	
Superiore																			
Gossenkoellesee	9.93	5.99	0.21	84.88	27.22	16.13	128	5.26	0.32	13	79	6.8	86	410	2.5	0.4	na	na	
Estany Redo	3.67	4.15	4.04	34.05	5.5	11.86	51.4	2.87	0.16	23	89	6.4	47	251	3	0.9	na	na	
La Caldera	3.945	0.11	2.82	42.13	21.41	6.875	70.4	6.12	0.51	10	70	8.1	343	249	3.5	0.5	na	na	
Starolesnianske	32.26	14.64	4.5	879.8	4.725	51.40	936	17.12	0.005	5	100	5.0	-3	394	8	1	na	93	
pleso																			
Nizne Terianske	13.72	0.69	1.05	25.45	2.805	15.45	43.7	1.65	0.11	35	94	6.5	77	616	3.5	0.4	na	10	
pleso																			
Dlugi Staw	18.17	0.29	0.06	1.96	0	18.52	20.5	0.11	0.003	90	100	5.6	5	603	<1	na	na	na	
Chuna	7.43	0.59	0.1	44.11	64.05	8.12	116	5.43	1.45	7	45	6.2	20	96	2	2.3	12	na	
Joerisee	14.98	2.93	0	14.77	16.62	17.91	49.3	1.21	1.13	36	66	7.0	118	995	11	na	na	na	

The ranges of bacterial numbers and biomass found in all samples are in **Table 3**. The average values of carbon biomass of bacteria in particular lakes ranged within one order of magnitude and represented a considerable component of pelagic biomass. The average biomass of the autotrophic microbial component – phytoplankton, varied within a range surpassing one order of magnitude. Maximum biomasses of phytoplankton were found in the lake with the highest total phosphorus concentration, the lowest pH and a low zooplankton biomass – Lake Starolesnianské in Tatra Mts.

The total pelagic biomass in the lakes under study fell within the range of 10 to 3000  $\mu\text{g C l}^{-1}$  during particular sampling days. The three main components are bacterio-, phyto- and zooplankton except of the three lakes in Tatra Mts where zooplankton was rather scarce. In different lakes, any of these components might be the prevalent one in seasonal peaks.

In 11 lakes with a fully elaborated total pelagic biomass, its values, apparently, corresponded to the average total phosphorus concentrations, except of the lake Jóri. In two lakes with average P concentrations not surpassing  $1 \mu\text{g l}^{-1}$  (Ovre Neadalsvatn and Długi Staw), the average total pelagic biomasses did not surpass  $30 \mu\text{g l}^{-1}$  C. One lake with an “extreme” P concentration of  $8 \mu\text{g l}^{-1}$  (Starolesnianske Pleso) showed 30 times higher total biomass. The rest of the lakes with 2.5 to  $3.5 \mu\text{g l}^{-1}$  P and lake Jóri with  $11 \mu\text{g l}^{-1}$  P showed total biomasses from 44 to  $128 \mu\text{g l}^{-1}$  C. The most acidified lakes within this cluster with pH below 6 (Lochnagar, Lago Paione Superiore) had the lowest autotrophic to heterotrophic microbial biomass ratios and the highest heterotrophic microbial biomasses.

**Pelagic food webs 2<sup>nd</sup> level** for the assessment of primary production and exudation, bacterial production and elimination were investigated fully in 7 lakes and partly (without primary production) in two lakes. Both the field and laboratory work was done by specialized teams (4 partners) during two ice-free seasons. In most cases, there were the first data on carbon fluxes in pelagic food webs measured in remote lakes. The range of some measured fluxes are shown in **Table 3**.

The total primary production was assessed, including algal exudation and bacterial utilization of algal exudates. The lowest total primary production was measured in Długi Staw, whereas the highest values were found in Starolesnianské pleso, which could be qualified as almost mesotrophic. The values of extracellular production (EOC), which provided a readily available organic substrate for pelagic bacteria, reached 70 – 80% in MOLAR lakes, whereas just 40% and less was found in meso- to eutrophic lowland lakes and reservoirs (Straškrabová *et al.* 1999b). In the lakes studied, the % of EOC was, at the average, inversely related to the value of total production: In the “mesotrophic” lake Starolesnianské, it did not surpass 47%, whereas in the extremely low productive Długi Staw, EOC % was 57-75%. Primary production per area could reach considerable values in deep lakes due to high transparency and, consequently, high depth of euphotic layer.

Consistently with this, bacterial production in lakes with different “trophy” (total primary production) was more related to absolute values of EOC (algal exudation) than to the values of total production and often it is comparable with the values found in meso- to eutrophic lowland lakes in winter. The elimination rates were often lower than production rates and this is in concordance with the scarcity of potential bacterivores in the lakes.

The main carbon fluxes in pelagic region of a MOLAR lake are shown in **Figure 12** (example of the epilimnion in Ovre Neadalsvatn). The major fluxes were: uptake of inorganic C (DIC) by phytoplankton, exudation of dissolved organic C and direct uptake of exudates by bacteria. All the other fluxes were by two orders lower. Several fluxes could not be measured and should be only estimated. The most uncertain flux, which might be of different significance in different lakes, is the input of organic carbon from external source and its availability to bacteria. The pool of non-biomass organic C is always the major organic C compartment in pelagial. In alpine lakes above timber line, the external organic C input was considered to be negligible compared to in-lake production.

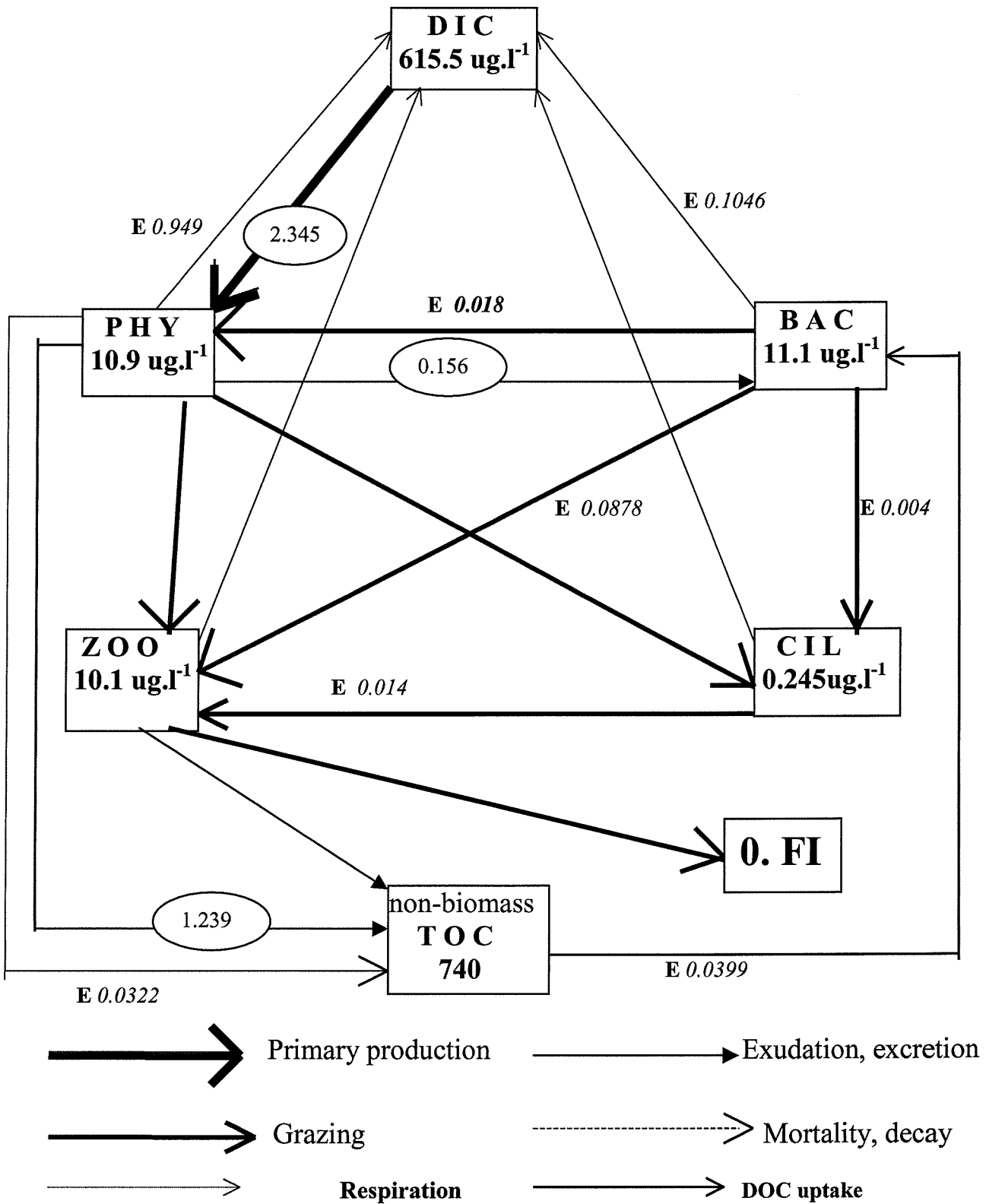
However, the results of MOLAR project showed that this is not always true. A low phytoplankton to heterotrophic biomass ratio in some lakes (Dhugi Staw, Lago Paione Superiore and Lochnagar) and also a high zooplankton to phytoplankton biomass ratio in the two latter lakes, suggested a significant external source besides the in-lake primary production. The same is indicated from estimates of carbon budget in Lake Redo (Camarero *et al.* 1999).

**Table 3.** Ranges of bacterial numbers and biomasses in all samples from the pelagial of 12 MOLAR lakes

Parameter	Total range	3 lowest values	3 highest values
numbers, $10^6 \text{ ml}^{-1}$	0.06 – 9.79	0.06, 0.08, 0.11	2.09, 2.73, 9.79
mean volumes, $\mu\text{m}^3$	0.01 – 1.46	0.01, 0.01, 0.03	0.60, 0.95, 1.46
mean lengths, $\mu\text{m}$	0.3 – 4.1	0.3, 0.4, 0.5	3.1, 3.9, 4.1
carbon biomass, $\mu\text{g l}^{-1}$	0.84 – 144.2	0.84, 1.40, 1.41	91.5, 113.5, 144.2

**Table 4.** Primary production and bacterial production in mountain lakes – ranges of measured values in 7 lakes. GPP-C – gross primary production expressed in C, EOC – extracellular production in % of GPP-C, THY – bacterial uptake of thymidine (range in parentheses – with higher specific activity of thymidine), LEU – bacterial uptake of leucine.

Parameter	Ranges of values found
GPP-C $\mu\text{g l}^{-1}\text{h}^{-1}$	0.06 - 17.0
EOC %	3 - 80
THY $\text{pmol l}^{-1}\text{h}^{-1}$	0.05 - 0.9 (1.2 – 15.1)
LEU $\text{pmol l}^{-1}\text{h}^{-1}$	0.7 - 50



**Figure 12.** Carbon flow chart in Ovre Neadalsvatn, epilimnion 0 – 3 m, Aug.19-21, 1996. All compartments (boxes) were directly measured except of fish. Fluxes in  $\mu\text{g.l}^{-1}\text{h}^{-1}$  (values in ovals-



directly measured, E-estimates based on measurements). DIC-dissolved inorganic C, TOC-total organic C, PHY-phytoplankton, BAC-bacteria, ZOO-zooplankton, CIL-ciliates.

### **5.1.6 Evaluate applicability of various critical load models to mountain lake ecosystems, and develop a linked chemical-biological model for scenario assessment**

The *MAGIC model* for trends and prognosis has been used for six lakes. Special workshops have been arranged to carry out the calculations and discuss the necessary data from the sites. Reporting for the sites are planned and started. A Workshop for deposition, water chemistry and modelling was arranged in London in November 1998.

MAGIC has been calibrated for all 6 lakes, and used to predict future trends in water chemistry given full implementation of the Oslo (1994) and Gothenburg (1999) protocols to the UN-ECE Convention on Long-range Transboundary Air Pollution. The 6 lakes are: Gossenköllesee (GKS), Estany Redó (RED), Ovre Neadalsvatn (NEO), Lochnagar (NAG), Starolesnianske Pleso (STA), Stavsvatn (SVN). The first three are circum-neutral and exhibit only minor acidification due to acid deposition, whereas the last 3 are acidified with high concentrations of aluminium and damage to fish and other organisms.

Stavsvatn (SVN) in southern Norway exemplifies the changes predicted by the MAGIC model given a future scenario of reduced acid deposition. There is a 12-year data record from this lake, which allows splitting of the data into a calibration period of 3 years (1986-88) and an evaluation (testing) period of 9 years (1989-1997). The model was driven by the measured deposition during this 12-year period. The results show close agreement between observed and modelled concentrations of major ions for the period (**Figure 13**).

The calibrated model when run for 50 years into the future under the scenario of full implementation of the Oslo protocol (reduced S deposition relative to the year 1980), indicates that the water quality in the lake will continue to improve.

Data from the 6 lakes were also used to calculate critical loads using MAGIC and several standard steady-state models. These results indicate that all methods give roughly similar estimates for critical loads. MAGIC shows that achievement of new steady-state following change in deposition occurs with lag times of years-to-decades depending upon such factors as soil characteristics and lake hydraulic retention time.

Uncertainties in predictions come from difficulties in predicting future nitrogen retention and release in mountain areas. In addition from the model application it is clear that year-to-year variations in climatic conditions influence the surface water chemistry. Lon-term change in climate can also affect future lake water quality.

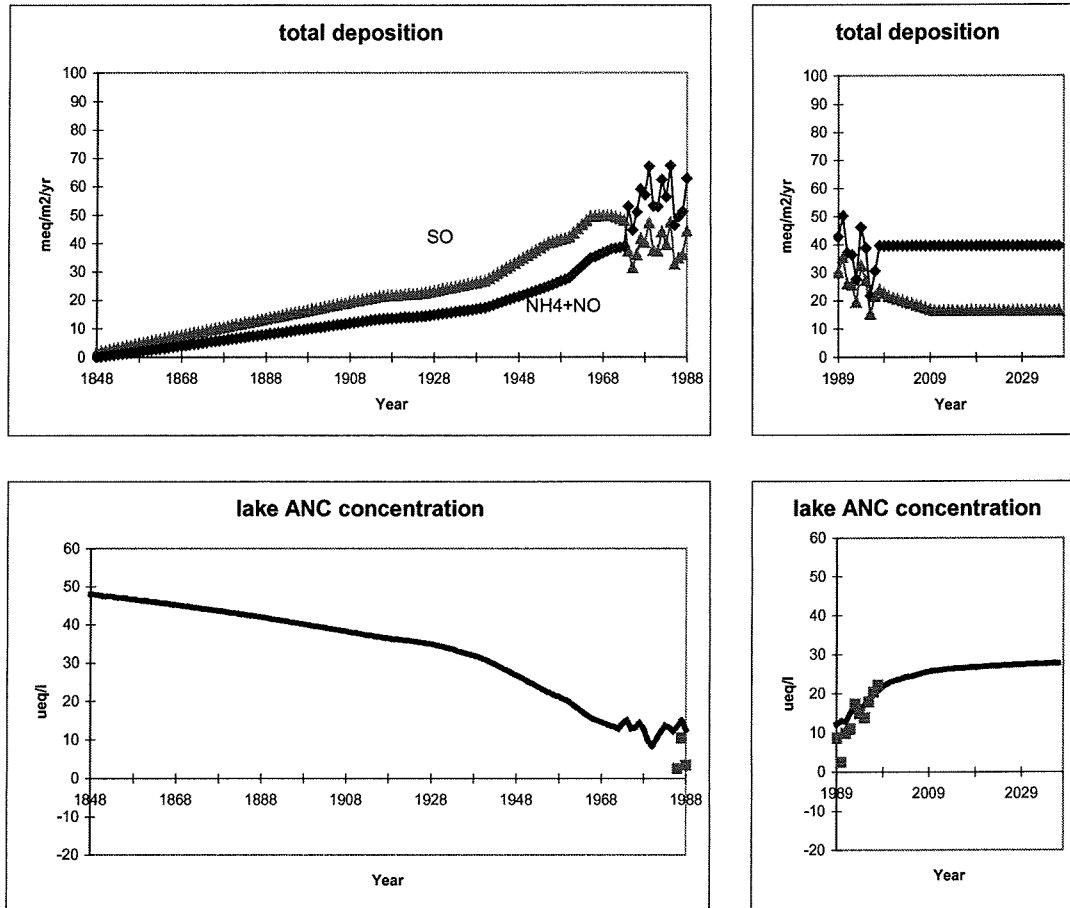
These model applications comprise the first step in extrapolation to entire mountain lake regions.

## Stavsvatn

Scenario: Oslo protocol

Hindcast period 1857 - 1997

Forecast period 1998-2047



**Figure 13.** MAGIC model calibration (left-hand panels) and prediction (right-hand panels) of lake water chemistry at Stavsvatn, southern Norway. Upper panels: historical (1848-1985), measured (1986-1997), and predicted (1998-2038) deposition of S and N. Lower panels: modelled (solid line) and observed (squares) ANC (acid neutralising capacity) in lakewater.

### 5.1.7 Application of static critical loads models to high mountain lakes, and assessment of their applicability for critical load and linked chemical-biological modelling

#### Methods

Critical loads for total acidity provide a measure of the sensitivity of freshwater bodies to the deposition of both acidifying sulphur and nitrogen deposition. For sulphur, the neutral marine input has to be subtracted from deposition inputs, because it is only the non-marine component which is accompanied by  $H^+$  (see **Table 4**). If it is assumed that chloride in precipitation is of marine origin, then using the known chemical composition of seawater it is possible to use measured chloride concentrations to subtract the proportion of each major ion which is delivered as neutral sea salt. For nitrogen, both oxidised (nitrate) and reduced (ammonium) forms are assumed to contribute in the same way to net acid deposition, because it is assumed that all ammonium is either taken up by terrestrial or aquatic biota, or nitrified to nitrate (resulting in a net release of acidity). Total N deposition is therefore used in the calculation of critical load exceedance (**Table 4**).

Static critical loads models have been applied to all 11 sites for which both water chemistry and acid deposition data are available (**Table 4**). The most simple, empirically based models require only water chemistry data for the calculation of critical load, plus a measure of acid deposition data to calculate critical load exceedance. Two such models are used here, the Steady State Water Chemistry model (SSWC - Henriksen *et al.* 1992) and the Diatom model (Battarbee *et al.* 1996, Allott *et al.* 1995).

The SSWC model employs a series of empirical relationships to determine the permanent buffering (in terms of base cation leaching) afforded by weathering processes, and from this determines the maximum flux of acid deposition which will maintain acid neutralizing capacity (ANC) above a pre-selected threshold value. The critical value of ANC can be chosen on the basis of known relationships between biological response and ANC. The most widely used thresholds are chosen to relate to the likelihood of damage to brown trout populations (see Lien *et al.* 1992, 1996).

The diatom model uses an empirically determined relationship between the ratio of lakewater calcium concentration and acid deposition to the status of the diatom population of a water body. In calibration lakes, lake sediments were used to determine which lakes had acidified, as defined by a change in the diatom population from pre-industrial conditions. The calibrated model requires only the chemical data described above. The data used for both models are the annual mean values.

Since the empirical critical load models take no account of N cycling in catchments, they cannot be used to assess the effects of changes in N deposition without assuming that nitrate leaching will not change (which is contrary to theories of N saturation in terrestrial systems). The First-order Acidity Balance (FAB) model is a process-based model which was developed to take account of the major sinks for N in order to assess the potential effects of changes in N deposition (Posch *et al.* 1997). Using the pre-industrial leaching rate of base cations from the SSWC model, FAB employs a mass-balance to determine those combinations of S and N deposition which will result in the selected critical ANC value. Since the FAB model quantifies the removal of N by soils, vegetation and in-lake retention, it requires certain lake catchment data as model inputs (**Table 4**), including lake: catchment area ratio, percentage cover of major soil types, and percentage cover of forest which is removed by logging (which is zero for all MOLAR sites). Note that Lago Paione Inferiore is assumed to have the same soil characteristics as the nearby Lago Paione Superiore. Since forestry is absent from MOLAR catchments, and grazing removal of vegetation is assumed to be minimal, the major sinks for N in the catchment are determined by soil type and in-lake retention.

There are two routes by which catchment soils can remove N from runoff passing through the catchment, denitrification and long-term immobilisation of N in soil organic matter. Denitrification processes, which release N back to the atmosphere primarily as N<sub>2</sub>O, require anaerobic conditions and are thus determined largely by soil type. In the FAB model, peat soils are assumed to be the main driver of denitrification, and a linear equation is used to determine the proportion of N inputs which are denitrified ( $f_{de}$ ):

$$f_{de} = 0.1 + 0.7f_{peat}$$

where  $f_{peat}$  is the proportion of peat soils in the catchment (Posch *et al.* 1997). Denitrification of N therefore accounts for between 10% (no peat soil present in catchment) and 80% (for 100% peat soil coverage of catchment) of net inputs to the catchment soils. Since peat is absent from all MOLAR WP1 sites,  $f_{de} = 0.1$ . However, one characteristic of the high-mountain MOLAR catchments is that soil cover is usually sparse, so here the soil-based sinks for N are weighted by the percentage of soil cover for each catchment (**Table 4**). Estimated soil cover varies from 8% in the catchment of Laghetto Inferiore, up to 70% for Estany Redó and Dlugi Staw.

Similarly, N immobilisation in soils is dictated by soil type and cover. Unlike input-dependent denitrification rates, however, N removal is assumed to occur at a fixed rate for each soil type. Literature based N immobilisation rates have been assigned to different soil types (Hall *et al.* 1997) and range from 1-3 kgN ha<sup>-1</sup> yr<sup>-1</sup> (0.071 - 0.214 keq ha<sup>-1</sup> yr<sup>-1</sup>). As for denitrification, N immobilisation rates have been adjusted to account for the percentage cover of soils within each catchment (**Table 4**).

In-lake retention of both S and N is an input-dependent process, determined largely by retention time, which is a function of lake: catchment ratio (**Table 4**) and runoff. It is calculated according to the method of Kelly *et al.* (1987), using literature-based values for the mass-transfer coefficients for N ( $S_N = 5.0 \text{ m yr}^{-1}$ ) and S ( $S_S = 0.5 \text{ m yr}^{-1}$ ) derived for lakes in North America and elsewhere (see Kelly *et al.* 1987, Dillon and Molot 1990, Posch *et al.* 1997).

### Results

SSWC and Diatom model critical loads are given in **Table 6**. For SSWC model applications, two values for the critical ANC threshold ( $ANC_{crit}$ ) have been selected, 0  $\mu\text{eq l}^{-1}$ , as used in the UK, and 20  $\mu\text{eq l}^{-1}$  as used in Norway and in a previous application of the model to AL:PE sites (Mosello *et al.* 1995). They indicate a wide range of acid-sensitivity in MOLAR sites. The lowest critical loads, indicating the most sensitive sites, are found at Starolesnianske Pleso in the Tatra Mountains, the two Norwegian sites (Ovre Neadalsvatn, Stavsvatn), Lago Paione Superiore in the Italian Alps, and Lochnagar, Scotland. The least acid-sensitive sites, indicated by the largest critical load values, are Jörisee and Laghetto Inferiore (Swiss Alps), and Gossenköllesee (Austrian Alps).

The critical load of three sites (Starolesnianske Pleso, Dlugi Staw in the Polish Tatra and Lago Paione Superiore) are exceeded using  $ANC_{crit} = 0 \mu\text{eq l}^{-1}$  in the SSWC model, while the use of  $ANC_{crit} = 20 \mu\text{eq l}^{-1}$  leads to increased exceedance at these sites plus the exceedance of critical load at an additional site, Lochnagar. The exceedance at Dlugi Staw despite its relatively high critical load value is due to the fact that it experiences the highest acid deposition inputs of all MOLAR WP1 sites (**Table 4**). The lowest observed values of lakewater ANC correspond with these exceeded sites, the exceptions being the two Norwegian sites which are not exceeding their critical loads despite very low ANC values (**Table 6**) Again, this is explained by the levels of acid deposition at these sites, which are very low.

Application of the diatom model produces lower critical loads for all sites because of the greater sensitivity of the model, and while the same four sites show exceedance (Starolesnianske Pleso, Dlugi Staw, Lago Paione Superiore, Lochnagar), Laghetto Inferiore is also slightly exceeded.

With the FAB model it is not possible to define a single value for a critical load, because both S and N are considered and behave independently, so that the critical load for one species is dependent on the critical load of the other. Instead, a critical load function (CLF) is generated for each site, whereby the series of paired critical loads for S and N can be plotted on axes of S and N deposition to define Deposition and catchment data for MOLAR WP1 sites (units in keq ha<sup>-1</sup> yr<sup>-1</sup> unless otherwise specified)

**Table 5.** Deposition and catchment data for MOLAR WP1 sites (units in  $\text{keq ha}^{-1} \text{yr}^{-1}$  unless otherwise specified)

Lake	Non-marine S deposition		Total N depn. ratio		Lake/cmt. cover (%)		Primary soil type		% of soil		Secondary soil type		% of soil		Weighted $N_{\text{imm}}$		Weighted $f_{\text{de}}$ fraction	
	S	N	ratio	cover	soil type	soil	$N_{\text{imm}}$	soil type	soil	$N_{\text{imm}}$	soil type	soil	$N_{\text{imm}}$	soil	$N_{\text{imm}}$	$N_{\text{imm}}$	$f_{\text{de}}$	
Ovre Neadalsvatn	0.08	0.20	0.031	42	Podzol	100	0.214		100	0.214		0.090	0.042		0.090	0.042		0.042
Stavsvatn	0.13	0.21	0.165	61	Podzol	100	0.214		100	0.214		0.131	0.061		0.131	0.061		0.061
Lochnagar	0.42	0.61	0.096	50	Alpine podzols	100	0.214		100	0.214		0.107	0.050		0.107	0.050		0.050
Lago Paione Superiore	0.40	0.78	0.026	30	Rankers	75	0.071	Dystric cambisols	25	0.071	0.021	0.071	0.030		0.071	0.021		0.030
Lago Paione Inferiore	0.40	0.78	0.012	30	Rankers	75	0.071	Dystric cambisols	25	0.071	0.021	0.071	0.030		0.071	0.021		0.030
Gossenköllesee	0.12	0.28	0.106	26	Rankers	90	0.071	Podzols	10	0.214	0.022	0.050	0.070		0.050	0.070		0.070
Estany Redó	0.29	0.38	0.155	70	Umbric leptosol	100	0.071		100	0.071		0.049	0.068		0.049	0.068		0.068
Starolesnianske Pleso	0.58	0.48	0.277	68	Rankers/lithosols	100	0.071		100	0.071		0.050	0.070		0.050	0.070		0.070
Długi Staw	0.85	0.77	0.024	70	Regosols/lithosols	54	0.071	Lithosols	46	0.071	0.050	0.021	0.010		0.021	0.010		0.010
Jörisee	0.13	0.21	0.044	10	Alpine podzol	100	0.214		100	0.214		0.017	0.008		0.017	0.008		0.008
Laghetto Inferiore	0.50	0.66	0.030	8	Alpine podzol	100	0.214		100	0.214		0.017	0.008		0.017	0.008		0.008

**Table 6.** Critical loads and exceedances for MOLAR WP1 sites (bold indicates critical load exceedance)

Lake	ANC $\mu\text{eq l}^{-1}$	SSWC MODEL			DIATOM MODEL			FAB MODEL			ANC <sub>crit</sub> =20 $\mu\text{eq l}^{-1}$		
		ANC <sub>crit</sub> =0 $\mu\text{eq l}^{-1}$	CL	Ex.	ANC <sub>crit</sub> =20 $\mu\text{eq l}^{-1}$	CL	Ex.	CLmin	CLmax	CLmaxN Exceedance	CLmin	CLmax	CLmaxN Exceedance
Ovre Neadalsvatn	27	0.55	-0.44	0.28	0.33	-0.24	0.09	0.55	0.72	-0.37	0.28	0.41	-0.10
Stavsvatn	20	0.51	-0.32	0.33	0.45	-0.30	0.11	0.56	1.14	-0.34	0.36	0.77	-0.16
Lochnagar	25	0.73	-0.13	0.54	0.36	<b>0.23</b>	0.10	0.77	1.25	<b>0.00</b>	0.57	0.96	<b>0.19</b>
Lago Paione Superiore	2	0.68	<b>0.05</b>	0.43	0.40	<b>0.29</b>	0.02	0.69	0.79	<b>0.39</b>	0.43	0.51	<b>0.64</b>
Lago Paione Inferiore	30	1.10	-0.37	0.84	0.65	-0.02	0.02	1.10	1.21	<b>0.01</b>	0.84	0.92	<b>0.27</b>
Gossenköllesee	100	1.67	-1.35	1.46	1.39	-1.23	0.02	1.75	2.57	-1.38	1.53	2.24	-1.17
Estany Redó	44	0.99	-0.55	0.74	0.77	-0.35	0.04	1.05	1.75	-0.52	0.79	1.31	-0.27
Starolesnianske Pleso	-18	0.34	<b>0.37</b>	0.13	0.27	<b>0.48</b>	0.03	0.38	0.86	<b>0.35</b>	0.15	0.36	<b>0.56</b>
Długi Staw	12	1.34	<b>0.19</b>	1.01	0.78	<b>0.72</b>	0.05	1.35	1.59	<b>0.13</b>	1.02	1.22	<b>0.45</b>
Jörisee	107	1.81	-1.48	1.58	1.28	-1.11	0.02	1.84	2.20	-1.52	1.61	1.93	-1.29
Laghetto Inferiore	38	1.73	-0.90	1.31	0.65	<b>0.05</b>	0.02	1.74	1.88	-0.64	1.32	1.43	-0.22

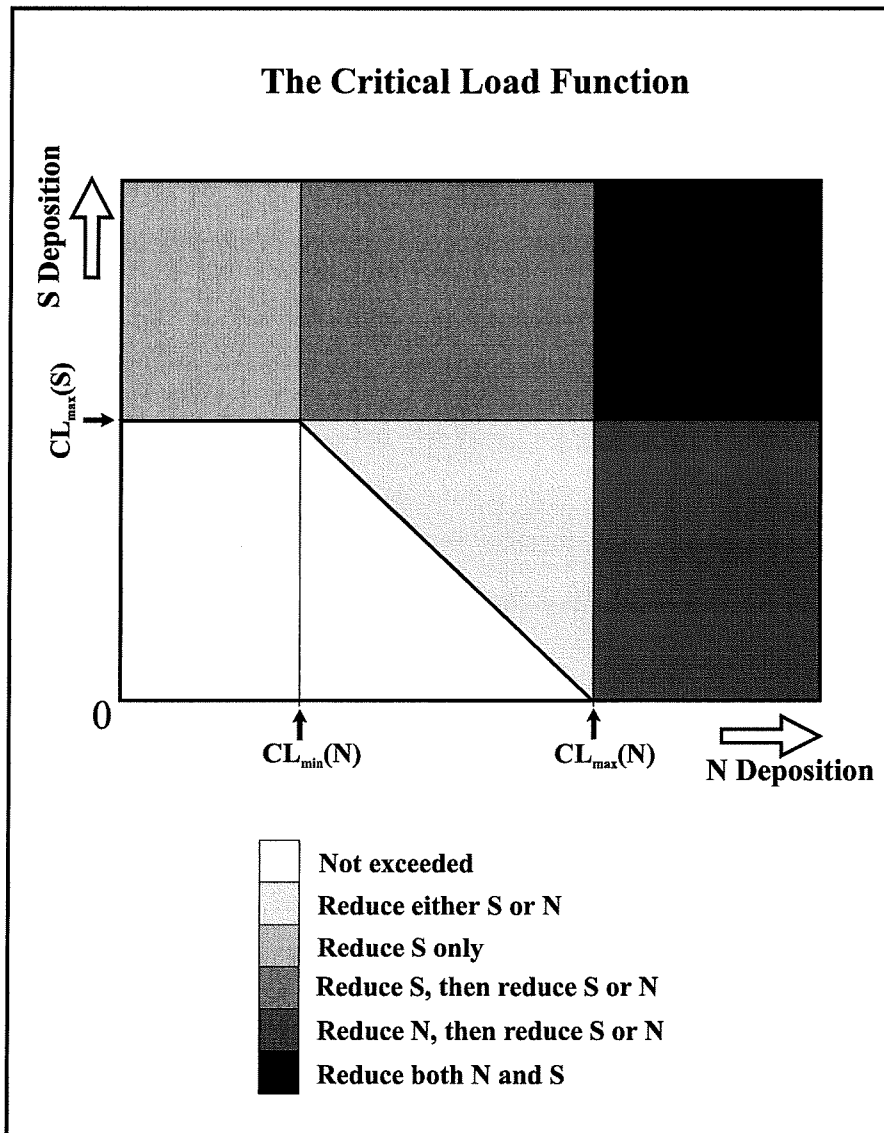
those combinations of S and N deposition which lead to critical load exceedance (see **Figure 14**). For any pair of values of S and N deposition, the position on the CLF determines whether S or N deposition, or some combination of the two, must be reduced to prevent critical load exceedance. The CLF for each MOLAR site, using  $ANC_{crit}$  values of  $0 \mu eq l^{-1}$  and  $20 \mu eq l^{-1}$ , is shown in **Figure 15**. The effect of using a more stringent value of  $ANC_{crit}$  can be clearly seen; values of both  $CL_{maxS}$  and  $CL_{maxN}$  are reduced (see also **Table 6**) leading to greater exceedances of the critical load.

Although it is not possible to determine a single critical load value, it is possible to calculate the exceedance of critical load as a flux of acidity (**Table 6**). Unlike the SSWC and diatom models, an exceedance with the FAB model does not indicate the figure by which deposition must be reduced in order to protect the site, because the reduction of S deposition would have a different effect on acidity fluxes from a reduction in N deposition. A FAB model exceedance therefore provides only a simple measure of potential harm, expressed as a flux of acidity which could be converted back into a value of ANC. A greater value of exceedance indicates that a lower (more negative if  $ANC_{crit} = 0 \mu eq l^{-1}$ ) ANC will ultimately result from the given level of deposition.

Since the FAB model predicts what the future leaching of nitrate will be at steady-state, rather than taking the current measured value of lakewater nitrate as an indication of the effect of N deposition (Curtis *et al.* 1998), it tends to generate greater values of critical load exceedance than either the SSWC or diatom models, although this is sometimes offset by the inclusion of an in-lake retention term for S which in the other models is assumed to be completely mobile and contributing to exceedance. For both values of  $ANC_{crit}$  there are five sites showing exceedance; Starolesnianske Pleso, Dlugi Staw, Lago Paione Superiore, Lochnagar and Lago Paione Inferiore. While Lochnagar and Lago Paione Inferiore are only marginally exceeded for  $ANC_{crit} = 0 \mu eq l^{-1}$  they show greater exceedance for  $ANC_{crit} = 20 \mu eq l^{-1}$ .

In most cases of exceedance with the FAB model, either N or S deposition could be reduced in order to protect the site (**Figure 14**). Nitrogen, and not just sulphur, is therefore contributing to exceedance at all these sites. At Starolesnianske Pleso  $CL_{maxS}$  is exceeded by S deposition, indicating that sulphur alone is sufficient to cause critical load exceedance regardless of whether N deposition is reduced. Similarly, at both Starolesnianske Pleso and Lago Paione Superiore (for  $ANC_{crit} = 20 \mu eq l^{-1}$ ) N deposition exceeds  $CL_{maxN}$ , and is therefore sufficient to cause exceedance even if S deposition were reduced to zero (**Figure 15**). Starolesnianske Pleso is the only site where both S and N deposition are sufficiently high to cause critical load exceedance on their own, and this is reflected by the negative ANC at the site.

It has been found that nitrate leaching from some British upland catchments is much lower than the deposition input flux of N, indicating N retention or removal by terrestrial or freshwater biota (Curtis *et al.*, 1998). This is reflected here by the horizontal distance between the points representing measured leaching flux and deposition on the CLF diagrams (**Figure 15**), which for all sites indicates a degree of N retention. However, in the same study the mobility of S in catchments generally resulted in sulphate leaching fluxes which were similar to deposition inputs (Curtis *et al.* 1998), i.e. the vertical distance between the two points on the CLF diagrams was very small.



**Figure 14.** The Critical Load Function defined by the FAB model

A striking feature of many of the CLF diagrams here (**Figure 15**) is that sulphate leaching appears to be greater than deposition inputs (for example at Ovre Neadalsvatn, Stavsvatn, Gossenköllesee, Jörisee and Laghetto Inferiore). Two possible mechanisms for such an observation are sulphur desorption or the weathering of sulphur bearing minerals. The desorption of sulphate from the soil exchange complex could occur in lake catchments which have experienced a reduction in S deposition, but while S emissions have been reduced across much of Europe in recent years this is only likely to be an important process in catchments with significant cover of deeper soils. In the 3 Alpine sites (Gossenköllesee, Jörisee and Laghetto Inferiore) the sparsity of soil cover would suggest that a weathering source of S is more likely. The source of the excess sulphur cannot, however, be confirmed without further study.

Vertical axis: non-marine S deposition  
 Horizontal axis: total N deposition

All units in  $\text{keq ha}^{-1} \text{ yr}^{-1}$

△ Current leaching  
 ◆ Current deposition

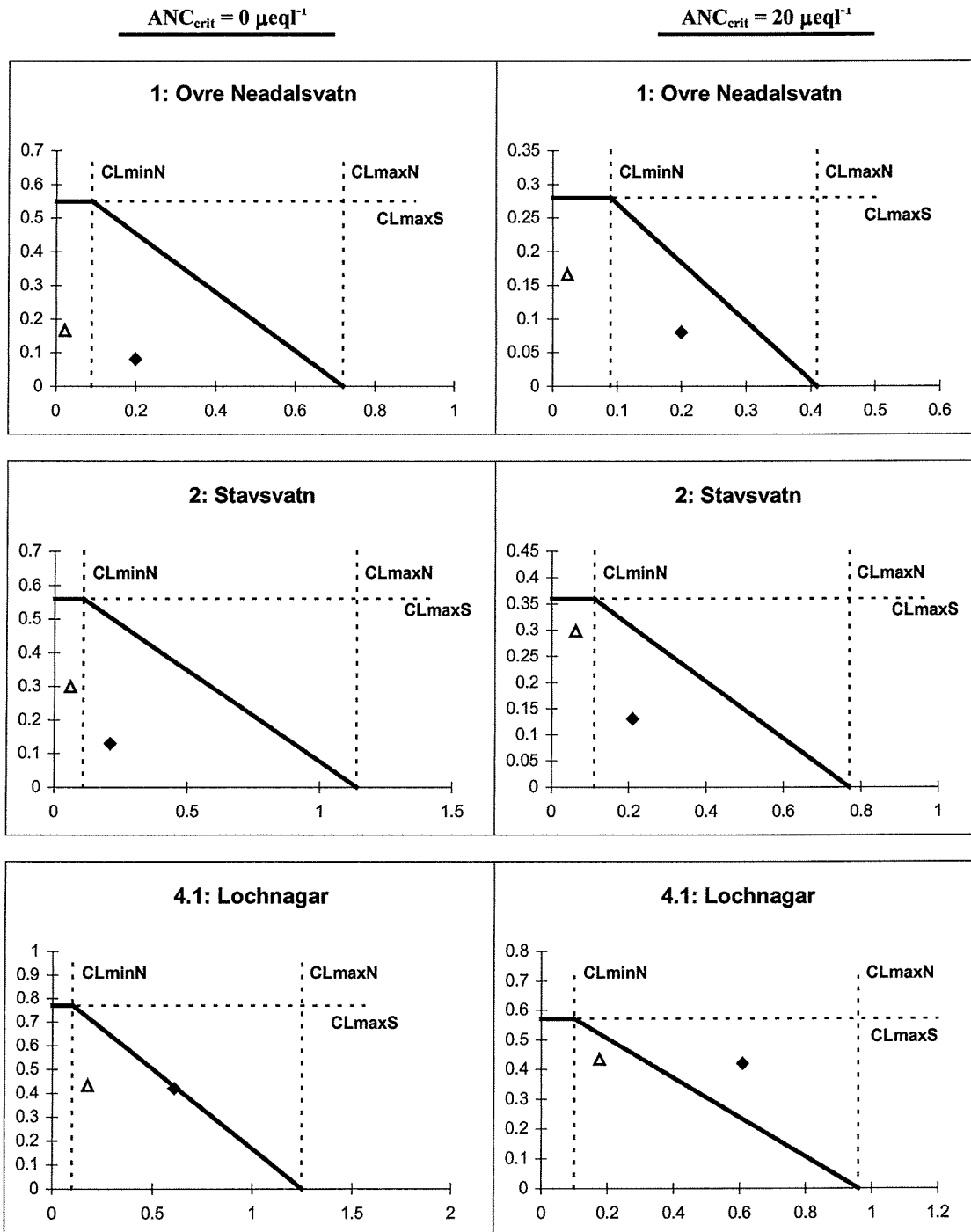


Figure 15. Critical Load Function diagrams for MOLAR sites



Vertical axis: non-marine S deposition  
 Horizontal axis: total N deposition

△ Current leaching  
 ◆ Current deposition

All units in  $\text{keq ha}^{-1} \text{ yr}^{-1}$

$\text{ANC}_{\text{crit}} = 0 \mu\text{eq l}^{-1}$

$\text{ANC}_{\text{crit}} = 20 \mu\text{eq l}^{-1}$

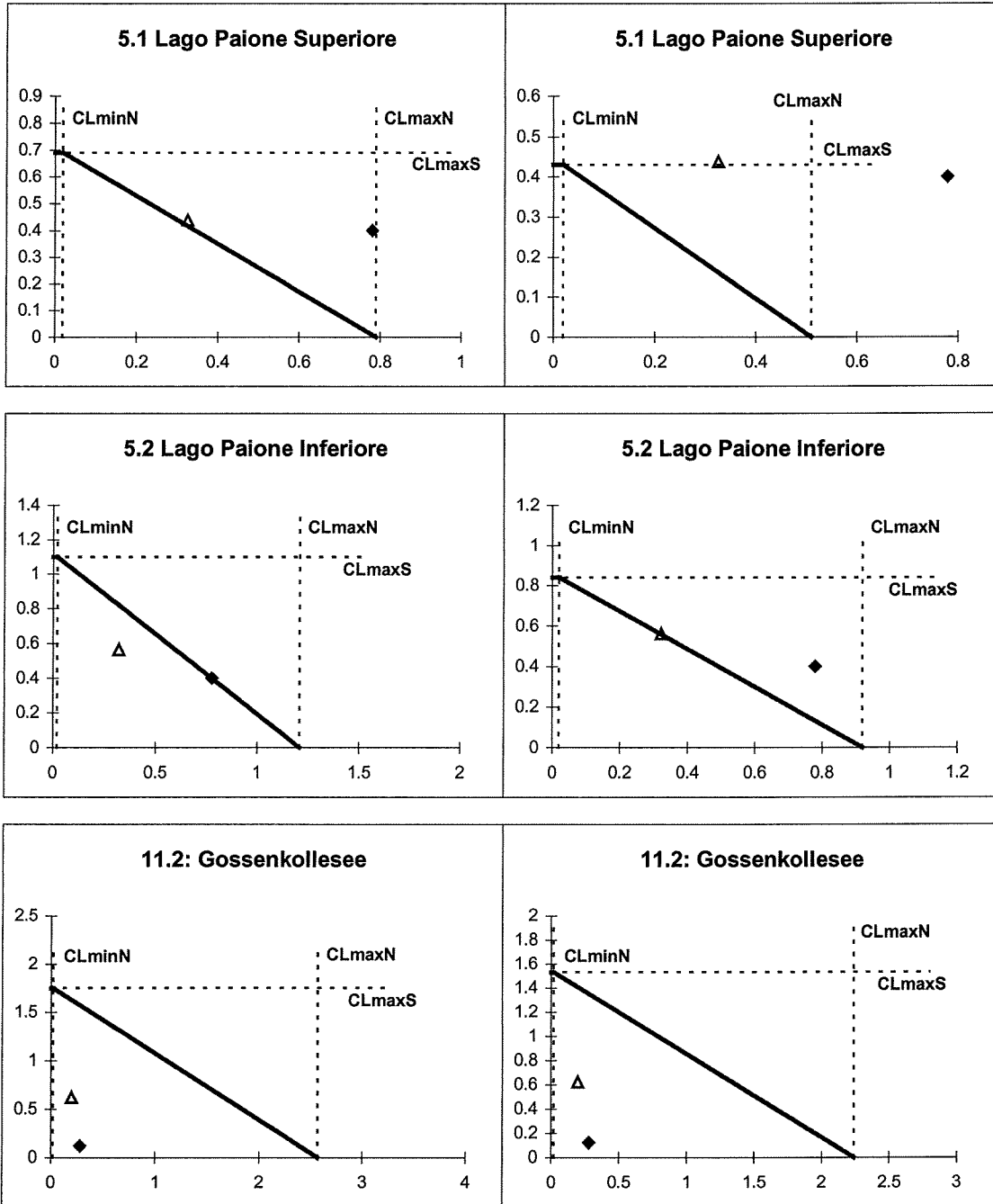


Figure 15: Critical Load Function diagrams for MOLAR sites (continued)

Vertical axis: non-marine S deposition  
 Horizontal axis: total N deposition

△ Current leaching  
 ◆ Current deposition

All units in  $\text{keq ha}^{-1} \text{ yr}^{-1}$

$\text{ANC}_{\text{crit}} = 0 \mu\text{eq l}^{-1}$

$\text{ANC}_{\text{crit}} = 20 \mu\text{eq l}^{-1}$

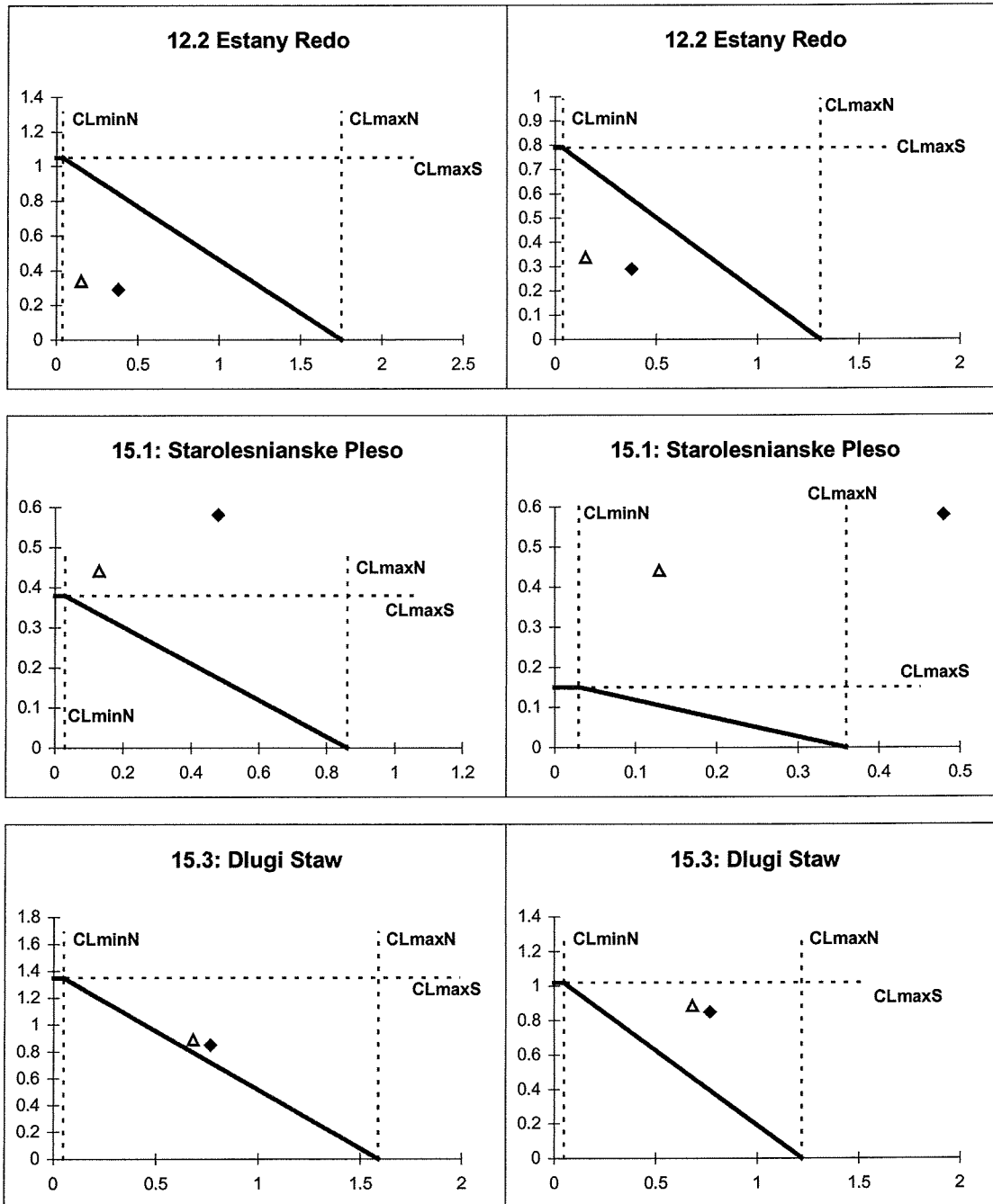


Figure 15: Critical Load Function diagrams for MOLAR sites (continued)

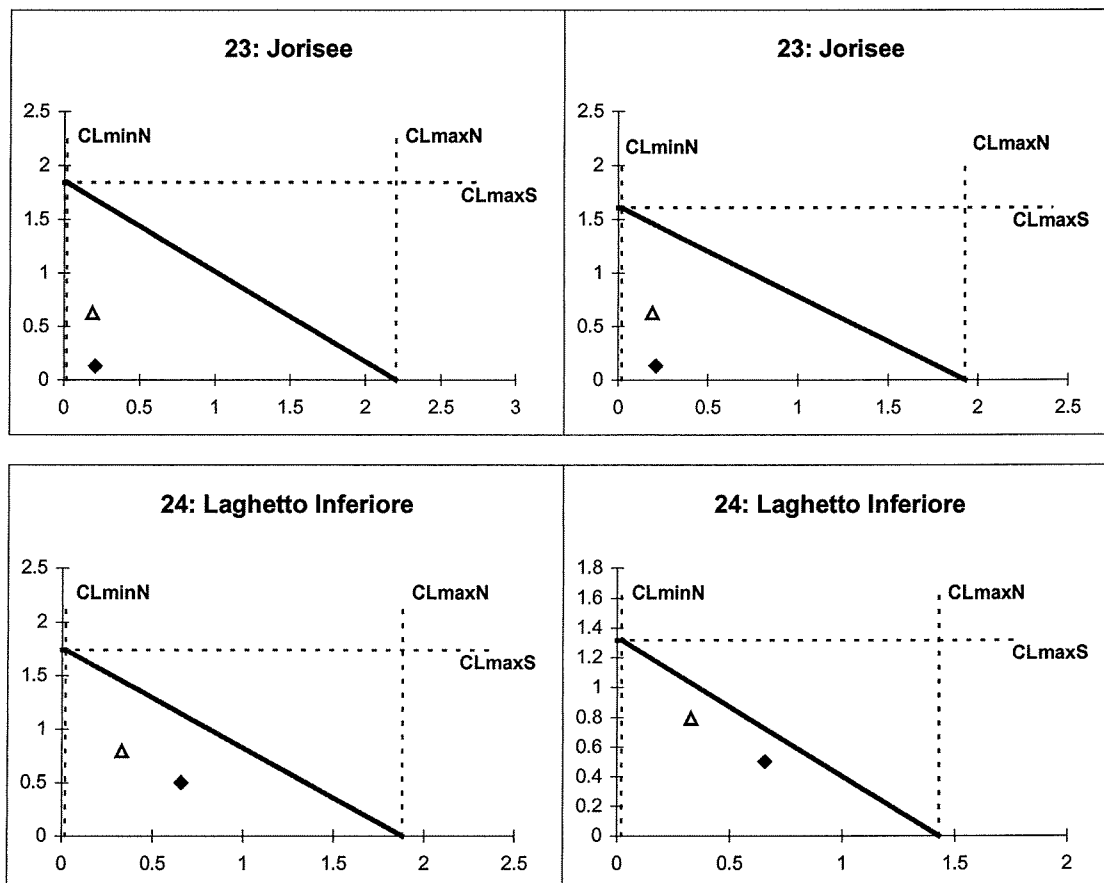
Vertical axis: non-marine S deposition  
 Horizontal axis: total N deposition

△	Current leaching
◆	Current deposition

All units in  $\text{keq ha}^{-1} \text{ yr}^{-1}$

$\text{ANC}_{\text{crit}} = 0 \mu\text{eq l}^{-1}$

$\text{ANC}_{\text{crit}} = 20 \mu\text{eq l}^{-1}$



**Figure 15:** Critical Load Function diagrams for MOLAR sites (continued)

*Discussion*

The chemical range of the MOLAR lake sites is reflected in the modelled critical load values, from acid-sensitive to very alkaline, insensitive conditions. The large variation in deposition inputs, from the very low levels in northern Norway and parts of the Swiss and Austrian Alps to the highly acid inputs in the Tatra mountains and parts of the Italian Alps, leads to a variety of responses in terms of critical load exceedance.

Three sites are exceeded according to all critical load models; Lago Paione Superiore, Starolesnianske Pleso and Długi Staw. Other sites have low critical loads which can lead to exceedance depending on the model used. Lochnagar is exceeded in all but one of the model applications, Lago Paione Inferiore is very close to exceedance according to the SSWC and diatom models while the FAB model shows that it is exceeded, and the otherwise insensitive Laghetto Inferiore is exceeded only according to the diatom model.

Low critical loads and ANC values at three of the remaining sites (Ovre Neadalsvatn, Stavsvatn and to a lesser degree, Estany Redó) indicate high or moderate degrees of acid-sensitivity, but these sites do not demonstrate critical load exceedance because of relatively low deposition levels. Only two of the MOLAR sites, Gossenköllesee and Jörisee, are extremely insensitive to acid deposition and they are both located in the central Alps. These two sites also show the greatest difference between deposition inputs of S and sulphate leaching (which is greater), indicating weatherable catchment mineralogies.

Critical load exceedance indicates that at some unspecified point in time, the critical chemical threshold will be crossed. With the SSWC and FAB models, this means that ANC will at some point decline to less than the selected critical value, whether 0 or 20  $\mu\text{eq l}^{-1}$ , and will therefore have an adverse effect on the target organism (e.g. brown trout populations). An exceedance with the diatom model indicates that the diatom flora is likely to have changed from pre-industrial conditions, and this can be tested by palaeolimnological investigation of lake sediment cores. None of the static models employed here can, however, indicate the likely timing of damage, which may have already occurred or which might result in several decades time. Only a dynamic model like MAGIC can predict the timing of acidification damage.

The sparsity of soil and vegetation cover in these high mountain catchments means that there is minimal capacity for retention of atmospheric acid inputs in the terrestrial part of the catchments, but the observation that N leaching is smaller than N inputs at all sites does indicate some degree of N retention. It is not possible to determine from current data whether this occurs in the terrestrial or in-lake part of the catchment. With the exception of sites like Gossenköllesee and Jörisee where high weathering rates seem to provide a large buffering capacity against acidification, these high-mountain lakes do seem to be very sensitive to acid deposition. It is evident that both sulphur and nitrogen inputs contribute to critical load exceedance at all affected sites, so future reductions in S deposition across Europe resulting from the implementation of the Second Sulphur Protocol of the UNECE could mean that nitrate becomes the dominant acid anion in the future.

Linked chemical-biological models are still under development, but the main potential for such models lies in the ability of critical load models to predict ANC, so that if the biological response to ANC can be determined it should be possible to predict the possible biological impacts of a specified deposition load.

## 5.2 MOLAR Work Package 2 (WP2)

### MEASURING AND MODELLING MAJOR ELEMENT AND POLLUTANT FLUXES IN MOUNTAIN LAKES AND THEIR IMPACT ON FISH

#### Topics

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- Deposition and snow pack analyses: ions, metals, radionuclides, PCBs, PAHs, SCPs
- Distribution (speciation) of  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ , organic pollutants and metals in lake water
- Fluxes of  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ , PCB, PAH, SCP to the catchment, the lake, and the sediment
- Uptake of PCB, PAH, and metals by fish: measurements and modelling

#### Sites

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##### Primary sites:

Gossenköllesee (GKS), Estany Redó (RED), Ovre Neadalsvatn (NEO), Lochnagar (NAG), Jörisee (JOR), Starolesnianske Pleso (STA)

##### Secondary sites:

Stavsvatn (SVN), Laghetto Superiore (LAG), Lago Paione Superiore (PAI)

#### Summary

The main goal of WP2, i.e. to measure the fluxes and pathways of ions, metals, radionuclides, persistent organic pollutants and spheroidal carbonaceous particles, has been achieved and high quality data on concentrations, inventories, distributions and fluxes of these parameters have been collected. An almost complete list of depositional fluxes to catchments, lake surface and sediments have been obtained for three lakes (GKS, RED, NEO) and an impressive number of measurements is now available for all six primary sites. Data analyses is completed, and evaluation and cross-comparison are under way. Conceptual models for the transport of SCPs, the deposition of radionuclides and the uptake of organic pollutants by fish have been developed. The results clearly show that high mountain lakes are remote though not pristine, and the selection of lakes has evidenced that there exists a degree of impact across Europe, for instance regarding the deposition of acids, heavy metals and organic pollutants. Since transport and redistribution of particles (SCPs), acids, metals, natural radioisotopes ( $^{210}\text{Pb}$ ), anthropogenic radioisotopes ( $^{137}\text{Cs}$ ) and chlorinated hydrocarbons such as DDT and DDE are dominated by very different meteorological, physical and chemical factors, a complex picture of impacts and responses emerges. Beside distance of source, air temperatures, altitude, geographical location, water chemistry, water renewal time, and snow melt processes play an important role. The reaction of the biota shows that chemical analysis of toxic substances can explain only part of the measured impact, and there are other environmental factors – inclusive food web structures –, which modulate the response of organisms. Although our results reflect the complex pattern of impacts, pathways and effects, there are still some open questions remaining, for instance regarding the role of hydrology and catchment characteristics.

**Table 6** provides an overview about measured parameters and shows that most analyses have been performed at the primary sites Gossenköllesee (GKS), Estany Redó (RED), Ovre Neadalsvatn (NEO), Lochnagar (NAG), Jörisee (JOR), and Starolesnianske Pleso (STA). Because of natural or legal constraints (presence or absence of fish, permits etc.) and depending on the availability of laboratory facilities on site (electricity, cabins etc.), three core sites (GKS, RED, NEO) have been established, from where a consistent and complete set of data is available. The most important results are summarized in **Table 7** that contains the characteristic data of the lakes. Some of them, however, are still preliminary and may be revised during the process of publication.

**Table 7.** Sampling at WP2 primary (GKS, RED, NEO, NAG, JOR, STA) and secondary sites (SVN, LAG, PAI). (\* Graniga Station at 1500 m in Val Bognanco)

Parameters / Sites	GKS	RED	NEO	NAG	JOR	STA	SVN	LAG	PAI
Air borne organics	+	+	-	-	-	-	-	-	-
Wet deposition: ions, nutrients	+	+	-	-	+	+	-	+	Gra*
Bulk deposition: ions, nutrients	+	+	+	+	+	+	+	-	+
Bulk deposition: metals	+	+	+	+	+	+	+	-	-
Bulk depos.: PCB, PAH	+	+	+	-	+	+	-	-	-
Bulk depos.: SCPs	+	+	+	+	+	+	-	-	-
Bulk deposition: <sup>210</sup> Pb	+	+	+	+	+	+	-	-	-
Snowpack: ions, nutrients	+	+	+	-	+	+	-	+	-
Snowpack: PCB, PAH	+	+	+	-	+	+	-	-	-
Snow pack: SCP, <sup>210</sup> Pb	+	+	+	-	+	+	-	-	-
Snow pack: metals	+	+	+	-	+	+	-	-	-
Hydrology, inlet, outlet	+	+	-	+	-	-	-	+	-
IN, OUT: ions, nutrients	+	+	-	+	-	-	-	+	-
IN, OUT: metals	+	-	-	+	-	-	-	+	-
IN, OUT: SCP	out	-	-	+	-	-	-	-	-
Lake water (LW) chemistry	+	+	+	+	+	+	+	+	+
LW: Metals (Pb, Cd, Hg)	+	+	+	+	+	+	+	-	+
LW: <sup>210</sup> Pb, <sup>137</sup> Cs partition coeff.	+	+	+	-	-	-	-	-	-
LW: Metal speciation	+	+	+	-	-	-	-	+	-
LW: PAH, PCB distribution	+	+	+	-	-	-	-	-	-
LW: SCP on GF/C filters	+	+	+	+	+	+	-	-	-
Traps: PCB, PAH, <sup>210</sup> Pb, <sup>137</sup> Cs, SCP	not PCB	+	-	SCP	+	+	-	-	-
Coring and sediment dating	+	+	+	+	+	+	+	-	-
Sediment water content, LOI	+	+	+	+	+	+	+	-	-
Sediment grain size analysis	+	+	+	+	-	+	UCL	-	-
Sediment SCPs	+	+	+	+	+	+	UCL	-	-
Sediment PCB, PAH	+	+	+	-	+	+	-	-	-
Sediment heavy metals, Hg, Se	+	+	+	+	+	+	+	-	-
Sediment magnetic susceptibility	+	+	+	-	-	+	-	-	-
Soil characteriz. (MAGIC)	+	+	+	+	+	+	1998	-	-
Soil inventory: <sup>210</sup> Pb, <sup>137</sup> Cs, SCP	+	+	+	+	+	1998	-	-	-
Fish: Heavy metals, PCB	+	+	+		+	fish- less	+	-	-
Fish: Histology, enzymes	+	+	+		+	fish- less	+	-	-

**Table 8.** Characteristic data, annual means and annual fluxes for WP 2 Lakes. (\* Preliminary data).

Station name	Gossen- köllesee	Estany Redó	Ovre Neå- dalsvatten	Lochnagar	Jörisee III	Staroles- nianske Pleso
Abbreviation	GKS	RED	NEO	NAG	JOR	STA

<b>1 Geography, geology, morphometry</b>						
Altitude (m)	2417	2240	728	785	2519	2000
Latitude,	47° 13' N	42° 38' N	62° 47' N	56° 58' N	46° 47' N	49° 10' N
Longitude	11° 01' E	0° 46' E	09° 00' E	03° 14' W	09° 59' E	20° 10' E
Mountain range	Alps	Pyrenees	Caledonian	Cairngorms	Alps	High Tatra
Country	Austria	Spain	Norway	UK	Switzerland	Slovakia
County/Region	Tyrol	Catalunya	Møre & Romsdal	Scotland	Graubünden	Tatra Mt.
Lake area (ha)	1.7	24	50	9.8	5	0.7
Max. depth (m)	9.9	73	18	24	21.8	4.1
Volume (m <sup>3</sup> )	78,000	7.750,000	1.950,000	820,000		11,750
Catchm. (km <sup>2</sup> )	0.20	1.55	16	1.02	1.1	0.027
Main lithology	Granite gneiss amphibolite	Granodiorite	Gneiss	Granite	Crystalline gneiss	Granite
Soil cover (%)	10	60		40		75

<b>2 Meteorology, hydrology</b>						
Mean Air T (°C)	0.5	3.8	<5.6	5.1	-1.0	
Ice cover (days)	240	153	250	80-100		
Precipitation (mm)	1300	1600	1700	1600		1300
Snow prec. (%)	40	48		<10		
Mean pH prec.	5.0	5.0	5.2	4.6	5.2	4.5
Water renewal time (days)	100	1095	23.5	300		
Σ PCB in air <sup>a</sup> (pg m <sup>-3</sup> )	573	526				
Σ PAH in air <sup>b</sup> (pg m <sup>-3</sup> )	1954	2800				

<b>3 Lake water</b>						
	<b>GKS</b>	<b>RED</b>	<b>NEO</b>	<b>NAG</b>	<b>JOR</b>	<b>STA</b>
Mean annual T		4.4	3.0			
Cond. ( $\mu\text{S cm}^{-1}$ )	21	12	12	24		15
pH	6.8	6.3	6.2	5.3		4.9
Alkal. ( $\mu\text{eq l}^{-1}$ )	85	41	32	11		-13
DN ( $\mu\text{g l}^{-1}$ )	250	240	66	300		476
DOC ( $\text{mg l}^{-1}$ )	0.45	0.76	0.73	0.8		2.75
TP ( $\mu\text{g l}^{-1}$ )	2.5	3.8	1	2.5		8.0
Chl a ( $\mu\text{g l}^{-1}$ )	1.7	0.7	0.38	2.0		
Pb total ( $\mu\text{g l}^{-1}$ )	0.283	0.230	0.059	0.503	2.190	1.715
Cd total ( $\mu\text{g l}^{-1}$ )	0.022	0.011	0.004	0.044	0.031	0.144
Cu total ( $\mu\text{g l}^{-1}$ )	0.300	0.267	0.243	0,100	0.650	0.200
Co total ( $\mu\text{g l}^{-1}$ )	0.028	0.030	0.021	0.083	0.060	0.070
Zn total ( $\mu\text{g l}^{-1}$ )	2.675	2.100	1.286	4.025	23.225	7.500
Cr total ( $\mu\text{g l}^{-1}$ )	0.250	<0.5	0.250	<0.5	0.600	2.500
Ni total ( $\mu\text{g l}^{-1}$ )	0.125	0.900	0.100	0.200	0.300	0.105
Mn total ( $\mu\text{g l}^{-1}$ )	0.700	1.200	1.157	8,500	4.833	9.100
V total ( $\mu\text{g l}^{-1}$ )	0.275	<0.2	0.100	<0.2	<0.2	0.100
As total ( $\mu\text{g l}^{-1}$ )	0.225	0.185	0.443	<0.1	1.630	0.110
Hg total ( $\mu\text{g l}^{-1}$ )	0.0043	0.0022	0.0015	0.0017	0.0056	0.0032
Pb diss. (nM)	1.0	0.5	0.1	2.9		
Cd diss. (nM)	0.05	0.2	0.2	<0.3		
Ni diss. (nM)	1.5	2.0	3.4	1.9		
Co diss. (nM)	0.2	0.2	0.5	1.3		
$^{210}\text{Pb}$ ( $\text{Bq kl}^{-1}$ )	4.6	1.3	1.5			
$^{210}\text{Pb}$ (% particulate)	89%	82%	76%			
$^{137}\text{Cs}$ ( $\text{Bq kl}^{-1}$ )	1.3	0.3	1.5			
$^{137}\text{Cs}$ (% particulate)	38%	21%	21%			



<b>3 Lake water (continued)</b>						
	<b>GKS</b>	<b>RED</b>	<b>NEO</b>	<b>NAG</b>	<b>JOR</b>	<b>STA</b>
$\Sigma$ PAH (pg l <sup>-1</sup> ) <sup>c</sup>	987	789	1147			
$\Sigma$ PCB (pg l <sup>-1</sup> ) <sup>d</sup>	106	62	25			
$\Sigma$ PCB (% part.)	82 %	63 %	47 %			
$\Sigma$ HCH (pg l <sup>-1</sup> ) <sup>e</sup>	992	2915	305			
$\Sigma$ DDT (pg l <sup>-1</sup> ) <sup>f</sup>	31	32	0.6			
$\Sigma$ Endosulphanes (pg l <sup>-1</sup> ) <sup>g</sup>	161	1146	134			

<b>4 Deposition: annual fluxes</b>						
H <sup>+</sup> (meq m <sup>-2</sup> )	12	16	10	38		37
SO <sup>4</sup> (meq m <sup>-2</sup> )	15	35	21	50		66
N (meq m <sup>-2</sup> )	34	52	34	58		54
Ca (meq m <sup>-2</sup> )	10	35	7	16		16
Pb (mg m <sup>-2</sup> )	2.1*	25.6*	1.2			
Cd (mg m <sup>-2</sup> )	0.12*	0.44*	0.014			
Hg (mg m <sup>-2</sup> )	0.013*		0.0041			
<sup>210</sup> Pb to catchment (Bq m <sup>-2</sup> )	163-225	120-262	128	90		190
<sup>210</sup> Pb to sediment (Bq m <sup>-2</sup> )	71	171-314	98	240	544	130
Sediment. rate (g cm <sup>-2</sup> )	0.01	0.01	0.01	0.03		
SCP flux to the sediment (m <sup>-2</sup> )	46.9	190.6	1.0	424.4	87.0	265.5
Total PAH to lake (mg m <sup>-2</sup> )	10-300	30-600				
Total PCB to the lake (mg m <sup>-2</sup> )	2-10	3-15				

<sup>a</sup> Sum of 28,31,52,101,118,138,153,180 in the particulate phase and the gas phase

<sup>b</sup> Sum of 22 PAH in the particulate phase and the gas phase

<sup>c</sup> Sum of 22 PAH in the particulate phase and the dissolved phase

<sup>d</sup> Sum of 28,31,52,101,118,138,153,180 in the particulate phase and the gas phase

<sup>e</sup> Sum of  $\alpha$ -HCH and  $\gamma$ -HCH in the dissolved phase

<sup>f</sup> Sum of *p,p'*-DDT and *p,p'*-DDE in the particulate phase and the gas phase

<sup>g</sup> Sum of Endosulfan-I, Endosulfan-II and Endosulfan sulfate in the dissolved phase

### 5.2.1 Spheroidal carbonaceous particles, SCP

The aims of this work were rather ambitious and many of the analyses had not been attempted previously (SCP in atmospheric deposition, lake and stream waters, snow) whilst others had no established sampling or analytical protocols in the literature (e.g. SCP in soil profiles). Protocols therefore had to be established and developed as part of the project. Start-up time was limited and so samples taken early in the sampling periods were used to determine whether, for example, the volumes being filtered were sufficient for analytical purposes. Adjustments were then made as necessary. In addition, no attempt had previously been made to determine the representativity of a single SCP core in a whole lake basin, or how the use of a single SCP profile taken from the deepest part of the lake might over-estimate the whole basin inventory. Similarly, it was unknown how soil SCP profiles vary within a catchment, or how episodic SCP deposition was at remote mountain sites subjected to varying depositional regimes. Almost 1000 SCP analyses have been undertaken and as a result information now exists on these questions. However, the short sampling period and low frequency of some of the sampling means that although far more is now known about deposition patterns and relative storage between sediments and soils, significant questions remain regarding inter-annual variability and the movement of SCP within and out of the system. These questions need to be answered if deposition is to be fully quantitatively linked to the sediment record such that reconstructions of past deposition can be made.

#### *Atmospheric deposition of SCP*

Samples of atmospheric deposition of SCP were taken approximately weekly at Ovre Neadalsvatn, weekly in summer and fortnightly in winter at Lochnagar and Gossenköllesee (except for periods of snow accumulation at the latter), weekly then monthly at Starolesnianske Pleso, monthly at Redo and whenever conditions permitted access at Jorisee. Where significant snow accumulation was present during the winter months, or where access was limited, sampling of snow pack was used instead of deposition such that at all sites an annual deposition of SCP could be calculated. Unfortunately, due to sampling problems these periods were not the same at all sites. In determining the number of SCPs deposited per unit area over this period, a total number deposited directly onto the lake and catchment could be calculated.

	Sampling Period	SCP (m <sup>-2</sup> )	No. deposited in sampling period	
			Lake	Catchment
Ovre Neadalsvatn	1997	16	2.86 x 10 <sup>9</sup>	8.86 x 10 <sup>10</sup>
Lochnagar	1997	81,358	7.97 x 10 <sup>9</sup>	7.48 x 10 <sup>10</sup>
Gossenköllesee	1997	3,421	5.82 x 10 <sup>7</sup>	1.03 x 10 <sup>8</sup>
Redo	4/97-3/98	57,223	1.37 x 10 <sup>10</sup>	7.50 x 10 <sup>10</sup>
Starolesnianske	1997	16,387	1.22 x 10 <sup>8</sup>	3.20 x 10 <sup>8</sup>

In addition, dry only and wet only sampling at Redo suggested that SCP deposition by these two means were approximately equal at this site for this sampling period.

#### *Lake sediments*

A single lake sediment core was taken from the deep water areas of each of the six sites, <sup>210</sup>Pb dated and analysed for SCPs. The resulting profiles agreed with those typical of Europe although some variation was observed compared with cores taken from the sites for AL:PE (1 and 2). As cores were taken from the deep-water areas only, the results have to be extrapolated in some way in order that a figure for the sediment basin as a whole can be derived. It is likely that if sediment focusing exists to any extent that SCP concentrations will be elevated in the deep-water area and therefore single cores are likely to overestimate SCP storage. However, it was unknown on what scale this over-estimates occurred as no full-basin inventories of SCPs had ever been undertaken.

At Lochnagar, 16 sediment cores, in addition to NAG8 (the dated MOLAR core), were analysed for SCP. The full SCP profile was produced for each core so that an inventory could be calculated for each. The sediment basin was sub-divided into areas each containing one representative core and the SCP value for this core then extrapolated for the corresponding area. In this way, a total SCP inventory was estimated for the lake. This multi-core approach showed that extrapolation from a single deep-water core can overestimate the SCP storage by two (surface estimate) to three (full core estimate) times. It is unknown whether these figures are similar at other sites, but does give some basis against which to compare other estimates of sediment focusing, such as using a comparison of  $^{210}\text{Pb}$  in soils and sediments. Full inter-comparisons between SCP data and  $^{210}\text{Pb}$  remain to be done but should provide far more interpretative detail.

Finally, a very good agreement was observed between SCP inventories and inventories of trace metals from atmospheric sources in the Lochnagar cores. An  $R^2$  of 0.85 - 0.87 was found for both Pb and Hg.

#### *Soil Cores*

A single soil core has so far been analysed for each site. Additional soil cores at Starolesnienske Pleso and Lochnagar have been received and analysed to try and ascertain some data on the extent of within catchment variability. In general, soil core data agreed with sediment and expected results i.e. highest concentrations / inventories at Lochnagar, Starolesnienske, lower levels at Redo, then Gossenköllesee and lowest at Øvre Neådalsvatn. This was the first time that SCP analyses had been undertaken at a number of sites and it was therefore interesting to observe the similarities between the profiles. The profiles were short and showed high concentrations in the surface sample followed by a rapid decay. The exception to this was Starolesnienske, which showed a broad peak with maximum SCP concentration at 7-8 cm depth.

A total storage of SCPs within lake sediments and catchment soils can therefore be estimated given knowledge of accumulating sediment areas and catchment soil areas. At Lochnagar it was found that 67 % of total deposited SCPs were stored within the soils and 33 % in sediments. Once again, this is in reasonable agreement with Pb and Hg where it is estimated that 80 – 90 % is stored within the catchment soils.

#### *Sediment traps*

Sediment trap sampling regimes varied considerably within the six sites. Monthly samples were obtained from 10m, 25m and 57m at Redo, approximately six monthly samples from Gossenköllesee, annual samples have been obtained from Lochnagar since 1990, and samples have so far been received from Starolesnienske and Jorisee but the data from Øvre Neådalsvatn are not yet available. Surface and deep water sediment trap comparisons are also to be made at Lochnagar. Little interpretative work has so far been done on the data. The situation at Redo, which potentially was the most interesting site, is complicated by the absence of particles in many of the traps / depths. Currently, it is unknown whether this is a sampling problem (insufficient sample) or an analytical (detection limit) problem. At Lochnagar, the long term trends are also of interest. Similar values are observed in all years although the values for 1994/5 and 1996/7 are slightly elevated and the interim year 1995/6 shows virtually double concentrations over previous values. The reasons behind this are currently unknown although a similar pattern is observed in  $\text{NO}_3^-$  deposition. SCP in deposition are known to agree well with acid ions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ) probably due to their similar sources and therefore the reason for this pattern may be depositional rather than, for example, increased erosion from the catchment.

#### *Lake and stream samples*

Lake and stream samples represent the source of greatest uncertainty in the complete SCP dataset and this is due to the impracticality of sampling large volumes at a high frequency. Such work had never been attempted before and so it was unknown what a suitable sampling volume would be. Initially, this was 20 litres, but after the first few months was changed to 'as much as possible' and varied between 40 and 300 litres. It is therefore impossible to say how SCP concentrations vary within the

lake water column through a year or what proportion are entering or leaving by discrete streams or during snowmelt. It is expected that SCP in lake water will vary considerably depending on depositional episodes, the particle settling velocities and the water residence times of the lakes. Similarly, the outflow concentrations are expected to vary accordingly. The scant data appear to support this, but much more detailed work is needed for confirmation.

Concluding, a vast number of data have been collated and summarised but have yet to be fully interpreted in the light of other available data (e.g.  $^{210}\text{Pb}$ , trace metals in deposition, meteorological data etc.). Samples are still being received and have yet to be analysed. It is envisaged that full data analysis will take some time but will yield a great deal of previously unknown information regarding the distributions of SCP within mountain lake ecosystems as well as information regarding deposition patterns and even possible source regions for episodes. However, a great deal of work remains if the movement of SCPs between lake and catchment and especially the level of loss to the system is to be fully understood.

### 5.2.2 Radionuclides

The fallout radionuclides  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$  and  $^7\text{Be}$  were measured in rainwater, soil cores, the water column and bottom sediments to validate models of transport processes through the lake/catchment system and to facilitate their use in reconstructing atmospheric fluxes of pollutants from sediment records.

Although concentrations of  $^{210}\text{Pb}$  and  $^7\text{Be}$  in rainwater show large fluctuations of timescales of 2-4 weeks, mean annual values are more consistent. At sites near the Atlantic seaboard (Redo, Ovre Neadalsvatn, Lochnagar) mean annual  $^{210}\text{Pb}$  concentrations all lie in the range 66-84 Bq  $\text{kl}^{-1}$ . Significantly higher concentrations (146-173 Bq  $\text{kl}^{-1}$ ) were recorded at sites from central Europe (Gossenköllesee, Starolesnianske). This pattern reflects the global west/east increase within landmasses due to a build up of  $^{222}\text{Rn}$  concentrations in the atmosphere as the prevailing winds transport air masses over the land surface. On a local scale, variations in  $^{210}\text{Pb}$  flux are largely controlled by variations in rainfall. From these results we will be able to make improved estimates of radionuclide fluxes at most European sites, enhancing their value as tracers.

In spite of the anticipated difficulties (limited suitable core sites, the impact of snow cover), the soil core results, used to determine long-term atmospheric fluxes, appear to quite good though analysis of the results is still in progress. At most sites calculation of the long-term mean (c.30 y)  $^{210}\text{Pb}$  flux gives values that are comparable with the short-term (2 y) values from direct measurements, providing evidence that the flux has remained constant at least on this time-scale. The one exception is Redo where the soil core measurements appear to record much higher fallout levels, possibly due to the long-term influence of Saharan dust inputs. The data on  $^{137}\text{Cs}$  will be used to reconstruct the record of  $^{137}\text{Cs}$  deposition.

Particulate and dissolved  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  have been measured in the water columns of Gossenköllesee, Redo and Ovre Neadalsvatn using an INFILTREX II water sampler. The particulate fraction was determined using 1  $\mu\text{m}$  and 0.45  $\mu\text{m}$  filters in series. The filters were dried and weighed to determine the suspended sediment concentrations and analysed for  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  by gamma spectrometry. The soluble fraction was determined using exchange columns with appropriate extraction materials. These were removed in four separate sections, dried and analysed for  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$ , again by gamma spectrometry. Fluxes of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  through the water column have been measured via concentrations on samples collected in sediment traps. Measurements have also been carried out on plankton and fish.

Although some of the data still needs to be analysed in detail, the main results are now clear.  $^{210}\text{Pb}$  concentrations in the water column are  $\sim 2\text{-}5$  Bq  $\text{kl}^{-1}$ , representing a c.40 times dilution of the rain

water. The ice cover has a clear seasonal influence and its effect is presently being modelled.  $^{137}\text{Cs}$  concentrations are in the range  $\sim 0.5\text{--}4\text{ Bq kL}^{-1}$ . Since there has been virtually no atmospheric fallout of  $^{137}\text{Cs}$  since 1986, the source must be either catchment runoff or remobilisation.  $^{210}\text{Pb}$  appear to be dominantly associated with particulates whereas  $^{137}\text{Cs}$  is mainly in the soluble phase.  $^{210}\text{Pb}$  fluxes through the water column are broadly in agreement with atmospheric fluxes. Comparisons with fluxes to bottom sediments calculated from sediment cores will be used to determine the impact of sediment focussing on sediment records.

### 5.2.3 Persistent organic pollutants in air, water, sediments and fish

#### *Methodology*

$\text{C}_{18}$  solid-phase disks have been observed to be useful for the measurement of organochlorine compounds (OC) and polycyclic aromatic hydrocarbons (PAH) at  $\text{pg/l}$  in atmospheric precipitation samples with reproducibilities of 5-15% and extraction efficiencies of 80-100%. Quantitation and detection limits of 0.14-3.5  $\text{pg/l}$  were achieved from the analysis of 0.25-10 l of water, e.g. bulk precipitation or snow. The use of  $\text{C}_{18}$  disks allows the determination of these organic pollutants in remote areas affording collection and extraction of large numbers of samples with limited instrumentation.

A method for the analysis of trace OC in large numbers of fish muscle samples has been developed. This method provides higher precision than that observed in the most uniform fish populations. Among all sample-handling steps, evaporation losses has been observed to constitute the main aspect of recovery decrease. These can be minimized to less than 10% when it is avoided that the extract go to dryness. In any case, the effect of these losses can be compensated by correction by a tetrabromobenzene surrogate. Sample grounding with sodium sulphate provides significant higher concentrations than freeze-drying. Soxhlet extraction for 18 h is sufficient to draw most OC from the muscle samples, no significant peaks representing measurable concentrations of these compounds have been found by further extraction after this period. Repeatability and reproducibility is smaller than the dispersion between fishes of similar length and age from the same lake for all compounds except a-HCH.

From the point of view of instrumentation (gas chromatography coupled to mass spectrometry using chemical ionization in the negative ion mode -GC-NICI MS-), the use of ammonia as reagent gas provides lower limits of detection and quantitation than methane for most OC. These lower limits allow the detection and quantitation of species with three and four chlorine substituents in aromatic rings which are difficult to determine at trace levels when methane is used as reagent gas. The use of ammonia as reagent gas also facilitates the quantitation of the DDT derivatives. The mass spectra obtained with ammonia and methane correspond to the molecular incorporation of thermal electrons rather than true chemical ionization reactions. Despite the differences in fragmentation patterns associated to these two reagent gases, the use of one or the other does not require changes in the compound-specific ions selected for the selected ion monitoring mode. In any case, calibration of all OC using straight lines and check for uniform slope values is needed for correct quantitation. Finally, a method based on HPLC-fluorescence at the excitation/emission wavelength pairs of naphthol (290/335 nm) and pyrenol (345/395 nm) on fish bile samples has been developed. The method has allowed to determine the concentrations of hydroxylated polycyclic aromatic hydrocarbons in fish from the lakes considered in the project. Concentration ranges between 69 and 990  $\text{ng/ml}$  bile have been found.

#### *Field studies*

High altitude lakes are remote but not pristine environments. All measurements performed on fish, water, air and sediments show that the concentrations of OC and PAH are similar to those found in sites with a moderate degree of contamination which is *a priori* unexpected when considering the long distance of these ecosystems from the pollution sources. The present project has shown that high

altitude lakes provide a good case for the study of long-range transport of persistent organic pollutants.

The study of fish concentrations and sediment inventories (430-2800 meters above sea level, 40-67°N) shows that lake elevation is the major variable determining the accumulation of low volatility OC such as 4,4'-DDE, 4,4'-DDT and penta- to hepta-chlorobiphenyls. These compounds are also significantly correlated with annual average air temperatures. In contrast, volatile OC (sub-cooled liquid vapor pressure  $> 10^{-2.5}$  Pa) do not exhibit any gradient with elevation. The results obtained in the study illustrate that in temperate regions global distillation of OC involves the selective retention of the low volatility compounds at the coldest areas. This fractionation effect is responsible for the accumulation of high concentrations of potentially harmful compounds in high altitude ecosystems. PAH do not show this trend with temperature. On the other hand, other aspects such as fish age, size and trophic status are relevant for the accumulation of OC in fish. In insectivores fish populations, however, the accumulation trends derived from these factors might be smaller than those observed as consequence of temperature effects.

A correlation between levels of lake sediment PAH, hydroxy PAH in fish and antioxidant compounds in fish (namely  $\beta$ -carotene and glutathion disulphide) has been found in the high altitude lakes considered in this study. This is the first case of a correlation identified between markers of environmental stress and a lake pollutant. The analysis of OC and metals have allowed to exclude any trend with these antioxidant markers in the case of these compounds. The sediment data show that PAH inventories in these high altitude lakes started to increase at the beginning of the century. Conversely, the increase of OC is observed in the seventies.

Atmospheric deposition shows a higher content in persistent organic pollutants in wet samples. The deposition fluxes exhibit rather constant values throughout the year.

#### **5.2.4 Metals in precipitation, lake water, sediments and fish**

##### *Metal concentrations in lakewater and precipitation*

A comparison of lakes and sites shows a large variation in metal concentration both in lakes and in atmospheric deposition (**Table 7**). Also in this respect, northern Norway seems to be one of the least polluted regions in Europe, although toxicologic studies showed that fish from Ovre Neadalsvatn seem to be especially affected by PAH (see below).

##### *Metal speciation in the water column*

Trace metal concentrations and their speciation have been determined in water column samples from Gossenköllesee, Redo and Ovre Neadalsvatn using anodic and cathodic stripping voltammetry in the Liverpool University Oceanography laboratory. Analyses have been carried out on both filtered (0.4  $\mu\text{m}$  and 0.1  $\mu\text{m}$ ) and unfiltered, samples.

Concentrations of Pb, Cd, Ni, Co have been determined at all three sites and in all fractions, and are in the ranges: Pb 0.3-1 nM, Cd 0.07-0.2 nM, Ni 1.5-3 nM, Co 0.2-0.6 nM. High Pb concentrations in the surface samples from Redo in summer are attributed to atmospheric inputs. Initial results suggest that these trace metals are mainly in the soluble phase. Enhanced concentrations in some species were recorded at mid-depths, possibly due to biological factors. Systematic comparisons between trace metals and radionuclides are presently being carried out.

##### *Metal concentrations in fish and sediments*

In 1997, a broad screening of the metal concentrations (Na, Mg, Ca, Ti, Mn, Fe, Hg, Co, Cu, Zn, As, Se, Pb, Sr, Mo, Ag, Cd, Cs, La, Ce) in kidney and liver, as well as Hg in muscle, was performed on a total of 89 individuals from 4 lakes (Arresjøen, Jörisee, Etang d'Aubé and Stavsvatn). The fish

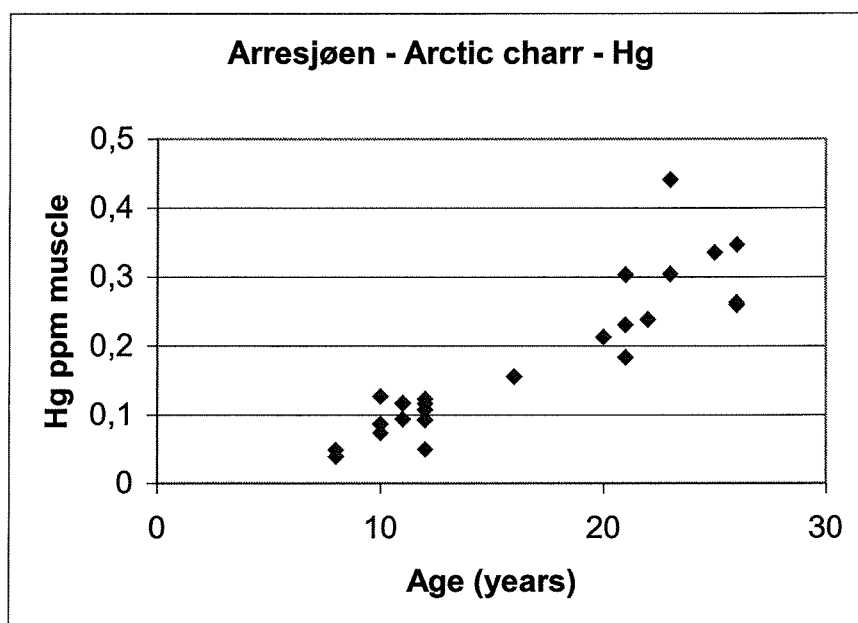
sampled from the MOLAR lakes in 1997 (Ovre Neadalsvatn, Redo, Gossenköllesee and resampling of Stavsvatn, Etang d'Aubé and Jörisee were analysed at NIVA in 1998 for mercury (Hg) in muscle, and metals in kidney and liver (Cd, Pb, Cu, and Zn, as well as Se, Cs and As). A total of more than 140 fish from the seven MOLAR lakes have been analysed.

As a part of a QCP, reanalyses of mercury in fish from lakes with old fish (>10 years) and populations possibly being piscivorous were performed. In addition, muscle samples from 143 fish sampled in MOLAR have been analysed at the University of Stockholm, Sweden, for the isotopes of  $^{15}\text{N}/^{14}\text{N}$  and  $^{13}\text{C}/^{12}\text{C}$ . This has been an additional project not originally planned for MOLAR. The relatively high fractionation rate of nitrogen through a food web can result in a difference in the isotope ratio of 3,3 ‰ between plankton feeding and piscivore fish of same species in a lake. The relative distribution of nitrogen isotopes in different individuals, indicative of specific trophic levels, can be used as a continuous variable by which trophic position may be quantified. Isotopic measurements will therefore provide a time-integrated measure of assimilated diet and an independent means of evaluating the diet of the consumer. This is an important variable especially when detailed stomach analyses are impossible to obtain.

In all lakes, except in Arresjøen, the Hg concentrations in fish were low (Rosseland *et al.* 1999, Rognerud *et al.* 2000) and lower than values generally observed in boreal areas in Scandinavia (Anderson *et al.* 1987, Fjeld and Rognerud 1993). Within the lakes Hg must be converted to methyl-Hg before accumulating in aquatic organism. The low temperature, low concentrations of DOC and organic content in the sediments, as observed in our lakes, are all factors associated with low methylation rates of Hg in the lakes (Ramlal *et al.* 1993). The high transparency of the MOLAR lakes also favours demethylation, which is a significant process reducing methyl-Hg concentration in lake water (St. Louis *et al.* 1996). The isotope data also indicate that these populations are feeding on a low trophic level. Thus, low methylation rates and low trophic level are possible explanations for low Hg levels in these lakes. However, the Hg concentration in the piscivorous Arctic charr population in Arresjøen (**Figure 16**) was 2-3 times higher than the other lakes. The sediment flux of Hg was the lowest observed in all lakes indicating that biomagnification is the main reason for high Hg concentrations in Arresjøen. This has been confirmed by the isotopes ratios of  $^{15}\text{N}/^{14}\text{N}$  and  $^{13}\text{C}/^{12}\text{C}$ . (Rognerud *et al.* 2000). By the new recommendations by EPA (US Environmental protection Agency), the oldest fish from Spitsbergen should not be eaten in an amount of 227 g (for a human of 70 kg) more than 2 times a month! This demonstrates that even that remote area is not undisturbed by man.

All data analysed at the other institutes (UIBK, CID-CSIC, CNRS) have been stored in a database at NIVA, in a form which might be used in a future ENSIS database. The data will be analysed in a multivariate statistical model. The results can also be coupled with the data from physiology and histology of each individual fish.

Observed concentrations of contaminants in fish are also a function of the "dose". We will use concentrations and accumulation rates of Hg, Se, Pb, Cd, Zn, As, Cs and POP's in surface lake sediments as a surrogate variable for the dose in each lake. Sediments are known to reflect atmospheric depositions of pollutants but they are also influenced by the local water quality and lake specific data as water renewal time and catchment size. Concentrations of metals in sediments have been analysed at SGab in Luleå, Sweden and the  $^{210}\text{Pb}$  datings necessary for calculating accumulation rates at the University of Liverpool. The basic hypothesis is that by including the "dose", water quality and food web position it will be possible to sort out the most influencing variables for bioaccumulation of contaminants in fish.



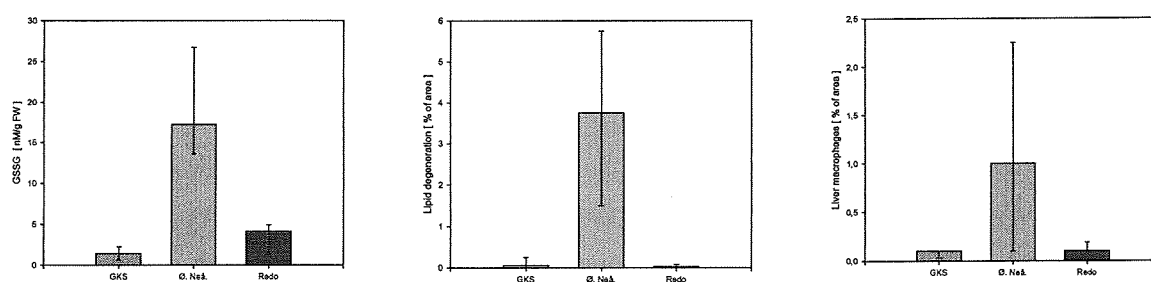
**Figure 16.** Mercury concentration in muscle versus age of individual fish sampled from a population of Arctic charr (*Salvelinus alpinus* L.) at Arresjøen, Spitsbergen, Norway.

#### *Fish physiology and histology*

Prior to the Annual MOLAR Meeting in Arcachon, France, in February 1999, a fish workshop was held in Arcachon at the Laboratory of CNRS-University of Bordeaux. The main focus was on the physiology of fishes in high mountain lakes, and the gill histology.

Fish were caught by gill nets and dissected at the lakes. A piece of the kidney and liver as well as one gill arch were fixed in buffered formaline for histology and sent to Innsbruck. From three lakes also frozen liver samples were brought to Innsbruck for biochemical analysis. Fish from these three lakes, Ovre Neadalsvatn, Gossenköllesee, and Redo were studied in more details. Analyses revealed that fish from Ovre Neadalsvatn show significant signs of environmental impact. Biochemical and histological data give evidence that these fish are stressed (**Figure 17**). However, data for metal accumulation (NIVA analyses) and organochlorine pollutant accumulation (J. Grimalt's analyses) indicate that Ovre Neadalsvatn is the least polluted site. One possible source for the observed environmental stress in Ovre Neadalsvatn are polycyclic hydrocarbons (PAHs) as visualized by bile analysis. The fish from this lake are especially rich in metabolites of PAH detoxification (Escartin and Porte 1999).





**Figure 17.** Biochemical and histological parameters of fish liver. For each of the three parameters, values from Gossenkøllersee (GKS, left in each figure), Ovre Neadalsvatn (Ø.Neå, middle) and Redo (right) are shown. Glutathione disulphide (GSSG, left figure) is a measure for oxidative stress. Lipid degeneration of liver cells (mid figure), and an increased number of macrophages (right figure) are also possibly induced by pollutants

*To conclude*, our study shows that high concentration of Hg, less volatile PCB congeners and ppDDE in piscivorous Arctic charr from lake Arresjøen was mainly caused by biomagnification in the food chain where cannibalism was the driving force. Shorter food chains and fish feeding on a lower trophic level (benthic invertebrates and terrestrial insects) were the most important factors explaining lower concentration of Hg and less volatile PCB congeners in fish populations from the European high mountain lakes. Our data indicate that atmospheric deposition affected by local sources may explain the higher concentrations of pesticides (ppDDT, ppDDE and lindane;  $\gamma$ -HCH) in fish from the Pyrenees compared to the other sites. We also confirm the hypothesis put forward by Grimalt *et al.* (1999) that age adjusted concentration of Hg and less volatile organochlorines in insectivorous brown trout populations are suitable media for monitoring changes of the bioavailability of these contaminants over time, as well as regional trends, in high mountain areas.

### 5.3 MOLAR Work Package 3 (WP3)

#### CLIMATE VARIABILITY AND ECOSYSTEM DYNAMICS AT REMOTE ALPINE AND ARCTIC LAKES

##### 5.3.1 Introduction

In this work package we have explored the relationships between short-term variations in weather patterns (from automatic weather stations) and water column behaviour and between longer-term climate trends (from 200 year long instrumental records) and proxy climate records from dated sediment cores. We have also attempted to calibrate dynamic lake models using water column data from the study sites with a view to forecasting probable lake behaviour under different climate scenarios.

##### 5.3.2 Sites selected

The lakes in this study share the same basic limnological characteristics. They are oligotrophic, typically dimictic and have a winter ice-cover and a summer thermocline. They are all situated above or beyond the regional tree-line, and they have poorly vegetated catchments.

Most of the sites were included in the AL:PE 2 study, and belong to the group of sites identified in that study to be least influenced by acid deposition and other pollutants. Additional sites that provide the study with a wider geographical and chemical range are located in Finland, Austria, Switzerland and Slovenia.

The sites are: Ovre Neadalsvatn (Norway), Saanajärvi (Finland), Gossenköllesee (Austria), Hagelsee (Switzerland), Jezero Ledvicah (Slovenia), L. Redo (Spain, Pyrenees), L. Cimera (Spain, Gredos, secondary site) and Terianske Pleso (Slovakia).

### 5.3.3 Objectives and results

#### *Objective 1:*

- *To obtain and harmonise instrumental weather records over the last 200 years for all study regions,*
- *To model the relationship between climate records for mountain weather stations (at study sites) with those for lowland stations, and*
- *To calculate surface water temperature and ice-cover at the study sites.*

Ten regions of Europe were selected for new homogenisation studies. In each region a local network of stations was identified allowing the construction of an independent climate series. Following homogenisation, time-series and spatial analysis of the 16 data sets (from 1781 to the present day) was used to provide an accurate base for validation work across the full range of remote sites in the project.

The accuracy of the individual reconstructions was tested using data from the on-site automatic weather stations. These showed a high skill factor for the model, especially for the Scottish and Norwegian sites. The poorest performance was observed for the Alpine sites owing to the occurrence of summer inversions.

The on-site temperature reconstructions allowed the calculation of annual and decadal means for each calendar month, an index of continentality (winter – summer means) and the period of ice-cover. Ice cover was calculated simply as the number of days with temperature below zero, or more accurately by subtracting the number of negative degree-days from the number of positive degree-days for each year. However, at Hagelseewli in Switzerland the relationship between air temperature and water temperature was poor due to the shading effect of a high cliff face on the south side of the lake.

#### *Objective 2:*

- *To assess the seasonal variability of physical, chemical and biological characteristics of study lakes.*

In order to assess how lake chemistry and biological communities respond to changes in ice-cover, light penetration, temperature change, stratification and mixing, essential water column data (temperature, oxygen, pH, conductivity and chlorophyll-a) were collected at bi-weekly intervals in the ice-free season, and at the beginning, middle and end of the ice-cover period depending on conditions. Samples for major ion (Ca, Mg, Na, K, alkalinity, Cl and SO<sub>4</sub>) and nutrient (N, P, dissolved SiO<sub>2</sub>) chemistry, phytoplankton (diatoms and chrysophytes) and zooplankton analysis were, on average, collected at monthly intervals. Benthic diatoms and chironomid sampling was carried out along transects perpendicular to the shoreline using scuba to sample deep-water habitats.

The data show that the lakes have surface temperature minima from 3.4 – 7.6<sup>0</sup> C to 9.6 – 14<sup>0</sup> C, range in chlorophyll a (Chl a) values from less than 1 µg l<sup>-1</sup> to about 4 µg l<sup>-1</sup> and are well oxygenated. However, several sites show severe deeper water oxygen reductions in winter with values between 0 and 4 mg l<sup>-1</sup>. The pH of the lakes reflects their catchment bedrock. The two calcareous lakes (Hagelseewli and Ledvicah) have pH values varying between 7.8 and 8.0, whilst most other sites on crystalline bedrock have acidic pH values varying between 5.3 (associated with the spring melt period) and 7.0.

The lakes vary seasonally with respect to heat flux, pH and Chl a concentration. The pH fluctuations are greatest at the most productive sites reflecting seasonal differences in production and respiration. Chl a values also fluctuate markedly through the year. In most cases peak values occur during autumn turnover, although at sites with longer ice-free periods, two maxima (spring and autumn) occur.

Vertical gradients are also marked with up to a 10<sup>0</sup>C difference occurring between the epilimnion and hypolimnion during summer stratification. The Chl a maximum typically occurs at the metalimnion, reflecting the optimum combination of light and nutrient concentration for algal photosynthesis. Rates of oxygen depletion vary according to lake depth and productivity, with losses being rapid and episodic in shallower lakes, slower and more progressive at deeper, oligotrophic sites. At some sites low hypolimnetic oxygen concentrations are accompanied by an increase in Mn indicating probable releases of phosphorus taking place.

*Objective 3:*

*- To harmonise taxonomy of key indicator taxa and model their distribution in relation to environmental variables.*

In MOLAR we have built on previous AL:PE knowledge by (i) harmonising taxonomic procedures with those of new participants (from Switzerland and Finland); (ii) developing a taxonomic system for chrysophytes and chrysophyte cysts and (iii) refining local and regional training sets for pH and temperature reconstruction.

*Objective 4:*

*- To establish long-term variability in ecosystem dynamics from recent palaeolimnological records and to compare the sediment record with the instrumental record of climate variability (see above).*

The longer term (decadal) lake variability was assessed from a high resolution analysis of recent sediments. The key biological remains (benthic and planktonic diatoms, chrysophyte cysts, cladocera and chironomids) were analysed, along with analysis C, N, pigments and the mineral fraction of the sediment derived from the lake catchment.

Replicate core samples of the upper sediment were taken with a wide-diameter piston corer from each site. The uppermost 20 cm of sediment was sub-sampled at contiguous 2 mm or 2.5 mm intervals to provide an average sample resolution of 5-10 years. In the laboratory the dry weight, wet density and loss-on-ignition of each sample was measured.

One core from each site was dated using <sup>210</sup>Pb, <sup>137</sup>Cs and <sup>241</sup>Am and a calendar year chronology was constructed for each dated core to allow comparisons between the sediment record and the instrumental temperature record.

Cores were correlated at each site on the basis of dry weight and loss on ignition measurements using sequence slotting procedures. This exercise allowed chronologies to be transferred between cores.

Data from all core analyses were transferred to the central database, and processed to make comparisons with the reconstructed instrumental climate record for the last 200 years. Linear regression analysis was used to find any potential relationships between the biological and sediment response variables and the instrumentally reconstructed climatic variables (= predictor variables). The species composition data for diatoms, chironomids, chrysophytes, and cladocerans, were summarised as principal component axes prior to being used as response variables. To harmonise the climatic predictors and the response variables, the climatic variables were smoothed along time with a LOESS regression.

Although many of the relationships between climate predictors and sediment responses were statistically weak the analyses indicated significant correlations between temperature and loss on ignition, diatom-inferred pH, and PCA axis 1 for diatoms and chironomids at some sites.

Data from cores at several sites shows clear evidence for the impact of climate change with increases in the proportion of planktonic diatom taxa occurring at a number of sites over recent decades.

*Objective 5:*

*- To model the relationship between weather patterns and water column dynamics and chemistry.*

The lake model DYRESM was explored to relate weather patterns to water column dynamics and chemistry. Despite progress in customising the model to mountain lake conditions difficulties were experienced with simulating the break-up of ice in spring. In addition the requirements for frequent wind input to the model were greater than the field data available.

The model AQUASIM was also evaluated. In this case the model simulates water column turbulence quite sensitively, but does not yet include the capacity to model ice behaviour.

### **5.3.4 Conclusions**

Air, water temperatures and ice-cover can be modelled with good skill at remote mountain lakes, using data transferred from lowland meteorological stations.

Fine resolution analysis of cores from remote mountain lakes situated in relatively unpolluted regions of Europe show coherent variations over the last 200 years that are probably related to climate influences.

Core records can be compared with instrumental climate records, although the accuracy of the comparison depends on sediment accumulation rates and the accuracy of sediment dating. A decadal resolution is possible in most cases.

Climate impact on mountain lakes is registered most clearly in the sediment by changes in organic matter, changes in diatom phytoplankton and changes in chironomid assemblage composition.

Currently available lake models need substantial modification, especially with respect to ice behaviour, if they are to be used to predict accurately the impact of future climate change on mountain lakes.

## **5.4 MOLAR Work Package 4 (WP 4)**

### **INTEGRATING ACTIVITIES**

Work package 4 (WP4) was devised as a programme of integrating activities convened by ECRC at University College London, NIVA and University of Bergen. The three field-based work packages (WP1-3) were linked and given coherence by a programme of integrated activities that ensured the standardisation and harmonisation of field and laboratory methods, the reporting of data, centralised storage, retrieval and analysis of data, and the presentation and dissemination of results.

#### **5.4.1 Specific objectives**

- To co-ordinate a programme of standardised and quality controlled field and analytical methods;*
- To extend and further develop an integrated and harmonised database;*
- To ensure the optimal use of database information to facilitate the application of multivariate statistical and modelling techniques to provide an integrated assessment of project results;*

*-To further develop a multidisciplinary network of environmental scientists to co-ordinate research, exchange knowledge and disseminate findings from studies of mountain lakes.*

#### *Standardisation and quality control of field and laboratory methods*

Standardised protocols for field sampling, laboratory analyses, chemical AQC and biological harmonisation developed within the precursor AL:PE project were amended and/or extended within MOLAR to account for new determinations and/or improvements in available methods. A series of workshops was held at the beginning of the project and detailed manuals were produced and distributed to all participating groups. Protocols and laboratory performance have been reviewed at regular workshops throughout the project.

Rigorous data quality control procedures for water chemistry and a programme of inter-laboratory calibration established within AL:PE were extended to new determinands and to deposition measurements. The intercalibration programme was extended to outside laboratories and linked to that managed by NIVA for the UNECE International Co-operative Programme on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters) and to the circuit of the Analytical Quality Control and Assessment Studies in the Mediterranean Basin (AQUACON) carried out by CNR in cooperation with the Environmental Institute of the Joint Research Centre of Ispra. Results were published in separate reports (Mosello *et al.* 1999, Hovind 1997).

A system of sample exchange and workshops was instigated to develop and extend the programme of taxonomic harmonisation established in AL:PE. The programme of quality control for invertebrates was linked to that currently managed at the University of Bergen for the UNECE ICP Waters. NIVA co-ordinated the analysis of test-fishing data within WP1 and WP2 and all ageing of fish was performed by a "certified" expert at NIVA to harmonise determination of fish age.

#### *Database development and statistical analysis*

The primary biological, chemical, and physical data from the various study sites in the AL:PE and MOLAR projects are stored on a centralised database developed at the University of Bergen. It includes, in a consistent and structured way, all the available geographical, climatic, catchment environmental, lake chemical, lake physical, lake biological, and sediment chemical and biological data.

The database is of the relational type and uses ACCESS software, this allows ease of exchange of data between laboratories and ease of data input via EXCEL.

Statistical analyses have been, and continue to be implemented to address a range of questions. Exploratory data analysis prior to any statistical analysis is done using SYGRAPH, CALI, CANODRAW, TILIA-GRAPH and TRANSFOR to look for outlying values and to assess the need for data transformations. Basic statistical analyses is done using SX, SYSTAT, and GENSTAT, whereas multivariate analysis of data from several sites involve CANOCO, TWINSPAN, CLUSTER, and SIRIUS. More specialised software (e.g. WACALIB, CALI) has been used for reconstructing lake-water pH from diatom assemblages preserved in the lake sediments.

The database will be ultimately transferred to NIVA where it will be developed and maintained in conjunction with ECRC-UCL and other AL:PE/MOLAR laboratories and centres and where it will be available for use in follow-up projects.

#### *Dissemination of results*

Data and preliminary findings from the project have been discussed and ratified at workshops and meetings of the scientists involved in each work package and at annual meetings of the full MOLAR group. Results have been presented in annual reports and consolidated in the final report. Particular emphasis has been placed on publishing the protocols and results of the project in the international

scientific literature. A list of publications and presentations from the project is appended to this report (**APPENDIX A**). An international conference on remote mountain lake ecosystems has been organised under the auspices of the MOLAR Steering Group led by the University of Innsbruck and will take place in Innsbruck in September 2000.

A Web page for the MOLAR project has been developed at Charles University Prague. It is continuously being reviewed and upgraded to present the objectives and results from the project; details of publications; and links to participating organisations and associated relevant projects. The web page is accessed on:

<http://prfdec.natur.cuni.cz/hydrobiology/molar/welcome.html>.

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## Appendix A.

### JOINT PUBLICATIONS

Both publications that are submitted to different journals and publications already published are cited, as well as conference presentations where only abstracts are available. See also MOLAR Home page on Internet (<http://prfdec.natur.cuni.cz/hydrobiology/molar/welcome/htm>)

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## **Appendix B.**

## **PART B**

### **DETAILED REPORT OF THE INDIVIDUAL PARTNERS**

Reporting period:

March 1996 - February 1999

Partner:

Environmental Change Research Centre, University College London

Principal Investigator:

Dr Simon Patrick

Scientific staff:

Prof. R.W. Battarbee, Dr Neil Rose, Dr Nigel Cameron, Mr Chris Curtis

Address:

26 Bedford Way, London WC1H 0AP, UK

Telephone: +44 171 436 9248

Fax: +44 171 380 7565

E-Mail: spatrack@geog.ucl.ac.uk

#### **I. OBJECTIVES FOR THE REPORTING PERIOD:**

##### Project Co-ordination

##### Work Package 1

- ⇒ completion of all static modelling and intercomparison of acidification status of WP1 sites and static modelling approaches,
- ⇒ assessment of the modelling issues specific to high mountain lakes,
- ⇒ completion of final report and manuscripts for publication.

##### Work Package 2

- ⇒ Establish a more quantitative link between atmospheric deposition of SCPs and the sediment record in mountain lakes,
- ⇒ construct a conceptual model to illustrate the expected pathways of SCPs deposited from the atmosphere into lake sediments, catchment soils or leaving the system via the outflow, sample the main compartments, atmospheric deposition, snowpack, lake and stream (inflow and outflow) waters, sediment traps, lake sediments and catchment soils at Lochnagar (Scotland),
- ⇒ develop suitable techniques for analysis of the various sampled media,
- ⇒ analyse and interpret all SCP samples from all WP2 sites (6).

##### Work Package 3

- ⇒ Identify mountain lakes in Europe least affected by acid deposition and other pollutants and assess (1) whether changes in the sediment record could be correlated with changes in the instrumental climate record over the last 200 years, (2) whether the instrumental climate record derived from lowland and other meteorological stations could be transferred to mountain locations using statistical modelling procedures, and (3) whether dynamic lake models could be calibrated using seasonal water column data and then used to explore lake response to different future climate scenarios,
- ⇒ co-ordinate the diatom analyses carried out at each of the WP3 study sites,

- ⇒ carry out diatom and chrysophyte analysis at the Norwegian study site, Øvre Neådalsvatn,
- ⇒ overall co-ordination, including the production of final reports and papers.

#### Work package 4

- ⇒ Co-ordinate a programme of standardised and quality controlled field and analytical methods,
- ⇒ extend and further develop an integrated and harmonised database;
- ⇒ ensure the optimal use of database information to facilitate the application of multivariate statistical and modelling techniques to provide an integrated assessment of project results,
- ⇒ to further develop a multidisciplinary network of environmental scientists to co-ordinate research, exchange knowledge and disseminate findings from studies of mountain lakes.

#### II. OBJECTIVES FOR THE NEXT PERIOD:

- ⇒ Completion of papers for publication,
  - ⇒ completion of papers and posters for High Mountain Lake Symposium, Innsbruck September 2000,
  - ⇒ continuation of methodological development and application under EMERGE project.
- III. Are there any particular problems ? Is your part of the project on schedule ?

The project has been completed on schedule

#### IV. MAIN RESULTS OBTAINED: *METHODOLOGY, RESULTS, DISCUSSION, CONCLUSIONS* (use other pages as necessary but preferably no more than 2)

##### Work Package 1

##### *Methodology*

The role of ECRC-UCL in this part of WP1 was the compilation of the catchment/soils database and the application of static critical loads models. The most simple, empirically based, static models require only water chemistry data for the calculation of critical load, plus a measure of acid deposition data to calculate critical load exceedance; two such models are used here, the Steady State Water Chemistry (SSWC) model and the Diatom model.

Since the empirical critical load models take no account of N cycling in catchments, they cannot be used to assess the effects of changes in N deposition without assuming that nitrate leaching will not change (which is contrary to theories of N saturation in terrestrial systems). The First-order Acidity Balance (FAB) model is a process-based model which was developed to take account of the major sinks for N in order to assess the potential effects of changes in N deposition. FAB employs a mass-balance to determine those combinations of S and N deposition which will result in a selected critical ANC value. Since the FAB model quantifies the removal of N by soils, vegetation and in-lake retention, it requires certain lake catchment data as model inputs, including lake:catchment area ratio, percentage cover of major soil types, and percentage cover of vegetation types. These data have been compiled in a catchment/soils database for WP1 sites.

Diatom and SSWC model (using critical ANC values of both 0 and 20  $\mu\text{eq l}^{-1}$ ) critical loads indicate a wide range of acid-sensitivity in MOLAR sites. The lowest critical loads, indicating the most sensitive sites, are found at Starolesnianske Pleso in the Tatra mountains, the two Norwegian sites (Øvre Neådalsvatn, Stavsvatn), Lago Paione Superiore in the Italian Alps, and Lochnagar, Scotland. The least acid-sensitive sites, indicated by the largest critical load values, are Jörisee and Laghetto Inferiore (Swiss Alps), and Gossenköllesee (Austrian Alps).

The critical load of three sites (Starolesnianske Pleso, Długi Staw in the Polish Tatra and Lago Paione Superiore) are exceeded using  $\text{ANC}_{\text{crit}} = 0 \mu\text{eq l}^{-1}$  in the SSWC model, while the use of  $\text{ANC}_{\text{crit}} = 20 \mu\text{eq l}^{-1}$  leads to increased exceedance at these sites plus the exceedance of critical load

at an additional site, Lochnagar. Application of the diatom model produces lower critical loads for all sites because of the greater sensitivity of the model, and while the same four sites show exceedance (Starolesnianske Pleso, Dlugi Staw, Lago Paione Superiore, Lochnagar), Laghetto Inferiore is also slightly exceeded.

For both values of  $ANC_{crit}$  (0 and  $20 \mu\text{eq l}^{-1}$ ) there are five sites showing FAB model exceedance; Starolesnianske Pleso, Dlugi Staw, Lago Paione Superiore, Lochnagar and Lago Paione Inferiore. While Lochnagar and Lago Paione Inferiore are only marginally exceeded for  $ANC_{crit} = 0 \mu\text{eq l}^{-1}$  they show greater exceedance for  $ANC_{crit} = 20 \mu\text{eq l}^{-1}$ . In most cases of exceedance with the FAB model, either N or S deposition could be reduced in order to protect the site. Nitrogen, and not just sulphur, is therefore contributing to exceedance at all these sites. At Starolesnianske Pleso both S and N deposition are sufficiently high to cause critical load exceedance on their own, and this is reflected by the negative ANC at the site.

The chemical range of the MOLAR lake sites is reflected in the modelled critical load values, from acid-sensitive to very alkaline, insensitive conditions. The large variation in deposition inputs, from the very low levels in northern Norway and parts of the Swiss and Austrian Alps to the highly acid inputs in the Tatra mountains and parts of the Italian Alps, leads to a variety of responses in terms of critical load exceedance. Three sites are exceeded according to all critical load models; Lago Paione Superiore, Starolesnianske Pleso and Dlugi Staw. Other sites have low critical loads which can lead to exceedance depending on the model used. Lochnagar is exceeded in all but one of the model applications, Lago Paione Inferiore is very close to exceedance according to the SSWC and diatom models while the FAB model shows that it is exceeded, and the otherwise insensitive Laghetto Inferiore is exceeded only according to the diatom model. Low critical loads and ANC values at three of the remaining sites (Øvre Neådalsvatn, Stavsvatn and to a lesser degree, Estany Redó) indicate high or moderate degrees of acid-sensitivity, but these sites do not demonstrate critical load exceedance because of relatively low deposition levels. Only two of the MOLAR sites, Gossenköllesee and Jörisee, are extremely insensitive to acid deposition and they are both located in the central Alps.

A striking feature of many of FAB model outputs is that modelled sulphate leaching appears to be greater than deposition inputs (for example at Øvre Neådalsvatn, Stavsvatn, Gossenköllesee, Jörisee and Laghetto Inferiore). Two possible mechanisms for such an observation are sulphur desorption from soils or the weathering of sulphur bearing minerals. Given the sparsity of soil cover in these high mountain catchments (the smallest value is 8% soil cover at Laghetto Inferiore) a weathering source of S seems more likely, but this cannot be confirmed without further study. Conversely, despite the general sparsity of soil and vegetation cover, the observation that N leaching is smaller than N inputs at all sites indicates some degree of N retention. It is not possible to determine from current data whether this occurs in the terrestrial or in-lake part of the catchment.

With the exception of sites like Gossenköllesee and Jörisee where high weathering rates seem to provide a large buffering capacity against acidification, these high-mountain lakes do seem to be very sensitive to acid deposition. It is evident that both sulphur and nitrogen inputs contribute to critical load exceedance at all affected sites, so future reductions in both S and N deposition across Europe resulting from the implementation of the Gothenburg Protocol of the UNECE could have important implications for the recovery of acidified sites.

Linked chemical-biological models are still under development, but the main potential for such models lies in the ability of critical load models to predict ANC, so that if the biological response to ANC can be determined it should be possible to predict the possible biological impacts of a specified deposition load, including the prediction of potential biological recovery.

## Work Package 2

Many of the analyses undertaken had not been attempted previously (SCP in atmospheric deposition, lake and stream waters, snow) whilst others had no established sampling or analytical protocols in the literature (e.g. SCP in soil profiles). Protocols therefore had to be established and developed as part of the project. In addition, no attempt had previously been made to determine the representativity of a single SCP core in a whole lake basin, or how an SCP profile from the deepest part of the lake might over-estimate the whole basin inventory. Similarly, it was unknown how episodic SCP deposition was at remote mountain sites subjected to varying depositional regimes. More than 900 SCP analyses have been undertaken so far and as a result a significant body of information now exists on these questions.

Samples of atmospheric deposition and snowpack were taken such that at all sites an annual deposition of SCP per unit area could be calculated. Therefore a total number of SCP deposited directly on to the lake and catchment could be calculated. In addition, dry only and wet only sampling at Redo suggested approximately equal contributions to total deposition. A single lake sediment core was taken from the deep water areas of each of the six sites, <sup>210</sup>Pb dated and analysed for SCPs. At Lochnagar, 16 sediment cores were analysed for SCP. This multi-core approach showed that extrapolation from a single deep water core can overestimate the SCP storage by 2-3 times. A single soil core was analysed for each site and in general these data agreed with expected results i.e. highest concentrations at Lochnagar, Starolesnienske > Redo > Gossenkollesee > Øvre Neådalsvatn. At Lochnagar it was found that 67% of total deposited SCPs were stored within the soils and 33% in sediments. This is in reasonable agreement with Pb and Hg.

Sediment trap sampling varied considerably within the sites and little interpretative work has so far been done on the data. Lake and stream samples represent the source of greatest uncertainty in the SCP dataset and this is due to the impracticality of sampling large volumes at a high frequency. Such work had never been attempted before. It is expected that SCP in lake water will vary considerably depending on depositional episodes, the particle settling velocities and the water residence times of the lakes. The scant data appear to support this, but much more detailed work is needed for confirmation.

When these data have been fully interpreted a great deal of previously unknown information regarding the distributions of SCP within mountain lake ecosystems as well as information regarding deposition patterns and even possible source regions for episodes will have been produced.



### Work Package 3

*Diatom analysis co-ordination:* Protocols for diatom analysis for MOLAR were based on those already established between participating laboratories for the AL:PE project. Workshops to harmonise methods and taxonomy were successfully held on schedule. One difference from the AL:PE project was the addition of sites in Switzerland (Jorisee) and Slovenia (Ledvica) with alkaline waters atypical of the much more acidic waters previously studied. Consequently, in some cases, regional rather than pan-European training sets were used to cope with the wider floristic diversity imposed by these sites. The results of diatom analyses from cores from the different sites were transferred to ECRC-UCL as planned for checking before transfer to Bergen for numerical analysis and integration into the palaeolimnological database and comparison with other proxy data from each site.

*Diatom and chrysophyte analysis at Øvre Neådalsvatn:* Øvre Neådalsvatn lies in the northern part of the Norwegian Mountains at an altitude of 728 m. The catchment geology is of gneiss with alpine soils vegetated with alpine heath and a significant proportion of bare rock. Parts of the catchment are grazed at a low intensity during the summer months. Using a gravity corer a total of six new sediment cores of between about 30-37 cm long were taken in September 1996 from the deepest point of the lake. The primary cores were extruded on site. These cores were designated the codes ØVNE 4 to ØVNE9. Samples from the cores ØVNE 4 and ØVNE 7 were analysed for  $^{210}\text{Pb}$ ,  $^{226}\text{Ra}$ , and  $^{137}\text{Cs}$  by direct gamma assay in the Liverpool University Environmental Radioactivity Laboratory. Diatom analysis was carried out on 60 contiguous samples taken at 2 mm intervals down to a depth of 12 cm in core ØVNE 4. This depth represents the time period from 1781 to 1996, and is therefore appropriate for comparison with reconstructed instrumental records of climate. The diatom assemblages are diverse and a total of 172 diatom taxa were identified in the sequence. The low counting sum means that the percentage curves, even for the dominant taxa, are rather noisy. However, the populations of dominant taxa are relatively stable with no visible changes in the abundance of common diatoms over the period of study. Diatom-based pH reconstruction using the AL:PE training set shows that there are relatively small variations in reconstructed pH over the period covered by the core. A plot of smoothed pH values, indicated by a LOIS smoother vary between pH 5.9 and 6.1 and only show a slight overall decrease in pH between 1781 and 1996.

A total of 81 chrysophyte stomatocyst taxa were identified. The cyst percentage data are somewhat noisy and significant changes in their percentages are not apparent. The assemblages are dominated by small unornamented cysts with pores. A number of other cysts show restricted distributions or maxima in parts of the profile. However, given the absence of ecological data for these cysts it is not possible to speculate on the reasons for these small changes. In order to consider the changes in the whole assemblages the variation in cyst composition was reduced to four principal components and these were regressed against reconstructed climate variables, but show no significant correlation with instrumental climate data.

*Co-ordination activities:* There have been no problems with co-ordination activities over the life-time of the project. Workshops have been held on schedule in association with the annual MOLAR workshop and more specialist WP3 workshops have also been held. The final specialist meeting held in Bergen in November 1998 brought together data from all sites and made comparisons between the proxy data and instrumental climate data. It was agreed at this workshop that the results of WP3 would be presented in the form of two special Journal issues, one in the *Journal of Paleolimnology* and the second in the *Journal of Limnology*. The manuscripts are now in review and publication is expected in 2001. ECRC-UCL is editing or co-editing both volumes.

V. List of Publications arising from the project (include copies):

Battarbee, R.W. Recent climate variability and remote mountain lakes in Europe. *Journal of Paleolimnology* (submitted)

Koinig, K.A., Kamenik, C., Schmidt, R., Agusti-Panareda, A., Appleby, P.G., Fott, J., Lami, A., Rose, N.L., Schnell, O.A., Tessadri, R., Thompson, R. & Psenner, R. Palaeoenvironmental changes in an

alpine lake (Gossenköllesee, Austria) over the last 200 years – the influence of air temperature on biological parameters. *Journal of Paleolimnology* (submitted)

Lotter, A.F., Appleby, P.G., Dearing, J.A., Grytnes, J.-A., Hofman, W., Kamenik, C., Lami, A., Livingstone, D.M., Ohlendorf, C., Rose, N.L., Sturm, M. & Thompson, R. The record of the last 200 years in the sediments of Hagelseewli (2339 masl), a high-elevation lake in the Swiss Alps. *Journal of Paleolimnology* (submitted)

Cameron, N.G., Schnell, O.A., Rautio, M.L., Lami, A., Livingstone, D.M., Appleby, P.G., Dearing, J.A. & Rose, N.L. High resolution analyses of recent sediments from a Norwegian Mountain lake and comparison with instrumental records of climate. *Journal of Paleolimnology* (submitted)

Korhola, A., Sorvari, S., Rautio, M., Appleby, P.G., Dearing, J.A., Hu, Y., Rose, N.L., Lami, A. & Cameron, N.G. A multi-proxy analysis of climate impacts on recent development of subarctic Lake Saanajärvi in Finnish Lapland. *Journal of Paleolimnology* (submitted).

Brancelj, A., Šiško, M., Muri, G., Kamenik, C., Appleby, P.G., Lami, A., Shilland, E., Rose, N.L., Brooks, S.J. & Dearing, J.A. Lake Jezero v Ledvici (N.W. Slovenia) – impacts of earthquakes and climate change to the lake ecosystem. *Journal of Paleolimnology* (submitted).

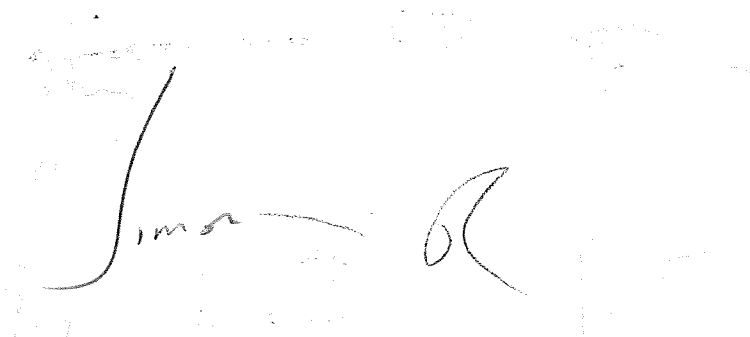
Rose, N.L., Harlock, S. & Appleby, P.G. (in press). The spatial and temporal distributions of spheroidal carbonaceous fly-ash particles (SCP) in the sediment records of European Mountain lakes. *Water, Air and Soil Pollution*.

N. G. Cameron, H. J. B. Birks, V. J. Jones, F. Berge, J. Catalan, R. J. Flower, J. Garcia, B. Kawecka, K. A. Koinig, A. Marchetto, P. Sánchez-Castillo, R. Schmidt, M. Šiško, N. Solovieva, E. Stefkova & M. Toro Valasquez (1999). Surface-sediment and epilithic diatom pH calibration sets for remote European mountain lakes (AL:PE Project) and their comparison with the Surface Waters Acidification Programme (SWAP) calibration set. *Journal of Paleolimnology* (in press)

Patrick, S., Battarbee, R.W., Wathne, B. & Psenner, R. (1998) Measuring and modelling the dynamic response of remote mountain lake ecosystems to environmental change: an introduction to the MOLAR project. In: K. Kovar, U. Tappeiner, N.E. Peters & R.G. Craig (Eds), *Hydrology, Water Resources and Ecology in Headwaters*. IAHS, 403-410.

Battarbee, R.W., Patrick, S., Wathne, B., Mosello, R. & Psenner, R. (1999) Measuring and modelling the dynamic response of remote mountain lake ecosystems to environmental change (the MOLAR project) - Proceedings of SIL, Dublin, August 1998.

Signature of Partner:



Date: April 4th 2000

**DETAILED REPORT OF THE INDIVIDUAL PARTNERS**

Reporting period: 1 March 1999 – 28 February 2000

Partner: University of Helsinki, UHEL

Principal Investigator: Atte Korhola

Scientific staff: Sanna Sorvari, Milla Rautio, Laura Forsström, Seppo Hassinen, Juhani Virkanen

Address: Lab of Physical Geography, University of Helsinki, PO Box 9 (Siltavuorenpenger 20 A), FIN-00014 Helsinki, Finland (*present address*: Department of Ecology and Systematics, University of Helsinki, P.O. Box 17, FIN-00014 Helsinki, Finland)

Telephone: +358-9-191 7512

Fax: +358-9-191 7301

E-Mail: [atte.korhola@helsinki.fi](mailto:atte.korhola@helsinki.fi)

**I. OBJECTIVES FOR THE REPORTING PERIOD:**

- Complete all physico-chemical and biological analyses of the contemporary data
- Collect and analyse all meteorological data
- Analyse supplementary cores for pigments and cladocera
- Complete all analyses of core material, including dating, SCP, mineral magnetics, pigments, C, N, S, chrysophytes, chironomids, diatoms, and cladocera.
- Carry out statistical analyses of the data
- Synthesize the results
- Report the results

**II. Are there any particular problems ? Is your part of the project on schedule ?**

- no problems were faced
- all the tasks were completed on schedule.

**III. MAIN RESULTS OBTAINED: *METHODOLOGY, RESULTS, DISCUSSION, CONCLUSIONS* (use other pages as necessary but preferably no more than 2)**

## METHODOLOGY

Water chemistry, including water column profiling, was sampled weekly during July and August 1997, once a month during September-October, and once in two months during the ice-cover period. Samples for major ions, TOC, SO<sub>4</sub>, Cl, Si, NH<sub>4</sub>-N, and NO<sub>2</sub>-N were sent immediately to the Laboratory of Physical Geography for analyses. Samples for total phosphorus and nitrogen were frozen and analysed later using the internationally agreed standards. Oxygen, pH, temperature and conductivity were measured *in situ* using equipments from HANNA Instruments. Alkalinity was measured in the laboratory within 24 hours.

Phyto- and zooplankton samples were taken bi-weekly during July and August 1999 from the deepest point of the lake (24 m) using five depths (0, 2, 5, 10, 23 m) and the samples preserved using Lugol's Iodine and Formalin, respectively. 250 ml was stored for phytoplankton and 10 l for zooplankton analyses (sieved through a 50  $\mu$ m mesh). Several vertical zooplankton hauls were taken simultaneously with water column profiling using a 200  $\mu$ m plankton net. A composite sample for chlorophyll-a was taken from ten depths simultaneously with the plankton sampling. 2-3 l of water were filtered immediately in the field from each depth, and the filters were frozen for analyses. Extraction was carried out using 90% acetone. After the extraction samples were filtered and measured the absorbance at the following wave-lengths: 750, 663, 647, 630, 480, 430 and 410 nm. The chlorophyll a concentrations were calculated after Jefferey and Humphrey (1975).

Epilithon diatom samples were collected twice a month during the open water season. Epilithic diatoms were removed from stones at the water depth of 40-50 cm along a *ca* 10 m stretch from the shoreline, using a toothbrush. Three stones were washed into a 250 ml polythene bottle; three composite samples were taken on each sampling visit.

Accumulated material was collected monthly during the open-water season using sediment traps; after the autumn overturn traps were left in the lake for the ice-cover period. For the biological transect, hard bottom samples were collected by diving. Continuous measurement of 7 meteorological variables (air temperature, epilimnetic water temperature, relative humidity, wind speed, wind direction, infra-red radiation, precipitation) was carried out by automatic weather station using 30 minute mean values. Due to problems associated with the energy supply, some interruptions in the operation of the station were faced during the mid-winter period.

Samples from Lake Saanajärvi master core (SAAN-4) were analysed for <sup>210</sup>Pb, <sup>226</sup>Ra, and <sup>137</sup>Cs by direct gamma assay in the Liverpool University Environmental Radiometric Research Centre, using Ortec GWL series well-type coaxial low background intrinsic germanium detectors. The separate cores were correlated with the master core by the sequence slotting technique. The variations in DW and LOI profiles, measured for each core in 2 mm resolution, were used in the correlations. The dated sediment cores were analysed for SCP, LOI, dry-weight, diatoms, cladocerans, chironomids, and total chrysophyte concentration using standard methods. Room temperature magnetic measurements were made on 95 weighed dried 0.2 cm contiguous samples in the depth range 1.0 - 20 cm in plastic film using a vibrating sample magnetometer, pulse magnetisers and spinner magnetometer. This

procedure provided continuous measurements of magnetisation in fields 0-1 T and remanence measurements following fields of 1T, -20 mT and -300 mT. Key magnetic parameters were calculated.

Sediment data was subjected to statistical analyses; relationship between biological change and climate was analysed by summarising the biological data first using principal components analysis (PCA). Linear regressions between the available sediment core variables (response variables) and reconstructed climate records (predictor variables) were then performed. Diatoms were used to reconstruct pH by weighted averaging partial least squares (WA-PLS) regression based on the AL:PE project calibration data-set of 118 lakes from European mountain regions. The data-set has been screened to include only appropriate arctic and alpine lakes and has a harmonised diatom taxonomy. The pH range in the data-set is 4.5-8.0. The predictive power of the training set, as assessed by statistical cross-validation, is 0.33 pH units for the 3-component WA-PLS model.

## RESULTS

Lake characteristics and selected chemical parameters are listed in Table 1. The lake was thermally stratified between the middle of July and the beginning of September (Fig. 1A). Maximum surface-water temperature, +14.6 C, was recorded at the beginning of August. The measured pH fluctuated between 5.4-7.5 (Fig. 1C). The pH was lowest during the snow melt period (June), whereas the values were relatively constant during the rest of the year. The hypolimnic oxygen concentrations were low (2.9 ppm) in the late spring (May/June); otherwise, the water was almost saturated. Alkalinity and conductivity were stable throughout the year.

Phytoplankton was dominated by chrysophytes and diatoms; also chlorophytes were quite abundant. Chlorophyll-a reached its maximum during the autumn overturn period (Fig. 1B). In general, the values were extremely low in comparison with more southerly sites. The crustacean zooplankton community consisted of ten species, of which the copepods *Cyclops abyssorum* and *Eudiaptomus graciloides* were most abundant. *Holopedium gibberum* was the dominant cladoceran taxon. Appendix 1 lists the preliminary species data of phyto- and zooplankton. Table 2 compares the abundance of calanoids, cyclopoids, and cladocerans during the sampling season. The more precise counting, and identification of rotifers, is in progress.

Sediment trap assemblages consisted mainly of suspended and resuspended planktonic diatoms (*Cyclotella* and *Aulacoseira* species). In general, the chitinous skeletal structures of Cladocera preserve better than soft-bodied Copepoda, resulting usually in a shift from Copepoda-dominating water column material to Cladocera-dominating sediment trap and fossil material - i.e. in the sediment copepods no longer are detectable. Diatoms were recorded in trap and sediment material even in the better way than in the water column.

**Table 1. Physiographic and water chemistry data for Lake Saanajärvi. The limnological values refer to epilimnetic measurements carried out in the lake during the 1996-1999 (July 4 1996- November 15 1999; n ≈ 25). Catchment area excludes water area.**

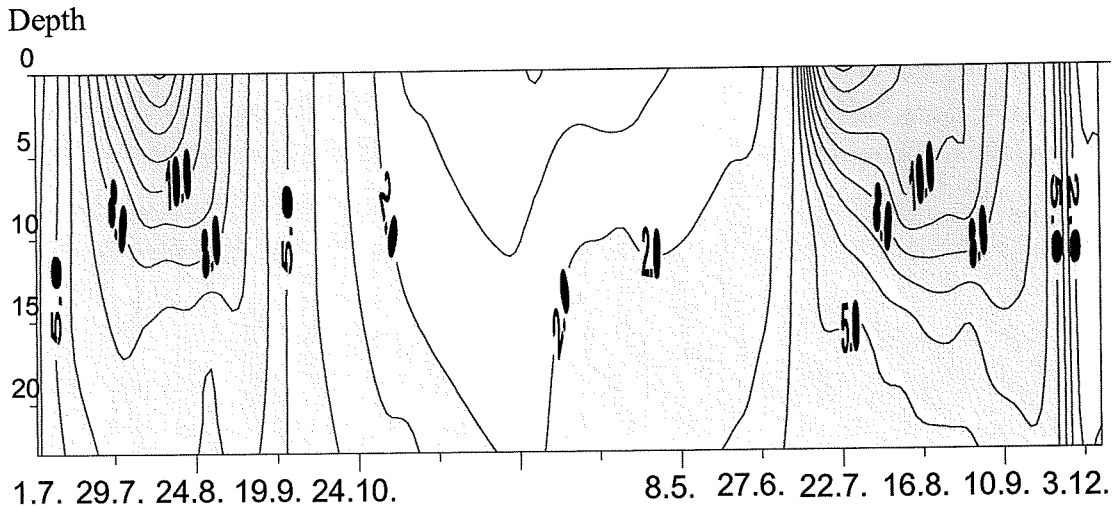
Parameter	Value	
Latitude	69°03'N	
Longitude	20°52'E	
Altitude (m a.s.l.)	679.4	
Catchment area (ha)	460.6	
Lake area (ha)	69.9	
Maximum lake depth (m)	24.0	
	Mean	Range
Secchi (m)	8.7	5.7-10.5
Water temperature (°C)	6.1	-0.2-14.6
pH	7.0	5.4-7.5
Conductivity ( $\mu\text{S cm}^{-1}$ )	28.2	24.6-37.0
Oxygen ( $\text{mg l}^{-1}$ )	9.7	8.5-12.7
Cl ( $\text{mg l}^{-1}$ )	1.59	0.68-2.84
SO <sub>4</sub> ( $\text{mg l}^{-1}$ )	4.2	0.8-5.9
Si ( $\text{mg l}^{-1}$ )	0.51	0.1-0.77
NH <sub>4</sub> -N ( $\mu\text{g l}^{-1}$ )	0.6	0.2-1.0
NO <sub>3</sub> -N ( $\mu\text{g l}^{-1}$ )	42	10-0.178
TP ( $\mu\text{g l}^{-1}$ )*	4.0	3.0-5.0
TN ( $\mu\text{g l}^{-1}$ )*	122.0	111.0-130.0
Ca ( $\text{mg l}^{-1}$ )*	2.8	2.5-3.1
K ( $\text{mg l}^{-1}$ )*	1.6	1.4-1.8
Na ( $\text{mg l}^{-1}$ )*	9.4	9.0-9.8
Mg ( $\text{mg l}^{-1}$ )*	5.9	3.8-7.6

\*marked parameters are measured open-water period in summer 1996

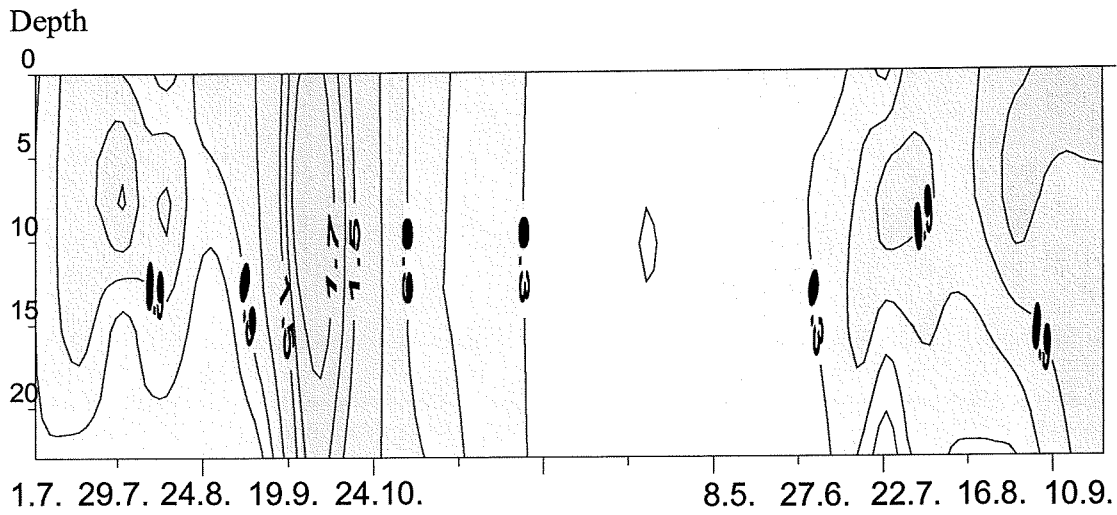
**Table 2. Calanoids, cyclopoids, and cladocerans during the sampling season.**

Group	Mean abundance ind./m <sup>3</sup>	Maximum abundance ind./m <sup>3</sup>	Minimum abundance ind./m <sup>3</sup>
Calanoida	439	626	200
Cyclopoida	131	330	5
Cladocera	81	180	5

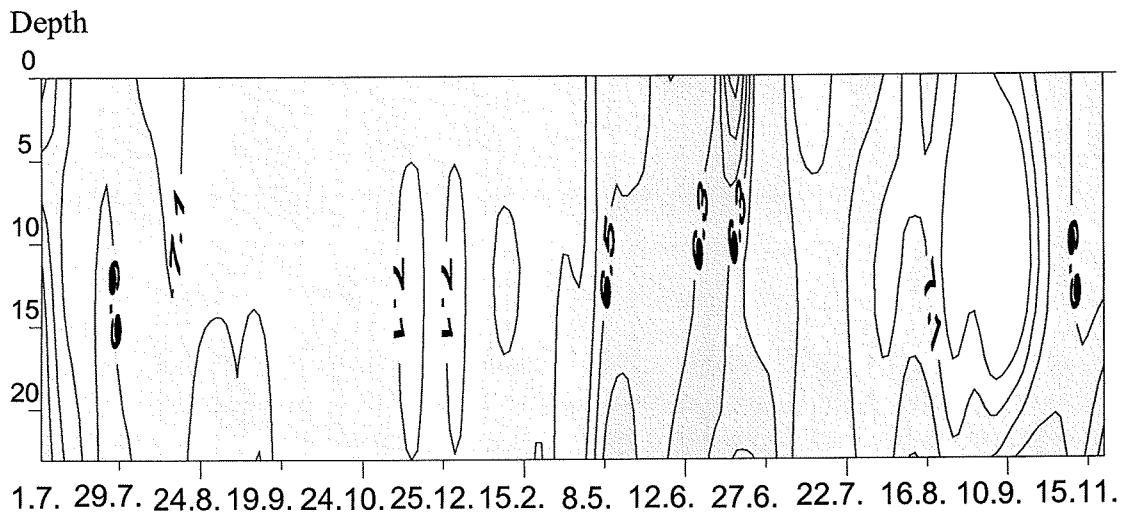
**A. Temperature (°C)**



**B. Chlorophyll-a (µg/l)**

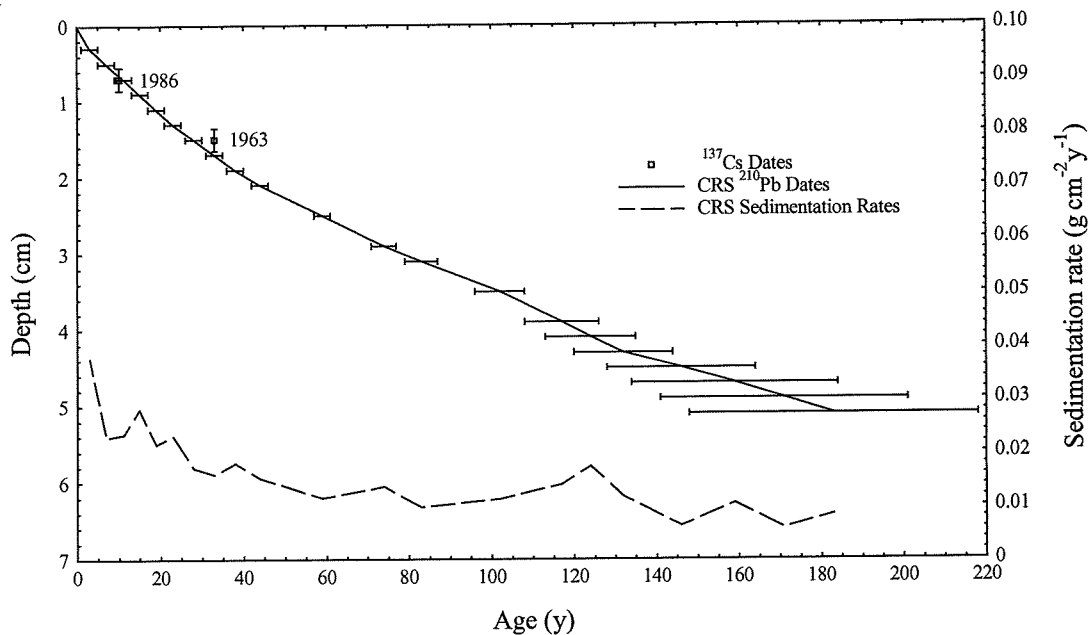


**C. pH**



**Fig.1. Seasonal fluctuation of temperature, chlorophyll-a, and pH in lake Saanajärvi. Table 2. Abundance of Calanoida, Cyclopoida and Cladocera**

In the dated master core equilibrium between total  $^{210}\text{Pb}$  and the supporting  $^{226}\text{Ra}$ , corresponding to ca. 150 years accumulation, was reached at a depth of about 6 cm. Unsupported  $^{210}\text{Pb}$  concentrations were a little irregular in the top 1.5 cm, but beneath this declined more or less exponentially with the depth suggesting relatively uniform sedimentation rates in the older sediments (Fig. 2). The  $^{137}\text{Cs}$  activity versus depth profile had two significant peaks, at 0.7 cm and 1.5 cm. It is presumed that the more recent feature records fallout from the Chernobyl reactor accident in 1986, and that the earlier feature records the 1963 fallout maximum from the atmospheric testing of nuclear weapons. This is supported by  $^{210}\text{Pb}$  dates (calculated using the CRS model) which place 1986 at a depth of ca. 0.6 cm and 1963 at a depth of ca. 1.7 cm. The mean sedimentation rate during the past 30 years is calculated to be  $0.025 \pm 0.005 \text{ g cm}^{-2} \text{ y}^{-1}$  ( $0.053 \pm 0.010 \text{ cm y}^{-1}$ ). The mean accumulation for the 150 years preceding ca. 1960 is calculated to be  $0.012 \pm 0.001 \text{ g cm}^{-2} \text{ y}^{-1}$  ( $0.024 \pm 0.002 \text{ cm y}^{-1}$ ). Sediment accumulation rates in the neighbouring cores are similar to those in the master core, suggesting relatively stable sedimentation conditions throughout the deeper basin. The chronology is confirmed by the SCP profile, with a clear increase in concentrations at ca. 4.2 cm. Magnitude of the record indicate a hemispherical background level of carbonaceous particles. Low sedimentation rates are typical to arctic lakes with low primary production.



**Fig. 2. Radiometric dating of the master core and dry matter accumulations rates.**

Responses to recent climatic changes in the sediment of Saanajärvi were studied by comparison of various biological and sedimentological proxies with the 200-year long climate record, specifically reconstructed for the site using a data-set of European-wide meteorological data. The multi-proxy evidence of simultaneously changing diatom, cladocera, and chrysophyte assemblages along with the increased rates of organic matter accumulation and pigment concentrations suggested that the lake had undergone a distinct typological change starting from the turn of the 20th century. This change, indicating an increase in lake productivity, paralleled a pronounced rise in the meteorologically reconstructed mean annual and summer temperatures in the region between ca. 1850 and 1930s. We postulated that, during the Little Ice Age, the lake was not, or was only weakly, thermally stratified during summer, whereas the subsequent increase in air and hence epilimnetic water temperatures resulted in the development of the present summer stratification. The increased thermal



stability of the lake created more suitable conditions for the growth of phyto- and zooplankton and changed the overall primary production from benthos to plankton. Mineral magnetic and carbonaceous particle records suggest long-distance pollution, particularly since the 1920s, yet the observed changes in lake biota and productivity can hardly be explained by this very minor background pollution; the 20th century species configurations are typical of neutral waters and do not indicate any response to pollution.

V. List of Publications arising from the project:

- Rautio, M. Sorvari, S. & Korhola, A. 2000. Crustacean zooplankton and diatom communities, their seasonal variability, and representativeness in the sediment of subarctic Lake Saanajärvi. *Journal of Limnology* (in press).
- Sorvari, S., Rautio, M. & Korhola, A. 2000. Seasonal dynamics of subarctic Lake Saanajärvi in Finnish Lapland. *Verh. Int. Ver. ges. Limnol.* in press.
- The MOLAR Water Chemistry Group (47 authors, including S. Sorvari, M. Rautio & A. Korhola) 1999. The MOLAR project: atmospheric deposition and lake water chemistry. *J. Limnol.* **58**: 88-106.
- Korhola, A., Sorvari, S., Rautio, M., Appleby, P.G., Dearing, J.A., Hy, Y., Rose, N. Lami, A. & Cameron, N.G. 2000. A multi-proxy analysis of climate impacts on recent development of subarctic Lake Saanajärvi in Finnish Lapland. *J. Paleolim.*, in press.
- Catalan, J., Ventura, M., Camarero, L., Granados, I., Thies, H., Lotter, A., Lien, L., Korhola, A., Sorvari, S., Rautio, M., Barbieri, A., Stuchlik, S. & Brancelj, A. 2000. Seasonal variability in remote mountain lakes: implications for climatic signals in their sediment record. *J. Paleolim.* (submitted).
- Sorvari, S. & Forsström, L. 2000. A two-year record of phytoplankton and diatom succession in subarctic Lake Saanajärvi in Finnish Lapland. *Polar Biology.* (in prep).
- Sorvari, S. & Korhola, A. 1998. Recent diatom assemblage changes in subarctic Lake Saanajärvi, NW Finnish Lapland, and their palaeoenvironmental implications. *J. Paleolim.* **20**: 205-215.
- Korhola, A. 1997. The suitability of northern freshwater ecosystems as indicators of climatic change. *Symp. on Climate Change Effects of Northern Terrestrial and Freshwater Ecosystems. Arktikum, Rovaniemi, Finland, 18th - 20th September, 1997.*
- Sorvari, S. & Korhola, A. 1997. Recent diatom assemblage changes in subarctic Lake Saanajärvi, NW Finnish Lapland - A Paleolimnological Approach. *Symposium on Climate Change Effects of Northern Terrestrial and Freshwater Ecosystems. Arktikum, Rovaniemi, Finland, 18th - 20th September, 1997.*
- Sorvari, S., Korhola, A. & Blom, T. 1997. Recent diatom assemblage changes in subarctic Lake saanajärvi, NW Finnish Lapland. *7th International Symposium on Palaeolimnology, 28 Aug. - 2 Sept. 1997. Heiligkreuztal, Riedlingen, Germany. Würzburger Geographische Manuskripte* **41**: 205-206.
- Korhola, A. 1996. Northern lakes as key witnesses for climatic change. *Universitas Helsingiensis* **3/1996**: 16-19.
- Korhola, A. 1996. Ilmasto jättää jälkensä järveen. Syrjäiset vuoristojärvet tutkijoiden arkistoina. [Climate leaves traces in lakes. Remote mountain lakes as archives of investigators] *Helsingin Sanomat*, Tiede ja Ympäristö. 17.2.1996.

Signature of Partner: *Atte Korhola*

Date: 1 May, 2000

**DETAILED REPORT OF THE INDIVIDUAL PARTNERS**

Reporting period: March 1996 – March 1999

Partner: University of Edinburgh

Principal Investigator: Roy Thompson

Scientific staff: Anna Agusti-Panareda

Address: Department of Geology and Geophysics  
The University of Edinburgh  
Edinburgh  
EH9 3JW

Telephone: 44-131-650-4907

Fax: 44-131-668-3184 E-Mail: roy@ed.ac.uk

**I. OBJECTIVES FOR THE REPORTING PERIOD:**

To:-

1. Collate, harmonise and analyse long-term instrumental climate records from the European lowlands and reconstruct climate change at the MOLAR WP3 and AWS sites.
2. Integrate and compare the climate reconstructions with the AWS monitoring.
3. Reconstruct variations in ice-cover and growth season at the MOLAR sites.
4. Correlate WP3 cores using LOI and DW measurements and generate a time-scale for all the cores by matching with the master PB-210 dated cores.

**II. OBJECTIVES FOR THE NEXT PERIOD:**

None

III. Are there any particular problems? Is your part of the project on schedule?

All the work has been completed.

IV. MAIN RESULTS OBTAINED: *METHODOLOGY, RESULTS, DISCUSSION, CONCLUSIONS*  
(use other pages as necessary but preferably no more than 2)

1. Long term climate reconstructions

We have assembled monthly series of temperature, pressure and precipitation from the European lowlands. The series have been carefully homogenised. Additional local climate records were also obtained to act as transfer series. This has allowed 217 year long climate reconstructions to be generated for all the 11 WP3 and AWS sites using a multiple regression approach. Cross-validation has been used to assess the skill of our method. The oceanic sites tend to have the lowest errors while, as anticipated, the more remote Iberian and Arctic sites have the largest errors. The monthly resolution and skill for all our reconstructions is more than adequate for assessing the climate record of the MOLAR sediment records. Furthermore we have shown that in the European area mountain climate change (in air-temperature) is very representative of lowland climate change and visa versa.

2. AWS and climate reconstructions

The AWS monitorings have allowed an independent check on the quality of our air-temperature reconstructions through a comparison of our 1997/98 air-temperature reconstructions and the on-site air-temperature measurements. In general excellent agreement is found between the two. AWS monitorings for the 1998/9 period thus remain to be compared. This data when combined with continued AWS monitoring, in EMERGE, will form a very useful database for high temporal resolution (daily) downscaling studies.

3. Reconstruction of ice-cover and growth season duration

Ice-cover and growth season have been reconstructed from the climatic analyses at all the WP3 sites. The error of our approach to ice-cover modelling has been validated by using historical data for two lakes in Finland. The average error in the duration of ice-cover, at these two lakes, is found with our model to be only four days.

4. Core-correlations and chronologies

Sequence slotting has been very successfully applied to sediment cores from all eight WP3 sites and generated core correlations. At many of the WP3 sites the core correlations are of extremely high quality so demonstrating stratigraphically intact sediment at the sites. At six of the WP3 sites these correlations allow the chronologies of the master cores to be transferred to the sister (undated) cores. Hence we have been able to position all the MOLAR biostratigraphic, magnetic and geochemical core data for these six sites onto a common time frame for between site comparison.

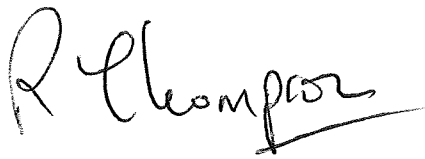
5. Database

A protected *www* database with 29 web pages was set up in Edinburgh in order to provide immediate and direct access to our results for all MOLAR participants.

V. List of Publications arising from the project (include copies):

1. Anna Agusti-Panareda, Roy Thompson and David M Livingstone, 2000. Reconstructing temperature variations at high-elevation lake sites in Europe during the instrumental period, *SIL*. (In press)
2. Anna Agusti-Panareda and Roy Thompson, 2000. Reconstructing air temperature variations at eleven alpine and arctic lakes in Europe from 1781 to 1997 AD. *J. Paleolimnology*. (Submitted)

Signature of Partner:

A handwritten signature in black ink, appearing to read "R Thompson". The signature is written in a cursive style with a long horizontal stroke at the end.

Date: 2000-04-10

Page 3 of 3

**DETAILED REPORT OF THE INDIVIDUAL PARTNERS**

Reporting period: 01/03/96 to 28/02/99

Partner: Norwegian Institute for Water Research (NIVA)

Principal Investigator: Bente M. Wathne

Scientific staff: Bjørn Olav Rosseland, Leif Lien, Sigurd Rognerud, Richard Wright,  
Ann Kristin Buan, Einar Kleiven (NIVA)  
Torunn Berg (Norwegian Institute for Air research, NILU).

Address: P.O. Box 173 Kjelsås  
N-0411

Telephone: +47 22185211

Fax: +47 22185200 E-Mail: bente.wathne@niva.no

**I. OBJECTIVES FOR THE REPORTING PERIOD:**

- Scientific co-ordination of MOLAR
- Co-ordinate WP 1 activities, including special responsibility for co-ordination of fish in WP 1,2, and water chemistry
- Site operator at Øvre Neådalsvatn, Stavsvatn and Arresjøen
- Sampling and analysis after the agreed MOLAR programme for Øvre Neådalsvatn, Stavsvatn, and Arresjøen
- Heavy metal analysis in deposition and lake water for WP 2 lakes after the MOLAR programme
- Ageing of all fish sampled in the MOLAR programme
- Analyses of heavy metals in liver, kidney and muscle in all fish from the MOLAR programme
- Analyses of isotopes of N and C in fish muscle from the MOLAR programme
- Report WP 1 results and edit annual progress report and final report for the total project
- Accomplish modelling activities within WP 1
- Complete database for chemistry and fish
- Prepare manuscripts for publication in international journals

**IV. MAIN RESULTS OBTAINED:**

*Scientific co-ordination*

The Annual Progress Reports have been prepared after the required form, including input from all project partners. The reports have been presented to Brussels and the MOLAR project group after each working year of the project. A MOLAR Manual describing the working methods, sampling and analysis within all scientific areas of MOLAR has been prepared, and this manual is also available for the public at the MOLAR homepage.

### *Sampling WP 1,2,3.*

The Norwegian lakes Øvre Neådalsvatn and Stavsvatn have been sampled according to the agreed plans apart from the sediment trap in Øvre Neådalsvatn, which was lost during the winter season 96/97 and not replaced. The active sampling period for the sediment trap is then from July to September 1996 only. The secondary site Arresjøen was sampled once in 1998.

### *Water and deposition chemistry, WP 1 and WP2.*

Seasonal variations in water chemistry have been followed for Øvre Neådalsvatn and Stavsvatn until the end of the sampling period in August 1998. Deposition sampling at Kårvatn close to Øvre Neådalsvatn and Møsvatn in the same area as Stavsvatn has also followed the plans. Deposition sampling and analysis at Kårvatn and Møsvatn are the responsibility of NILU.

Several workshops have been held during the reporting period discussing a.o. intercalibration exercises and quality control actions. The MOLAR labs as a total have performed well compared to the total number of laboratories participating in the intercalibrations.

Results for lake water chemistry for all 12 MOLAR lakes for 1996, 1997 and 1998 are stored by CNR and NIVA and after QA sent to the MOLAR database at UIB. Intercalibration exercises have been carried out both by CNR and NIVA. The water chemistry data base is now at NIVA and in Pallanza as well as at the University of Bergen.

Annual variations have been described and annual means have been calculated for each site. The ion concentrations have quite a wide range of variation (88-3360  $\mu\text{eq l}^{-1}$ ), from very diluted to highly buffered waters. The corresponding range of variation of conductivity is 6-148  $\mu\text{S cm}^{-1}$  at 25 °C. The pH values are in the range 4.9-6.0 in 8 of the 23 lakes, while three lakes (La Caldera, Hagelsee and Jezero v Ledvici) show values higher than 7.5. Alkalinity is very high for Jezero v Ledvici and Hagelsee (1303 and 1167  $\mu\text{eq l}^{-1}$ ), ranges between 118-343  $\mu\text{eq l}^{-1}$  for lakes Jörisee, Saanajärvi and La Caldera, and is lower than 50 and 20  $\mu\text{eq l}^{-1}$  in 15 and 7 lakes, respectively. Sulphate ranges from 11 to 252  $\mu\text{eq l}^{-1}$ ; the highest values show that atmospheric deposition cannot be considered as the only source of sulphate, but in some cases (e.g. Hagelsee, Jezero v Ledvici, Schwarzsee ob Sölden) there is also a sulphate contribution deriving from watershed weathering. Nitrate concentrations are very low (below 10  $\mu\text{eq l}^{-1}$ ) in the northernmost lakes in Norway (Øvre Neådalsvatn, Stavsvatn, Limgambergjtjern and Arresjøen), Finland (Saanajärvi), Russia (z. Chuna) and Spain (Laguna Cimera). The highest values (36-42  $\mu\text{eq l}^{-1}$ ) are found in the lakes in the Tatra Mountains (N. Terianske and Dlugi Staw). The lakes in the Alps show values between 15-26  $\mu\text{eq l}^{-1}$ , with the lowest value for Hagelsee (12  $\mu\text{eq l}^{-1}$ ). Nitrate concentration is also relatively low (below 12  $\mu\text{eq l}^{-1}$ ) in the lakes in Spain (Redó, Cimera and La Caldera).

The most important event affecting water chemistry is the snow melt, which in all the lakes causes a more or less sharp decrease in alkalinity, pH, calcium and major ion concentrations.

A synthesis paper of WP 1 on deposition and water chemistry has been produced.

### *Metal analysis in fish, WP2.*

NIVA has been responsible for the metal analyses in fish tissue and organs. In 1997, a broad screening of the metal concentrations (Na, Mg, Ca, Ti, Mn, Fe, Hg, Co, Cu, Zn, As, Se, Pb, Sr, Mo, Ag, Cd, Cs, La, Ce) in kidney and liver, as well as Hg in muscle, was performed on a total of 89 individuals from 4 lakes (Arresjøen, Jörisee, Etang d'Aubé and Stavsvatn). The fish sampled from the MOLAR lakes in 1997 (Øvre Neådalsvatn, Redo, Gossenköllesee and resampling of Stavsvatn, Etang d'Aubé and Jörisee were analysed at NIVA in 1998 for mercury (Hg) in muscle, and metals in kidney and liver (Cd, Pb, Cu, and Zn, as well as Se, Cs and As). A total of more than 140 fish from the seven MOLAR lakes have been analysed.

As a part of a QCP, reanalyses of mercury in fish from lakes with old fish (>10 years) and populations possibly being piscivorous were performed. In addition, muscle samples from 143 fish sampled in MOLAR have been analysed at the University of Stockholm, Sweden, for the isotopes of  $N^{14}/N^{15}$  and  $C^{14}/C^{12}$ . These are important variables especially when detailed stomach analyses are impossible to obtain, as isotopic measurements will provide a time-integrated measure of assimilated diet and an independent means of evaluating the diet of the consumer. This has been an additional project not originally planned for MOLAR, but has demonstrated the importance for future projects like EMERGE.

All data analysed at the other institutes (UIBK, CID-CSIC, CNRS) have been stored in a database at NIVA, in a form which might be used in a future ENSIS database. The data have partly been analysed in a multivariate statistical model. The results can also be coupled with the data from physiology and histology of each individual fish.

#### *Sediment analysis.*

Observed concentrations of contaminants in fish are also a function of the "dose". We have used concentrations and accumulation rates of Hg, Se, Pb, Cd, Zn, As, Cs and POP's in surface lake sediments as a surrogate variable for the dose in each lake. Sediments are known to reflect atmospheric depositions of pollutants but they are also influenced by the local water quality and lake specific data as water renewal time and catchment size. Concentrations of metals in sediments have been analysed at SGab in Luleå, Sweden and the lead 210 datings necessary for calculating accumulation rates at the University of Liverpool. The basic hypothesis is that by including the "dose", water quality and food web position it will be possible to sort out the most influencing variables for bioaccumulation of contaminants in fish.

#### *Fish Workshop*

Two major workshops on fish have been held during the MOLAR project, both in Arcachon, France, and hosted by CNRS and the University of Bordeaux. The first workshop was held prior to the sampling period in June 1996, and representatives for the national laboratories responsible for performing the testfishing and analysing the different fish tissues, participated in the workshop. Based on the practical performance under field conditions, several procedures had to be revised. A video tape was made showing the different modified procedures, and circulated to all laboratories prior to the field work in 1996. Kits for special tissue and blood sampling was sent from each responsible institution to the different groups, according to manual. With only few exceptions, sampling were performed as planned, and samples delivered successfully to the analysing laboratories by special mail. The second workshop was held prior to the Annual MOLAR Meeting in Arcachon, France, in February 1999. The main focus was on the physiology of fishes in high mountain lakes, and the gill histology. Besides the fish group in MOLAR, special invited participants were attending.

#### *Major findings – Fish*

We have in our AL:PE and MOLAR lakes only few examples where a pollution load of heavy metal can have given effects that interfere with normal ecology through changes in behaviour and reproduction success. We have, however, a few sites within MOLAR where a pollution load have accumulated in fish (muscle, liver and kidney), to give concentrations that by eating can lead to health risk for the consumers.

Examples of components that have such effects are heavy metals, especially Hg, Cadmium (Cd) and lead (Pb). Mercury is the "badest" in the metal group. While most other heavy metals "bioconcentrate" (= higher concentration in fish than in water), and bioaccumulate (increased concentration by increased age and size), mercury is the only heavy metal that show biomagnification through the food chain. In AL:PE 2 and MOLAR, we have found levels of Mercury, that is clear above reference levels for unpolluted areas. At Spitsbergen, Lake Arresjøen contain a population of Arctic charr that eat other fish (carnivorous) and become very old (more than 30 years of age), which

lead to both bioaccumulation and biomagnification. By the new recommendations by EPA (US Environmental Protection Agency), the oldest fish from Spitsbergen should not be eaten in an amount of 227 g (for a human of 70 kg) more than 2 times a month! These levels set a limitation to the use of fish as a natural food source with "unlimited" exploitation.

From AL:PE 2 ad MOLAR, we found that the trout liver in 12 out of 15 lakes (80%) had a level of Cd in liver that exceeded the recommended level for consumption given by the authority in Germany and the Netherlands. In Øvre Neådalsvatn, the lake which for years has been considered as the best reference lake for pristine environments in Europe, we even found results from a potential PAH pollution so strong that we could see histological changes in the liver of the fish.

Our results give signals that even "remote areas" of Europe is not undisturbed by man. One can always argue that few people eat trout liver or have a daily fish meal from alpine lakes, but again it reflects pollution in "remote areas" at levels which are significant.

### *Modelling*

The *MAGIC model* for trends and prognosis has been used for six lakes. Special workshops have been arranged to carry out the calculations and discuss the necessary data from the sites. Reporting for the sites are planned and started. A Workshop for deposition, water chemistry and modelling was arranged in London in November 1998.

MAGIC has been calibrated for all 6 lakes, and used to predict future trends in water chemistry given full implementation of the Oslo (1994) and Gothenburg (1999) protocols to the UN-ECE Convention on Long-range Transboundary Air Pollution. The 6 lakes are: Gossenköllesee (GKS), Estany Redó (RED), Øvre Neådalsvatn (NEO), Lochnagar (NAG), Starolesnianske Pleso (STA), Stavsvatn (SVN). The first three are circum-neutral and exhibit only minor acidification due to acid deposition, whereas the last 3 are acidified with high concentrations of aluminium and damage to fish and other organisms.

Stavsvatn (SVN) in southern Norway exemplifies the changes predicted by the MAGIC model given a future scenario of reduced acid deposition. There is a 12-year data record from this lake, which allows splitting of the data into a calibration period of 3 years (1986-88) and an evaluation (testing) period of 9 years (1989-1997). The model was driven by the measured deposition during this 12-year period. The results show close agreement between observed and modelled concentrations of major ions for the period. The calibrated model when run for 50 years into the future under the scenario of full implementation of the Oslo protocol (reduced S deposition relative to the year 1980), indicates that the water quality in the lake will continue to improve.

Data from the 6 lakes were also used to calculate critical loads using MAGIC and several standard steady-state models. These results indicate that all methods give roughly similar estimates for critical loads. MAGIC shows that achievement of new steady-state following change in deposition occurs with lag times of years-to-decades depending upon such factors as soil characteristics and lake hydraulic retention time.

Uncertainties in predictions come from difficulties in predicting future nitrogen retention and release in mountain areas. In addition from the model application it is clear that year-to-year variations in climatic conditions influence the surface water chemistry. Long-term change in climate can also affect future lake water quality.

### V. List of Publications arising from the project:



- Battarbee, R.W., Patrick, S., Wathne, B.M., Mosello, R., Psenner, R. 1998. Measuring and modelling the dynamic response of remote mountain lake ecosystems to environmental change (the MOLAR project). Proceedings of SIL Congress Dublin 1998, Abstract book pp. 144.
- Grimalt, J.O., Fernandez, P., Berdie, L., Vilanova, R., Catalan, J., Psenner, R., Hofer, R., Appleby, P.G., Rosseland, B.O., Massabuau J-C., Battarbee, R.W. and Lien, L., 2000. Selective Trapping of Organochlorine Compounds in Mountain Lakes of temperate areas. (MS subm. Nature April 2000)
- Massabuau, J-C., Rosseland, B.O., Laurent, P. et al. 2000. Towards limits of life in low-mineralised pristine waters: the trout case study. (Manuscript to be submitted Nature, May 2000).
- Mosello, R., Boggero, A., Marchetto, A. Wathne, B.M., and Lien, L. 1998. Chemistry of headwater lakes studies in the EU project "Acidification of mountain lakes: palaeolimnology and ecology (AL:PE)". - In: Kovar, U. Tappeiner, N.E. Peters, R.G. Craig (Eds), Hydrology, water resources and ecology in headwaters, Proceedings of the HeadWater'98 conference, Merano: 395-401. International Association of Hydrological Sciences Publ. No. 248, IAHS Press, Wallingford.
- Mosello, R. et al. (The MOLAR Water Chemistry Group). 1999. The MOLAR Project: atmospheric deposition and lake water chemistry. In: Straškrabová, V., C. Callieri & J Fott (Eds), Pelagic food web in mountain lakes. Mountain Lakes Research Program. J. Limnol., 58(2): 88-106.
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- Patrick, S., Battarbee, R.W., Wathne, B.M., Psenner, R. 1998. Measuring and modelling the dynamic response of remote mountain lake ecosystems to environmental change: An introduction to the MOLAR project. ). - In: Kovar, U. Tappeiner, N.E. Peters, R.G. Craig (Eds), Hydrology, water resources and ecology in headwaters, Proceedings of the HeadWater'98 conference, Merano: 403-410. International Association of Hydrological Sciences Publ. No. 248, IAHS Press, Wallingford.
- Patrick S., Battarbee R. W., Wathne B.M. and Psenner, R. 1997. Measuring and modelling the dynamic response of remote mountain lake ecosystems to environmental change: an introduction to the MOLAR project. European Conference on environmental and societal Change in Mountain Regions Oxford, UK, December 1997.
- Patrick S., Battarbee R. W., Wathne B.M. and Psenner, R. 1997. Measuring and modelling the dynamic response of remote mountain lake ecosystems to environmental change: an introduction to the MOLAR project. Advanced data analysis for modelling and assessment of biogeochemical effects of air pollution in temperate ecosystems CIEMAT, Madrid, October 1997.
- Psenner, R., Mosello, R., Boggero, A., Marchetto, A., Wathne, B.M., Lien, L 1998. Mountain lake research (MOLAR): Atmospheric deposition and Lake Water Chemistry. Proceedings of SIL Congress Dublin 1998, Abstract book p. 234.
- Rognerud, S., Grimalt, J.O., Hofer, R., R. Lackner, R., Rosseland, B.O., Massabuau, J-C., and Lien, L. 2000. Mercury, and organochlorine contamination in brown trout (*salmo trutta*) and arctic charr (*Salvelinus alpinus*) from high mountain lakes in Europe and the Svalbard archipelago. (MS) Rognerud, S., Grimalt, J.O., Hofer, R., R. Lackner, R., Rosseland, B.O., Massabuau, J-C., and Lien, L. 2000. Mercury, and organochlorine contamination in brown trout (*salmo trutta*) and arctic charr (*Salvelinus alpinus*) from high mountain lakes in Europe and the Svalbard archipelago. (MS)
- Rosseland, B.O. 1999. Miljøgifter i fisk fra høvfjellsjøer- resultater fra EU prosjektene AL:PE, AL:PE 2 og MOLAR.. (Environmental pollutants in fish from highmountain lakes – results from the EU projects AL:PE, AL:PE 2 and MOLAR). Vann 3B, 688-702. (In Norwegian)
- Rosseland, B.O., Lien, L., Morrison, B., Massabua, J-C., Hofer, R, Rodriguez, D., Grimalt, J., Moiseenko, T, Gals, J. and Birks, J. 1998. AL:PE Projects. Fish population studies. SIL XXVII Congress, "Water of Life", Ireland, Aug. 1998, Abstract book, p. 259.

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- Wathne, B.W. and Hansen, H. (Eds.) 1997. MOLAR. Measuring and modelling the dynamic response of remote mountain lake ecosystems to environmental change: A programme of Mountain Lake Research. MOLAR Project Manual. NIVA-report SNO 3710-97. 179 p.
- Wathne, B.W. (Ed.) 1998. MOLAR. Progress Report 2/1998. Measuring and modelling the dynamic response of remote mountain lake ecosystems to environmental change: A programme of Mountain Lake Research. NIVA-report SNO 3864-98. 110 p
- Wathne, B.W. (Ed.) 1999. MOLAR. Progress Report 3/1999. Measuring and modelling the dynamic response of remote mountain lake ecosystems to environmental change: A programme of Mountain Lake Research. NIVA-report SNO 4070-99. 124 p

Signature of Partner:

Date:

1/3-99

Bente M. Wathne

**DETAILED REPORT OF THE INDIVIDUAL PARTNERS**

Reporting period: 1 March 1996 to 28 February 1999

Partner: UINN-IZ University of Innsbruck  
Inst. of Zoology & Limnology

Principal Investigator: Dr. Roland Psenner

Scientific staff: Dr. Hansjörg Thies  
Dr. Ulrike Nickus\*  
Dr. Rudolf Hofer  
Dr. Reinhard Lackner

Address: Institute of Zoology and Limnology  
Technikerstr. 25  
A-6020 Innsbruck

\*Institute of Meteorology and Geophysics  
Innrain 52  
A-6020 Innsbruck

Telephone: +43 512 507-6130

Fax: +43 512 507-6130 E-Mail: roland.psenner@uibk.ac.at

**I. OBJECTIVES FOR THE REPORTING PERIOD:**

The work at our site, Gossenköllesee (GKS) comprised the following topics:

Bulk deposition and snow pack: ions, <sup>210</sup>Pb, PCB, PAH, SCP

- Lake water physics and chemistry
- Hydrology and mass balance
- Distribution (speciation) of <sup>210</sup>Pb, PCB, PAH, and metals in lake water
- Sedimentation of <sup>210</sup>Pb, PCB, PAH, SCP
- Sediment cores: PCB, PAH, <sup>210</sup>Pb, <sup>137</sup>Cs, SCP
- Soil inventory of <sup>210</sup>Pb and <sup>137</sup>Cs in the catchment
- PCB, PAH, and metals in fish
- Modelling the transport of elements and pollutants

Most of the field work has been done in the two hydrological years from 1 October 1996 to 30 September 1998. In this time period we have

- collected and evaluated meteorological data;
- sampled and analysed lake water, tributaries, snow and rain
- sampled organic micropollutants from air and lake water (with the group of Dr. Joan Grimalt), heavy metals for chemical speciation (together with Dr. Stan van den Berg) and radioactive lead in precipitation and lake water (with Dr. Peter Appleby);
- collected sediment cores and benthic invertebrates.
- In addition we have studied microbial food webs (structure and dynamics) and fish (histochemistry, physiological stress factors, metals and micropollutants)

IV. MAIN RESULTS OBTAINED: *METHODOLOGY, RESULTS, DISCUSSION, CONCLUSIONS*  
(use other pages as necessary but preferably no more than 2)

**RESULTS**

Water chemistry sampling and analysis has been done at Gossenköllesee (GKS) lake water, tributaries, springs, snow and rain according to the MOLAR project manual. All major ions and nutrients were sampled weekly or biweekly. Analytical quality control has been performed in cooperation with Bente Wathne and Rosario Mosello. Samples for heavy metals were taken from GKS surface and precipitation and sent to Norway for analysis. Sampling for heavy metal speciation and radionuclides in lake water of GKS was done in March and July by Peter Appleby and Stan van den Berg. Organic micropollutants in air and surface water have been collected in March and July 1997 by Rosa Vilanova, Pilar Fernandez and Guillem Carrera Ruiz. Large volume samples have been filtered for SCPs in Summer 1997 and sent to Neil Rose after filtration on Whatman GF/C filters. Microbial food web studies have been performed according to the MOLAR manual. Fish have been sampled in GKS, Jörisee, Ovre Neodalsvatn, Redo and Stavsvatn; they were processed on site, or sent to Innsbruck, France, Spain and Norway for further analysis. Histological sections of liver, gills and kidney were prepared and partly evaluated. Three additional sediment cores have been taken for contemporary chironomids and sent to Gunnar Raddum. Sediment traps for diatoms and chrysophytes (monthly) and SCPs and Pb (3 July, 29 November) have been taken. Soil samples have been taken in July by Peter Appleby. The MAGIC Model has been applied to GKS in January 1998 by Dick Wright, NIVA, and Chris Curtis, UCL, in cooperation with Uli Nickus and Hansjörg Thies. Schwarzsee ob Sölden (SOS), the secondary site, was sampled on 18 September 1997 for water chemistry.

**DISCUSSION**

The most important aspect of the work done at our site is that we have now a better understanding of transport processes in high mountain lakes: beside the transport of water (hydrology, e.g. water exchange rates measured by lithium tracers in an additional project) we have excellent data about distribution and transport of solutes (mass balance approach for major ions) but also of substances which differ extremely in their physical behaviour and transport routes: volatiles such as PCBs and PAHs, natural and anthropogenic radioisotopes such as  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ , metals originating from the bedrock and air pollution (Pb, Cd, Ni, Co), and true particles such as fly ash (SCP, spheroidal carbonaceous particles). In addition, we have gathered not only „objective“ pollution data, such as PCB, PAH, and metals accumulated in sediments and different organs of fish, but also „subjective“ measurements which indicate to how much stress fish populations are exposed. So we can not only provide a comparison of different lakes, the so-called WP2 lakes (i.e. 6 primary and 3 secondary sites), but we can give a broader view of transport of substances in high mountain lake ecosystems, for instance regarding the state and the effects of major pollutants (PCB, metals) on top predators.

One major problem was the restricted time for data evaluation because we have followed 2 hydrological years at Gossenköllesee (1 October 1996 – 30 September 1998). For this reason, publication of the results is still under way, and a large number of papers will be presented at the International Symposium on High Mountain Lakes and Streams, Innsbruck, 4-8 September 2000.

What is still missing, what could not be achieved? We have to admit that „simple“ high mountain lakes are rather complex systems (e.g. hydrology, Winter cover, snow melt ...) which need new approaches and new tools. The distribution of work into different workpackages could be optimized

because sampling for so many specific and sophisticated measurements needs more than just basic skills. Thus not all samples could be evaluated; for instance, we had not enough sample volume for counting SCPs in snow, or the material collected in sedimentation traps was not always sufficient for quantitative evaluations. Some of these problems can be avoided if there is a more rapid response between people responsible for their sites and the analyst. Analyses which needed the presence of an experienced team and heavy equipment (for instance air quality measurements,  $^{210}\text{Pb}$  and metal speciation etc.) worked nicely, thanks to the facilities at our station at the shore of Gossenköllesee, but turned out to be difficult undertakings at lakes other lakes studied within workpackage 2.

## CONCLUSIONS

The results clearly show that not only Gossenköllesee but high mountain lakes in general are remote though not pristine. The selection of lakes has evidenced that there exists a degree of impact across Europe, for instance regarding the deposition of acids, heavy metals and organic pollutants. Since transport and redistribution of particles (SCP), acids, metals, natural radioisotopes ( $^{210}\text{Pb}$ ), anthropogenic radioisotopes ( $^{137}\text{Cs}$ ) and chlorinated hydrocarbons such as DDT and DDE are dominated by very different meteorological, physical and chemical factors, a complex picture of impacts and responses emerges: beside distance of source, air temperatures, altitude, geographical location, water chemistry, water renewal time, and snow melt processes play an important role. The reaction of the biota shows that chemical analysis of toxic substances can explain only part of the measured impact, and there are other environmental factors – inclusive food web structures – which modulate the response of organisms. Although our results reflect the complex pattern of impacts, pathways and effects, there are still some open questions remaining, for instance regarding the role of hydrology and catchment characteristics.

### V. List of Publications arising from the project (include copies):

- Battarbee, R.W., Patrick, S., Wathne, B.M., Mosello, R., Psenner, R. 1998. Measuring and modelling the dynamic response of remote mountain lake ecosystems to environmental change (the MOLAR project. ). Proceedings of SIL Congress Dublin August 1998.
- Berdie, L., and J.O. Grimalt. 1998. Assessment of the sample handling procedures of a man power minimized method for the analysis of organochlorine compounds in large numbers of fish samples. *J. Chromatogr. A* **823**, 373-380
- Berdie, L., M. Santiago-Silva, R. Vilanova and J.O. Grimalt. 1997. Retention time repeatability as a function of the injection automatism in the analysis of trace organochlorinated compounds with high-resolution gas chromatography. *J. Chromatogr. A* **778**, 23-29
- Berdie, L., M. Santiago-Silva, R. Vilanova, P. Fernandez and J.O. Grimalt. Detector linearity in the routine analysis of organochlorinated compounds by GC-ECD and GC-MS. *Anal. Chem.*, Submitted for publication
- Carrera, G., P. Fernandez, R. Vilanova and J.O. Grimalt. 1998 Analysis of trace polycyclic aromatic hydrocarbons and organochlorine compounds in atmospheric deposition by solid-phase disk extraction *J. Chromatogr. A* **823**, 189-196
- Chaler, R., R. Vilanova, M. Santiago-Silva, P. Fernandez and J.O. Grimalt. 1998. Enhanced sensitivity in the analysis of trace organochlorine compounds by negative ion mass spectrometry using ammonia as reagent gas. *J. Chromatogr. A* **823**, 73-79
- Escartin, E. and C. Porte. 1999. Biomonitoring of PAH pollution in high-altitude mountain lakes through the analysis of fish bile. *Environ. Sci. Technol.*, in press
- Fernandez, P., R. Vilanova and J.O. Grimalt. 1996. PAH distributions in sediments from high mountain lakes. *Pol. Arom. Comp.* **9**, 121-128

- Grimalt, J.O., L. Berdié, P. Fernandez, R. Vilanova, R. Psenner, R. Hofer, B.O. Rosseland, P.G. Appleby, J. Catalan, J.C. Massabuau and R.W. Battarbee. Selective cold trapping of organochlorine compounds in high altitude lakes. *Nature*, Submitted for publication
- Koinig K.A., Sommaruga-Wögrath, S., Schmidt, R., Tessadri, R., Psenner, R. 1998. Acidification processes in high alpine lakes – Impacts of atmospheric deposition and global change. In: Haigh, M.J., Krecek, J., Rajwar, G.S., Kilmartin, M.P.: *Headwaters: Water Resources and Soil Conservation. Proceedings of Headwater '98*: 45-54
- Koinig KA, Schmidt R, Psenner R (1998) Effects of Air Temperature changes and acid deposition on the pH history of three high alpine lakes, *Proceedings of the 14th International Diatom Symposium* (in press)
- Koinig KA, Schmidt R, Wögrath S, Tessadri R, Psenner R (1998) Climate Change as the primary cause for pH shifts. *Water, Air, Soil Pol* **104**:167-180
- Koinig KA, Sommaruga-Woegrath S, Schmidt R, Tessadri R, Psenner R (1998) Acidification processes in high alpine lakes - Impacts of atmospheric deposition and global change. Conference Volume of the Head Water Conference 1998, Meran (in press)
- Koinig, K.A. 1998. Palaeolimnology of high mountain lakes – The impact of climate change and atmospheric deposition on past pH changes and sediment chemistry, Thesis, University of Innsbruck and Austrian Academy of Sciences.
- Koinig, K.A., Schmidt, R., Psenner, R. 1998. Driving forces for pH shifts in high alpine lakes – The impact of climate change versus acid deposition, *Würzburger Geographische Manuskripte* **41**: 109.
- Kopáček J., Stuchlík E., Fott J., Veselý J., Hejzlar J. 1998. Reversibility of acidification of mountain lakes after reduction of nitrogen and sulfur emissions in Central Europe. *Limnology & Oceanography*.
- Kopáček, J., E. Stuchlík, V. Straškrabová and P. Pšenáková. 1999. Factors governing nutrient status of mountain lakes in the Tatra Mountains. *Freshwat. Biol.* in press
- Nickus, U. 1999. Meteorological records of Gossenköllesee (2413 m, Kühtai, Tyrol). *Mitteilung Nr. 3*, Institute of Meteorology and Geophysics, University of Innsbruck (in press)
- Nickus, U., Thies, H., Kuhn, M. & Psenner, R. 1998. The snow cover at a headwater site in the Tyrolean Alps: seasonal and local variability of atmospheric trace substances in the snow pack. in: *Hydrology, Water Resources and Ecology of Mountain Areas* (Tappeiner et al., eds.), 39-42. European Academy Bozen.
- Patrick, S., Battarbee, R.W., Wathne, B.M., Psenner, R. 1998. Measuring and modelling the dynamic response of remote mountain lake ecosystems to environmental change: An introduction to the MOLAR project. ). - In: KOVAR, U. TAPPEINER, N.E. PETERS, R.G. CRAIG (Eds), *Hydrology, water resources and ecology in headwaters, Proceedings of the HeadWater'98 conference, Merano*: 403-410. International Association of Hydrological Sciences Publ. No. 248, IAHS Press, Wallingford.
- Pernthaler, J., Glöckner, F.O., Unterholzner, St., Alfreider, A., Psenner, R., & Ammann, R. 1998. Seasonal Community and Population Dynamics of Pelagic Bacteria and Archaea in a High Mountain Lake. *Appl. Env. Microbiol.* **64**: 4299-4306
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- Sommaruga-Wögrath S, Koinig K, Schmidt R, Tessadri R, Sommaruga R, Psenner R (1997). Temperature effects on the acidity of remote alpine lakes. *Nature* **387**: 64-67.
- Straskrabova, V. C. Callieri, P. Carrillo, L. Cruz-Pizarro, J. Fott, P. Hartman, M. Macek, J.M. Medina\_sanchez, J. Nedoma & K. Simek. 1999. Investigations on pealgic food webs in mountain lakes – aims and methods. *J. Limnol.* **58**: 77-87
- Thies, H., Nickus, U. & Psenner, R. 1998. Response of discharge and water quality in headwater brooks on distinct hydroclimatic conditions in the Tyrolean Alps. *IAHS Publ. no. 248*, 491-497.
- Thies, H., Nickus, U., Arnold, C., Schnegg, R., Wille, A. & Psenner, R. 1999. Biogeochemistry of a high mountain lake in the Austrian Alps. *Verh. Int. Verein. Limnol.* (in press)

- Vilanova, R., P. Fernandez and J.O. Grimalt. 1998 .Atmospheric persistent organic pollutants in high altitude mountain lakes. A preliminary study. In:*Sea-air exchange: processes and modelling*. Edited by J.M. Pacyna, D. Broman and E. Lipiatou. Office for official publications of the European Communities. Luxembourg. 1998. pp. 209-215.
- Wille, A., Sattler, B., & Psenner, R. 1999. Lake Ice Microbial Communities (LIMCO) – Biology of a periodic ecotone. Extended abstract. *Verh. Int. Verein. Limnol.* (in press)
- Wille, A., Sonntag, B., Sattler, B., & Psenner, R. 1999. Abundance, Biomass and Size-Structure of the Microbial Assemblage in the high mountain lake Gossenköllesee (Tirol, Austria) during the ice-free period. *J. Limnol.* **58**: 117-126

Signature of Partner:

A handwritten signature in black ink, appearing to read "Rolf Süssner". The signature is written in a cursive style with a large, prominent initial 'R'.

Date: 10 May 2000

## PART B

### DETAILED REPORT OF THE INDIVIDUAL PARTNERS

Reporting period: 01.02.1998 – 28.02.1999

Partner: OAW.IL, Institute of Limnology, Austrian Academy of Sciences

Principal Investigator: Prof. Dr. Roland Schmidt

Scientific staff: Dr. Karin A. Koinig, Mag. Christian Kamenik

Address: Gaisberg 116, A-5310 Mondsee, Austria

Telephone: +43 (0)6232 3125-24

Fax: +43 (0)6232 3578

E-Mail:  
roland.schmidt@oeaw.ac.at

#### I. OBJECTIVES FOR THE REPORTING PERIOD:

- a) Sampling and counting of epilithic and epiphytic littoral and pelagic diatoms of the Austrian site, Gossenköllesee (GKS).
- b) Diatom and chrysophycean cyst evaluation of sediment trap samples of GKS.
- c) Chrysophycean cyst evaluation of GKS2, Terianske Plezo, Jezero Ledvicah, and Hagelsee.
- d) Grain size measurements on GKS.
- e) Statistical treatment of field data.
- f) Sampling support for additional analyses of GKS.

#### II. OBJECTIVES FOR THE NEXT PERIOD:

Final statistical treatment of field data for publication.



## PART B

II. Are there any particular problems ? Is your part of the project on schedule ?

On schedule.


III. MAIN RESULTS OBTAINED: *METHODOLOGY, RESULTS, DISCUSSION, CONCLUSIONS*  
(use other pages as necessary but preferably no more than 2)

See additional pages.

IV. List of Publications arising from the project (include copies):

For the Austrian site Gossenköllesee 3 publications are in preparation (see publication list).

Signature of Partner:



Date: 07.4.2000

Page 2 of 2

## **Contributions of OAW.IL to the overall project**

- Diatom analyses of the sediment core Gossenköllesee (GKS)
- Chrysophyte cyst analyses of the sediment cores GKS, Terianske Plezo (Slovakia), Jezero v Ledvici (Slovenia), and Hagelseewli (Switzerland).
- Chrysophyte cyst and diatom sediment-trap analyses of GKS.
- Harmonisation of chrysophyte cyst taxonomy.
- Epilithic and epiphytic diatom transects of GKS.
- LOI, C/N, and grain size measurements of GKS.

### **1. Diatom sediment core data (GKS)**

The diatom subsamples were prepared according to standard techniques as described in Battarbee (1986).

A total of 67 diatom species were observed. The species composition was dominated by benthic *Fragilaria* (*F. brevistriata*, mean 23 %; *F. cf. lapponica* “X-large”, 11 %; *F. pseudoconstruens*, 9 %, *F. oldenburgiana*, 1.4 %), and planktonic *Cyclotella* (*C. cf. gordonensis*, 10 %; *C. cyclopuncta*, 7 %; *C. comensis*, 6 %). The other taxa with an average abundance of more than 1 % were predominantly *Achnanthes* (*A. levanderi*; 3 %; *A. minutissima*, 2.2 %; *A. oestrupii* , 1.3 %; *A. altaica*, 1.1 %; *Aulacoseira valida*, 1.8 %, and *Cymbella minuta*, 1.06 %). All of these species occurred throughout the core, indicating no major changes in the limnochemical conditions. No pH inference was applied, as several abundant species (accounting for 15 to 50 % of diatom assemblage) are not included in any current calibration data set.

The relative abundance of planktonic (total of all *Cyclotella*) species approximately followed the mean annual air temperature at GKS (Figure 1). During warm periods abundances of planktonic diatoms were higher than during cold ones. These findings match well with the observations of monthly changes in the recent diatom community of GKS. Low numbers of pelagic diatoms were found below the ice. Living diatoms were observed in the slush layer of the ice-cover: During onset of the ice-cover in November, *Cyclotella* was the most abundant taxon in the slush layers. However, a few weeks later a benthic community with *Fragilaria* and *Achnanthes* established which persisted until ice break in June (Koinig et al., in press). The relation between pelagic diatoms and air temperature is assumed to be predominantly driven by the duration of the ice-cover, as has also been discussed by Smol (1988) and Douglas & Smol (1999).

The divergence between air temperature and abundance of planktonic diatoms around 1975 was at highest during a period when not only temperature but also precipitation was low. Dry winters can cause an earlier ice break and consequently a longer vegetation period for *Cyclotella*, even if annual temperatures are low. Furthermore, during this period retrodicted temperature was low, when compared with measured Alpine or local (Innsbruck) data. The variation of planktonic diatoms better followed the annual air temperatures than seasonal pattern.

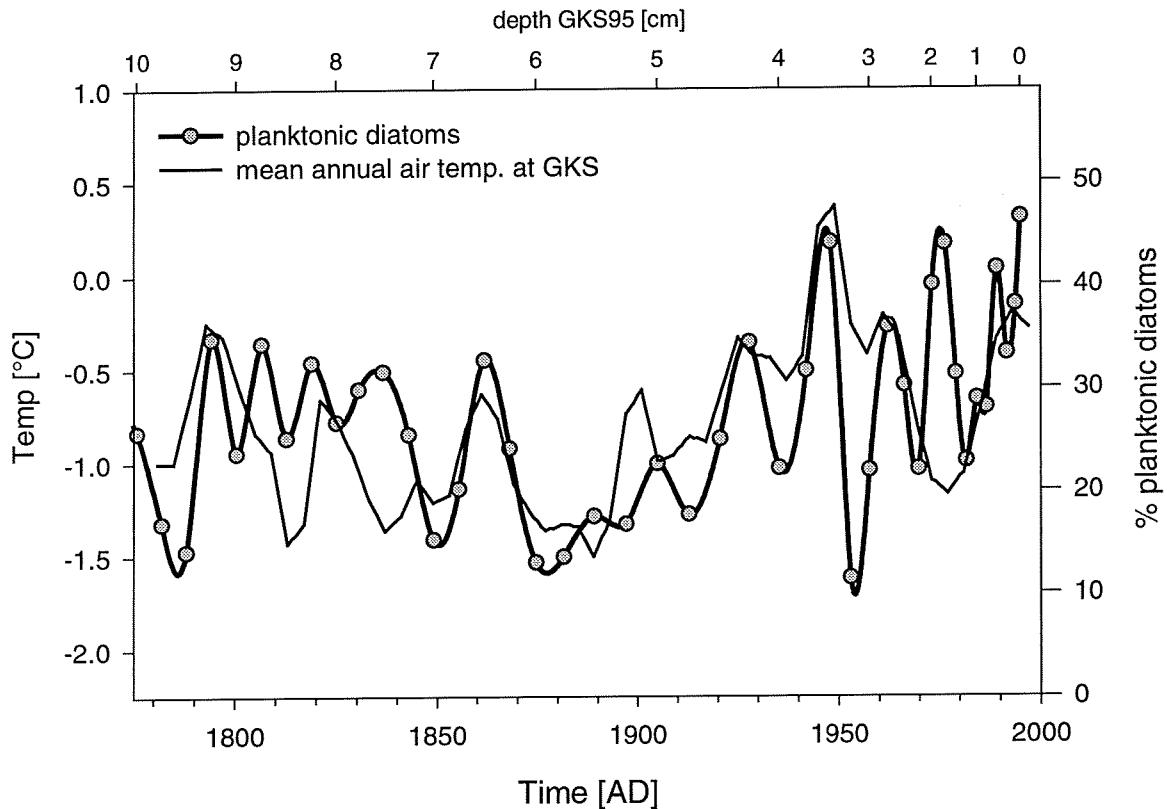


Fig. 1. Abundances of planktonic diatoms (*Cyclotella* spp.) in Gossenköllesee versus mean annual air temperatures.

## 2. *Chrysophyte stomatocysts*

Sediment traps of the Blösch-Type were exposed in the 4 lakes and sampled monthly during one or two years. For the detection of the whole morphological variability of the stomatocysts, sediment-trap as well as sediment core samples of the 4 lakes were counted in SEM (JEOL JSM 35). For harmonisation (taxonomic workshops) and descriptions of new types, a cyst data base with digital pictures (4000 size measurements) was established. In GKS, for example, 10 from a total of 36, in Jezero v Ledvicah 7 from 23 cyst types were described as new.

## 2.1. Sediment core data

The time spans from the last 150 (Jezero v Ledvici ) until about 900 years (Nižné Terianske Pleso).

In Gossenköllesee the sediment records revealed complex interactions between human impact, catchment processes, and climate. Alpine pastures and settlements have been important sources for nutrient influx in Alpine lakes. High productivity in GKS prior to approx. 1200 AD might have been favoured by both, temperature increase, indicated by pronounced glacier retreat during the 10<sup>th</sup>/11<sup>th</sup> century, and alpine farming. Historical records mention perennial settlements near Gossenköllesee prior to 1303 AD, and intensive sheep and cattle farming in this area during High Medieval times and later on. Chrysophyte cysts together with algal pigments indicate changes in nutrient concentrations (Fig. 2) in the middle of the 18<sup>th</sup> century. The food web in GKS may have been influenced when at the end of the 15<sup>th</sup> century the arctic charr (*Salmo trutta morpha fario* L.) was introduced in the lake. A decline in carbon, nitrogen, alloxanthin (cryptophytes) and canthaxantin (grazers) may indicate the removal of grazers by fish. Changes in C/N ratio, iron, manganese and mineral magnetism indicated increased detrital input from the catchment, probably by erosion processes. However, effects of climate and changes in land-use might overlap; e. g. during the time of "Little Ice Age", as indicated by a high C/N ratio, changes in metals and mineral magnetism, and historical records (restrictions of high alpine farming).

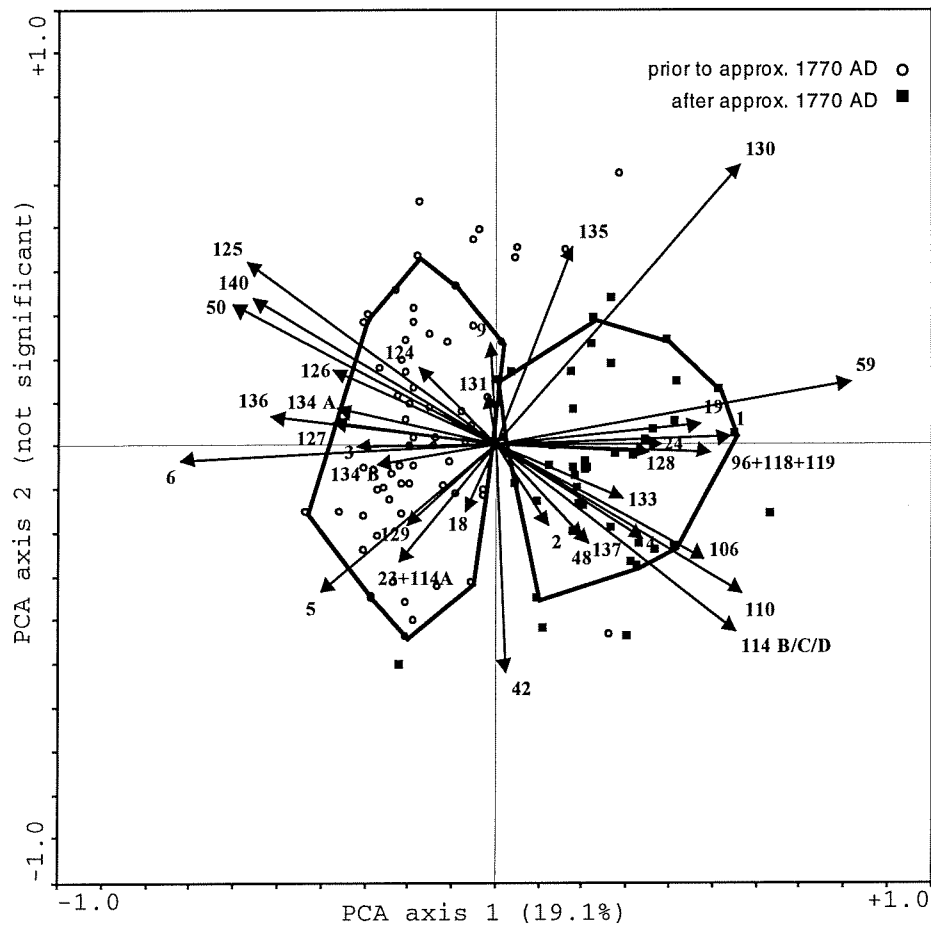


Fig. 2: PCA, summarizing the main changes in the stomatocyst assemblage composition in Gossenköllesee. PCA-axis 1 is statistically significant and separates zone I from zone II. Stomatocysts with small variance are not illustrated. Envelops combine 90% of the samples within one zone. Stomatocyst types dominating in zone I (ST # 6, ST # 125, ST # 5, ST # 126, ST # 127) are predominantly found in slightly meso- to eutrophic lakes, or assumed to have a wide tolerance concerning trophic status, whereas stomatocyst types prevailing in zone II (ST # 59, ST # 110, ST # 114 D, ST # 118, ST # 119, ST # 106, ST # 19) mainly occur in oligotrophic alpine and subalpine lakes (Kamenik et al., 2000).

## 2.2. Sediment trap data: stomatocyst seasonality

Sediment trap data from two years observation in GKS indicated a distinct seasonality of stomatocyst distribution (Fig. 3) which was related to ice setting and ice break.

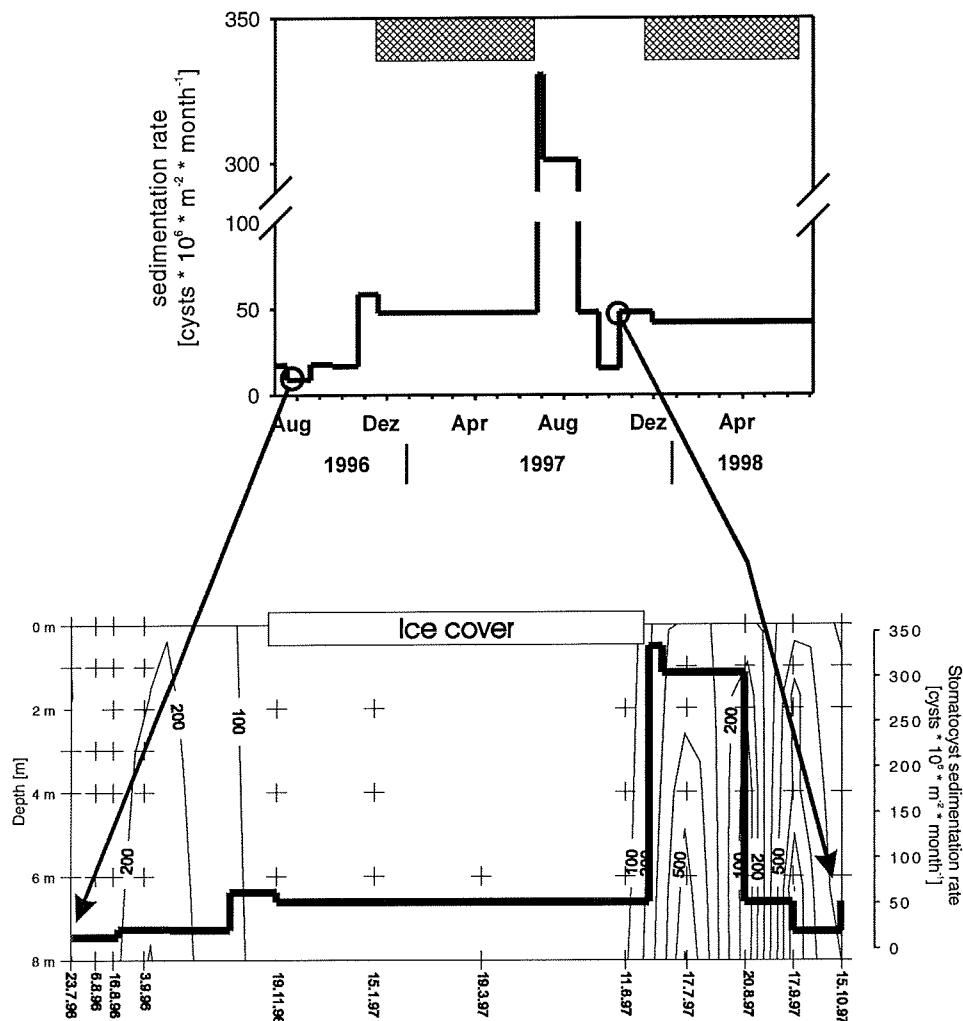


Fig. 3: Sedimentation rates of total stomatocysts and total number of vegetative chrysophyte cells in Gossenköllesee from 1996 to 1998. Grey boxes indicate ice cover. Crosses illustrate sampling points of phytoplankton samples (Kamenik et al., 2000).

### 2.3. Temperature relations

Mean monthly air temperatures, retrodicted from instrumental records for the last 200 years, show significant relation with the stomatocyst assemblage compositions of the sediment core data of all four lakes. Partial RDA (Redundancy Analysis) revealed that June air temperature significantly influenced stomatocysts in Jezero v Ledvici (1830 m a.s.l.) and Nižné Terianske Pleso (1941 m a.s.l.). In Hagelseewli (2339 m a.s.l.), where ice cover can remain the whole year, the stomatocyst assemblage composition was significantly affected by mean August - October air temperature. In Gossenköllesee (2417 m a.s.l.), which is exposed to SSE, the stomatocyst distribution was significantly influenced by autumn air temperature (Fig. 4). We suggest that these differences are due to different ice-break dates of the lakes. Hence, chrysophyte stomatocysts are a potential tool for seasonal palaeoclimate.

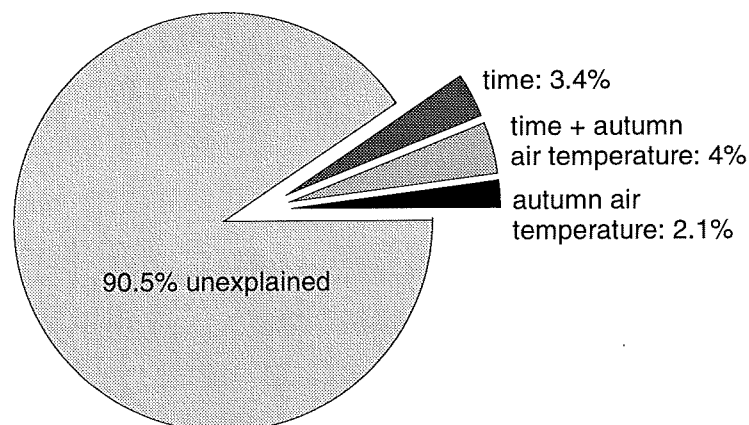


Fig. 4: Application of variance partitioning on factors significantly influencing the stomatocyst assemblage composition in Gossenköllesee and the amount of variance explained (Kamenik et al., 2000).

Publications:

KAMENIK, C., K.A. KOINIG, R. SCHMIDT, A. LAMI, P.G. APPLEBY, J.A. DEARING, R. THOMPSON & R. PSENNER. Eight-hundred years of environmental changes in a high alpine lake (Gossenköllesee, Tyrol) inferred from sediment records. *J. Limnol.*, (submitted).

KAMENIK, C., R. SCHMIDT, K.A. KOINIG, A. AGUSTÍ-PANAREDA, R. THOMPSON & R. PSENNER. The Chrysophyte stomatocyst composition in a high alpine lake (Gossenköllesee, Tyrol) in relation to seasonality, temperature and land-use. *Beih. Nova Hedwigia*, (in press).

KOINIG, K.A., KAMENIK, C., SCHMIDT, R., AGUSTI-PANAREDA, A., APPLEBY, P., FOTT, J., LAMI, A., ROSE, N., SCHNELL, O.A., TESSADRI, R., THOMPSON, R., PSENNER, R. Palaeoenvironmental changes in an alpine lake (Gossenköllesee, Austria) over the last 200 years – the influence of air temperature on biological parameters. *Journal of Paleolimnology* (submitted).



## PART B

### DETAILED REPORT OF THE INDIVIDUAL PARTNERS

Reporting period: 1-3-1996 to 28-2-1999

Partner: UNIVERSITAT DE BARCELONA, DEPARTAMENT D'ECOLOGIA. (UBCN.DE)

Principal Investigator: Jordi Catalan

Scientific staff: Lluís Camarero, Marisol Felip, Maria Rieradevall, Marc Ventura, Sergi Pla, Frederic Bartumeus, Dora Rodríguez, Lourdes Encina, Manuel Toro, Ignacio Granados

Address: Diagonal 645, Barcelona, E-08028, Spain

Telephone: +34 93 4021512

Fax: +34 93 4 11 14 38

E-Mail: catalan@bio.ub.es

#### I. OBJECTIVES FOR THE REPORTING PERIOD:

Field work and analytical work:

- On site measurements of sulphur and nitrogen deposition on L. Redó (Pyrenees)
- Monthly measurements of surface water chemistry in L. Redó
- Invertebrate sampling during the ice-free period in L. Redó
- Monthly sampling of the pelagic food web in L. Redó
- Measurement of phytoplankton and bacteria activities in L. Redó
- Installation of an automatic weather station in L. Redó
- Snow collection and chemical composition measurement in L. Redó
- Sediment particle sampling in Lake Redó
- Monthly measurements of physical, chemical and biological characteristics in the water column of L. Redó (Pyrenees) and L. Cimera (Gredos)
- Development of taxonomic system for chrysophytes
- Harmonise taxonomic procedures for key indicator taxa
- Sediment coring in L. Redó and L. Cimera

Numerical work:

- Data processing of the data obtained in relation with the different work packages for L. Redó and L. Cimera.
- Model development and applications related with the objective of work package 3.

#### II. PROBLEMS AND ACHIEVEMENT OF THE PROPOSED SCHEDULE

During the development of the project there were not major problems and schedule was followed without major deviation, particularly considering the nature of the fieldwork in extreme climatic conditions. There were episodic troubles with powering the automatic weather station and the sensor recording lake level, which appeared to be very sensitive to lighting. All analytical work was finished in schedule and the results were presented in different thematic workshop (Pallanza, Blatna, London, Arcachon, Bergen,) to the rest of participants.

Physical modelling of the water column resulted unsuccessful because the failure of the available models in reproducing the cooling of the lake at the right rate. It follows from that experience that convection driven cooling routines should be improved in those models.

#### IV. MAIN RESULTS OBTAINED: *METHODOLOGY, RESULTS, and DISCUSSION, CONCLUSIONS* (use other pages as necessary but preferably no more than 2)

##### WP1: *Mountain lake ecosystem response to acid deposition*

Deposition measurements were carried out on monthly-integrated samples at the lake station. However, we collected weekly and daily samples at a lower altitude and we have compared them with the monthly lake deposition. In 1997-98, we found no differences between the two sites; thus we could use the data on the lower station to follow the deposition in the lake catchment with much higher resolution. However, in 1998-99, although for most of the period the two sites were comparable, the annual deposition was significantly higher in the locality at higher elevation due to a few episodic events of much higher deposition. This result opens the question on which is the role of unusual episodes in establishing altitude differences in ion deposition in high mountains. A longer time series is needed to properly answer this question. The comparison of the chemical composition of the deposition with data from previous years (1987, 1994) has shown a trend of decreasing base cations in the past two years. These trends were reviewed in a joint publication with data from other sites (The Molar Chemistry group, 1999).

In co-operation with R. Wright (NIVA) and C. Curtis (UCL), FAB and MAGIC models were applied to Lake Redó. The lake was not acidified; thus the models were used to test future scenarios related to possible changes in sulphur and nitrogen emissions and to possible climate change and associated variations in dust deposition. The main conclusions were that the lake could hardly be acidified, even under the worse case considered; but, on the other hand, it is very sensitive to changes in base cation deposition; its alkalinity can vary up to 100% within reasonable future scenarios. Models were calibrated using measured data from 1997. Hindcasting of chemistry from previous years for which data was available (1984, 1994) was poor, indicating that a key process in the alkalinity balance of the lake is not properly taken into account by the model. The catchment of this lake (like most mountain lakes at high elevation) is poorly vegetated, chemical weathering of rocks may be more significant than in more vegetated catchments, we guess that this process might be the main source of discrepancy for hindcasting. The writing of these results for publication is in progress.

##### WP2. *Measuring and modelling major element and pollutant fluxes in mountain lakes and their impact on fish*

A large set of data have been collected on organic contaminants, SCPs and metals in collaboration with other partners, which using Pb-210 as tracer allowed to develop a first model illustrating the process from atmosphere to sediments. Concerning organochlorinated compounds, it appeared that fish are responsible for a large part of the flux of these compounds through the lake. Their importance is similar to sediments, but given their much lower surface, it means that their role is extremely important (Grimalt et al., submitted). Further research is needed, therefore, to understand the basis of the mechanisms supporting this fish role.

##### WP3. *Climate variability and ecosystem dynamics at remote alpine and arctic lakes*

Mean monthly temperature reconstructions for the last 200 years on L. Redó and L. Cimera sites were carried out by Roy Thompson and Anna Panareda from Edinburgh. Reconstructions were based on instrumental record from different meteorological stations around Europe and local and on-site weather stations measuring during the MOLAR project development. The trends that appeared in the reconstruction were compared with the sediment record of multiple variables (loss on ignition, pigments, diatoms, chironomids, cladocera,...). In the case of L. Redó, a clear response to warming during the last 50 years was demonstrated for two plankton diatoms (*Cyclotella pseudostelligera*, and *Fragilaria nanana*), *Acroperus harpae* (cladocera), and several chironomid species. Seasonal water column sampling, sediment traps, and an analysis of the physical consequences of this warming using a dynamic

physical model (DYRESM) indicated that the responses in biota were likely due to a warming of the epilimnion during late summer and autumn, rather than any significant change in the depth and deepening patterns of the thermocline (Catalan et al., in press). L. Cimera's (Central Spain) reconstructions showed that the locality is very sensitive to climate changes, warming was particularly visible in the chironomid response (Granados & Toro, submitted).

Studies on water column seasonality at 9 WP-3 sites provided the basis for analysing the implications of seasonal variability for detecting climatic signals in the sediment record of these lakes (Catalan et al., submitted). The lakes studied covered a broad range of size and latitudinal distribution. Nevertheless, they share a series of features (deep oxygen maxima, oxygen depletion in deep layers during winter, pH drop during thaw, etc.), which indicated that the underlying main processes are the same for all of them. From the patterns of variability we can distinguish mainly two sorts of potential signatures, which can be described as "species responses" and "system responses". The former comprehends episodic, short but strong events, which signal in the sediments must be carried by species signatures that immediately responded to such variability: e.g. pH drops during thaw, temperature peaks in the water column, intensity of specific productive periods. The latter comprehends changes that affect to the whole lake biochemistry and are reflected in the sediments, either by changes in total fluxes of materials or by changes in the whole set of species. Shallow, small lakes are in general more suitable for recording responses to episodic fluctuations in annual weather forcing; large lakes may succeed better in recording trends, because of their higher inertia. Overall residence time is the key aspect, lakes with high renewal rate, although potentially sensitive to climate fluctuations are bad candidates to have a good record in their sediments.

Sediment traps and regular sampling of the organism population also allowed for improving the understanding of the plankton food-web and the seasonal fluctuations of benthic communities. Up to now, it has been shown that although these lakes are located in poorly vegetated catchments, the role of inputs of dissolved organic carbon from outside the lake are likely more important than the incorporation of carbon by primary production. On the other hand, seasonal changes in chrysophytes provide potential for reconstructions of fluctuations in climate seasonality using the cyst remains that they left in the sediment (Pla, 1999).

#### List of publications:

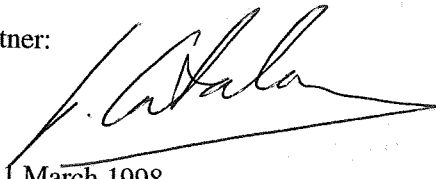
- Camarero, L., M. Felip, M. Ventura, F. Bartumeus, J. Catalan. 1999. The relative importance of the planktonic food web in the carbon cycle of an oligotrophic mountain lake in a poorly vegetated catchment (Redó, Pyrenees). *Journal of Limnology*, 58: 203-212.
- Camarero, L.; Catalan, J. 1998. Development of monitoring methods and modelling at Lake Redó, Spain. *Integrated monitoring: environmental assessment through model and empirical analysis*. Ed. Finnish Environment Institute M. Forsius, R. Guardans, A. Jenkins, L. Lundin and K.E. Nielsen (eds). pp: 87-91
- Catalan, J., M. Ventura, L. Camarero, I. Granados, M. Toro, H. Thies, U. Nickus, A. F. Lotter, L. Lien, A. Korola, A. Barbieri, S. Stuchlik, A. Brancelj. (submitted). Seasonal variability in remote mountain lakes: implications for detecting climatic signals in the sediment record. *Journal of Paleolimnology*.
- Catalan, J., Pla, S., Rieradevall, M. Felip, M., Ventura, M., Buchaca, T., Camarero, L., Brancelj, A., Appleby, P. G., Lami, A., Grytnes, J.A., Agustí-Panareda, A., Thompson, R. (in press). Lake Redó ecosystem response to an increasing warming in the Pyrenees during the twentieth century. *Journal of Paleolimnology*.
- Felip, M.; Bartumeus, F.; Halac, S.; Catalan, J., 1999. Microbial plankton assemblages, composition and biomass, during two ice-free periods in a deep high mountain lake (estany Redó, Pyrenees). *Journal of Limnology*, 58(2):193-202.

- Granados, I. & M. Toro. (submitted) Recent warming in a high mountain lake (Laguna Cibera, Central Spain) inferred by means of fossil chironomids. *Journal of Limnology*
- Grimalt, J.O; Fernández, P.; Berdié, L., Vilanova R.M., Catalan, J; Psenner, R.; Hofer, R.; Appleby, P.A., Rosseland, B.O.; Massabuau, J.C.; R.W. Battarbee. (submitted) Selective trapping of organochlorine compounds in mountain lakes of temperate areas. *Nature*.
- Pla, S. 1999. *Chrysophycean cyst from the Pyrenees and their applicability as paleoenvironmental indicators*. Ph.D. thesis. Universitat de Barcelona.
- The MOLAR water chemistry group. 1999. The MOLAR project: atmospheric deposition and lake water chemistry. *Journal of Limnology*, 58(2):88-106.

Signature of Partner:

Jordi Catalan

Date: Barcelona 1 March 1998



## **PART B**

### **DETAILED REPORT OF THE INDIVIDUAL PARTNERS**

Reporting period: March 1996 to February 1999

Partner: Instituto del Agua. Universidad de Granada

Principal Investigator: Prof. L. Cruz-Pizarro

Scientific staff: Dr. P. Sánchez-Castillo  
Dr. P. Carrillo  
Dr. I. Reche  
Dr. M. Villar-Argaiz  
J.M. Medina-Sánchez

Address: Instituto del Agua. Universidad de Granada  
Ramón y Cajal num 4. 18071 Granada. España

Telephone: + 34. 958. 243093/8018  
Fax: + 34. 958. 243094  
E-Mail: lcruz@goliat.ugr.es

#### **I.OBJECTIVES FOR THE REPORTING PERIOD:**

Completion of the tasks included in WP1 for Lake La Caldera and, partly ( Assess the seasonal variability of physical, chemical and biological characteristics of sites) in WP3.

### II. MAIN RESULTS OBTAINED:

As mentioned before, we have mostly been involved in WP1 and have been responsible for providing data about: major water chemistry; 1<sup>st</sup> and 2<sup>nd</sup> level of microbiology; contemporary zooplankton and contemporary diatoms.

We have actively participated in the chemistry intercomparison exercises performed

Our main methodological contribution to the Project was related to the proposed techniques for the measurements of primary production, phytoplankton extracellular released carbon and bacterial production.

Samples for water chemistry and 1<sup>st</sup> level of microbiology were taken in 28 occasions for three consecutive years. Sampling was conducted weekly at three/four depths along the vertical profile at a central deepest fixed station. Biological processes (2<sup>nd</sup> level of microbiology) were performed in a total of 10 occasions.

For sampling and analysis we have strictly followed the standard techniques and protocols agreed by convenors and lead laboratories (compiled in the Project manual).

It is important to point that after several years of persistent drought and consistent volume reduction, the lake became completely recovered in 1996 and from then on, the "usual" morphometric characteristics were registered, although the ice-free period for the studied years was shorter than the registered in previous ones. On the other hand, by middle September 1996, an exceptional precipitation event represented an input of nutrients to the lake, associated with Saharan dust.

#### *Lake water physical and chemical characteristics:*

Lake La Caldera exhibited a weak Thermal stratification in mid-summer, with maximum surface-bottom differences ranging from 3.5 °C and 6.7 °C. During the remaining of the season the lake had a uniform temperature profile and surface-bottom differences did not surpass 2°C.

In relation to the chemical variables measured in the lake water, the most noticeable characteristics in comparison with other sites included in the project (and also with previous data from this lake) are:

A very high pH values, always greater than 7.5; a moderate Alkalinity values (194 to 373 µeq/l) with very wide range of variation during the ice-free period; a rather high Calcium content with values (average for the water profile) ranging from 176 to 298 µeq/l and, on average, a medium/high measured conductivity values ( between 27 and 37.5 µS/cm.

Total Phosphorus (TP) usually ranged between 3.3 and 7.3 µg P/l , although a strong increase ( of about 10 fold the P of the lake) was punctually registered in September 1996 as a result of the already commented external (atmospheric) input. Particulate Phosphorus (PP) was the dominant P fraction (>55%), except for the above mentioned increase, when PP accounted for less than 20% and Total Dissolved Phosphorus (TDP), over 80%.

Nitrogen was found mainly as inorganic forms, Dissolved Inorganic Nitrogen (DIN) representing more than 50% of Total Nitrogen (TN). DIN (and especially NO<sub>3</sub>) slowly decreased over the summer. According to Morris & Lewis (1988), DIN/TP (by weight) ratio values exceeding 12, implies a strong likelihood of P limitation, and in fact, this was the case of La Caldera for the study period except for the sporadic atmospheric load of P.

### *Pelagic Food Webs*

The autotrophic community in lake La Caldera was composed by nanoplankton species as is characteristic for oligotrophic systems. We have not found autotrophic picoplankton in the lake. *Chromulina nevadensis* was the dominant species for most of the ice-free period, being replaced by *Chlorella sp* by the middle/end of the summer period. Both of them show a remarkable population decline at the end of the ice-free period.

Chrysophyceae reached its maximum density and biomass values in September of 1996: 21000 – 30400 cells/ml, which represented the higher values ever registered in the lake, and  $> 55 \mu\text{gC/l}$ , respectively (averages values for the water column), immediately after the dust (nutrient) deposition event. Both Chrysophyceae and Chlorophyceae reached lower densities (ca. 12000 cell/ml) and accounted  $>80\%$  and  $>60\%$  of total algal biomass, respectively, in 1997.

Other less important species, in terms of population densities and biomass, such as *Amphidinium sp*, *Rhodomonas minuta*, *Ochromonas sp* and *Cyanarcus sp* were also present.

Phytoplankton seasonal succession showed a common basic pattern over the studied years. However, there were moderate differences on the water profile in both abundance and biomass of the major algal groups. It is remarkable the high values of phytoplankton biomass ( $257 \mu\text{g C/l}$ ) at the bottom depth immediately after thaw in 1996. The development of a *Cryptomonas sp* with a large cell volume was responsible for this situation.

*Chromulina nevadensis* showed marked seasonal differences in size and morphology: after ice-out, cells with big pyrenoids (mean cell volume  $30\text{--}40 \mu\text{m}^3$ ) developed, while cell volume gradually decreased to mean values of  $5\text{--}8 \mu\text{m}^3$  by the end of the ice-free period.

Chlorophyll a values ranged (on average for the water profile) from 0.2 to  $1.8 \mu\text{g/l}$ . These values are close to the lowest ones ever measured in the lake. The pattern of variation in the water column (peaks at intermediate depths) conforms that obtained in previous records but it is interesting to point both the unusual peak found after the thaw, and a consistent decrease along the summertime.

The heterotrophic bacterial community of lake La Caldera was composed of free small coccus-like and rod shaped forms. Filamentous bacteria were scarce. Most coccus-forms could be identified as virus-like particles because of their small size and polyhedral shape. The seasonal dynamic of the bacterial community showed limited inter-annual differences. Maximum bacterial densities were reached at bottom depths in late August during 1996, whereas for 1997 a fairly homogeneous vertical distribution was observed, with minimum differences in abundance and biomass in the water profile.

It is remarkable the extremely low values for bacterial abundance (always below  $10^6$  cell/ml) and biomass (never reaching  $30 \mu\text{g C/l}$ ) measured in this lake.

Ciliates were very scarce. Individual samples never surpassed during the 1997 sampling period  $24$  cell/l, which represents  $3491 \text{ pg C/l}$ . Such values are much lower (by three orders of magnitude) than those reported for 1996 and a negative correlation with greater sized (Rotifera and Crustacea) zooplankton densities seem to be evident. Maximum densities were reported during thawing and no individual record was observed since the middle of the ice-free period.

Heterotrophic nanoflagellates were also very poorly represented in the pelagic community. Average values for the water column (total HNF assemblage) were around 100 cell/ml which mean biomass values never greater than  $0.3 \mu\text{g C/l}$ . Their contribution to the particulate organic carbon pool in the lake is more than two orders of magnitude lower than bacterial one.

Zooplankton community composition was simple and we did not observe major inter-annual differences in composition. A calanoid copepod, *Mixodiaptomus laciniatus*, was the main zooplankton species. Rotifers (*Hexarthra bulgarica*) and cladocerans (*Daphnia pulicaria*) were usually present at low abundance.

*M. laciniatus* comprised over 90% of zooplankton abundance and biomass. Biomass (mean values for the water profile) ranged from 0.002 to 60  $\mu\text{g C/l}$ , showing very great differences among years. *D. pulicaria* and *H. bulgarica* accounted for less than 5% of zooplankton abundance and biomass. For most of the ice-free period, naupliar and copepodite stages of *M. Laciniatus* dominate in the lake.

Zooplankton showed a heterogeneous vertical distribution. Overall, species concentrated at the highest depths during the time of the sampling (mid-day) and especially during the sunny days, when zooplankton biomass at the bottom exceeded over three times that of surface.

The autotrophic/heterotrophic (A/H) ratio showed significant inter-annual differences (particularly when compared with data obtained in previous "dry" years) and averaged between 2.2 and 5.7. Bacteria constituted a minor proportion of the plankton biomass. Phytoplankton was the main contributors and zooplankton, although contributing significantly to the overall biological community, was a non important fraction in 1996, the year when ciliates reached maximum abundance and biomass.

Gross Primary Production (GPP) measurements ranged between 0.37 and 3.25  $\mu\text{g C/h}$ , quite comparable to previous values registered for this lake. However, the depicted seasonal pattern was different as the maximum values were measured by the end of the summer. The highest autotrophic production was measured in late August. A consistent vertical pattern was always observed, the maximum values measured very close to the bottom.

Extracellular released products, fluctuated between 0.045 and 1.46  $\mu\text{g C/h}$ , which represent between 22% and 69% of GPP.

Bacterial production (BP) ranged between 0.065 and 0.03  $\mu\text{g C/h}$ . The percentage of BP in relation to GPP was extremely low (from 0.5% to 3.9%). This sharply faced up to the expected values for such oligotrophic system. These results suggest a weak coupling between phytoplankton and bacteria which hardly can be related to the "lack" of extracellular carbon available to bacteria. BP measurements were rather constant in time and no clear vertical pattern was observed.

To depict the pattern of the carbon (energy) flux in the pelagic food web and get a deeper insight into the mechanisms involved in structuring the algal community in the lake ( particularly, the relative importance of external forces: atmospheric inputs and ice-melting processes vs biologically driven recycle processes) we did measure the algal and zooplankton elemental composition (C,N,P) and their changes over time. In summary, we were able to identify three general seasonal conceptual models representing the nutrient flux among the major compartments of the pelagic zone. While ice-melting processes dominated the nutrient flow at thaw, biologically driven processes such as zooplankton recycling, became relevant as the season and zooplankton ontogeny progressed. The stochastic nature of nutrient inputs associated with atmospheric events can promote rapid transitional changes between a biologically (autochthonous resources) and a externally (allochthonous resources) driven community.



### III. LIST OF PUBLICATIONS ARISING FROM THE PROJECT :

Medina-Sánchez, J.M., M. Villar-Argaiz, P. Sánchez-Castillo, L. Cruz-Pizarro & P. Carrillo. 1999. Structure changes in a planktonic food web: biotic and abiotic controls. *J. Limnol.* 58(2): 213-222

MOLAR Water Chemistry Group. 1999. The MOLAR Project: atmospheric deposition and lake water chemistry. *J. Limnol.* 58(2): 88-106

Straskrabová, V., C. Callieri, P. Carrillo, L. Cruz-Pizarro, J. Fott, P. Hartman, M. Macek, J.M. Medina-Sánchez, J. Nedoma & K. Simek. 1999. Investigations on pelagic food webs in mountain lakes – aims and methods. *J. Limnol.* 58(2): 77-87

Villar-Argaiz, M. 1999. *Redes tróficas pelágicas: Una perspectiva estequiométrica*. PhD Thesis. Universidad de Granada. Granada. Spain. 242 pp

Villar-Argaiz, M., J.M. Medina-Sánchez, L. Cruz-Pizarro & P. Carrillo. 2000. Life history implications of calanoid *Mixodiaptomus laciniatus* in C:N:P stoichiometry. *Verh. Internat. Verein. Limnol.* 27: 000-000

Villar-Argaiz, M., J.M. Medina-Sánchez & P. Carrillo. Relationship between N:P ratio and growth rate during the life cycle of a calanoid copepod : An *in situ* measurement. *Oikos*. In press

Villar-Argaiz, M., J.M. Medina-Sánchez & P. Carrillo. Linking life history strategies and ontogeny: a stoichiometric approach. *Ecology*. In press

Villar-Argaiz, M., J.M. Medina-Sánchez, L. Cruz-Pizarro & P. Carrillo. Inter- and intra-annual variability in phytoplankton community. The influence of allochthonous vs autochthonous P sources. *Freshwat. Biol.* Submitted.

Villar-Argaiz, M., J.M. Medina-Sánchez & P. Carrillo. Seasonal variation in the elemental content ratios of phytoplankton and bacteria in a high mountain lake. *Aquatic Microbial Ecology*. Submitted

Signature of Partner:



Date: Granada April 15, 2000.

## MOLAR REPORT 1999

Jean-Charles Massabuau

**Contractor:** Centre National de la Recherche Scientifique (CNRS)  
**Subject area:** Fish, fish physiology  
**Leading scientist:** Jean-Charles Massabuau  
**Scientific staff:** Suzanne Dunel-Erb (CNRS, Strasbourg), Jean Forgue (Univ. Bordeaux I), Bernard Rivier (Cemagref, Aix en Provence), Charles Roqueplo (Cemagref, Bordeaux).  
**Address:** Laboratoire d' Ecophysiologie et Ecotoxicologie des Systèmes Aquatiques, UMR 5805 (Univ. Bordeaux I & CNRS) Place du Dr Peyneau 33120, Arcachon, France  
**Telephone:** +33 (0)5 56 22 39 25  
**Fax:** +33 (0)5 56 22 39 26  
**e-mail:** massabuau@lnpc.u-bordeaux.fr

### I OBJECTIVES FOR THE REPORTING PERIOD

- Organising fish physiology sampling in selected European lakes
- Analysing fish blood and selected parameters of gill histology (scanning microscopy) for the lakes sampled during the programme.
- Interpreting fish blood data combined with gill histology (scanning microscopy) for the lakes sampled during the programme.
- Realising and producing 2 films "Looking for arctic charr in remote mountain lakes" and "A protocol for fish sampling in the field".
- Organising the 1999 Molar meeting in Arcachon.
- Producing a draft for an interdisciplinary paper on "Toward limits of life in low mineralised water: the brown trout case".

### II MAIN RESULTS OBTAINED

#### Physiological analysis

When studying the ecology of remote mountain lakes and the role biotectors can play as early alarm of air born pollution and climate changes, a basic question is to understand how fish succeed to live in such extreme biotopes where low mineralisation is the first major stress. Taking advantage of the palette of water ionic composition observed in the Molar lakes, we studied the minimal concentration of key ions (Na, Cl, Ca, alkalinity) compatible with fish life. The aim of the study was to gain more insights into the basic knowledge necessary to interpret secondarily contamination processes in the brown trout *Salmo trutta*.

Basically, it is worthwhile noticing that fish in such situation must develop two strategies of adaptation:

- First, they must reduce the ionic leaks by decreasing their gill permeability. It was classically known from laboratory experiments that the calcium ion play a key role to solve this problem but, to our knowledge, there was no field data about values of minimum water calcium concentration compatible with fish life in these biotopes.

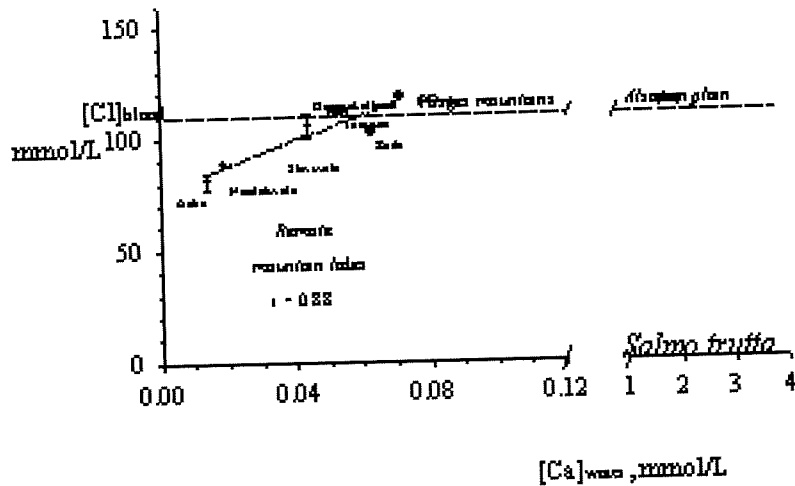


Figure 1: Relationship between blood chloride concentration ( $[Cl]_b$ ) in brown trout *Salmo trutta* and water calcium concentration in remote mountain lakes. It is only in lakes where  $[Ca]_w < 30 \mu\text{mol}\cdot\text{L}^{-1}$  that brown trout caught with gill nets can not maintain a normal  $[Cl]_b$ .

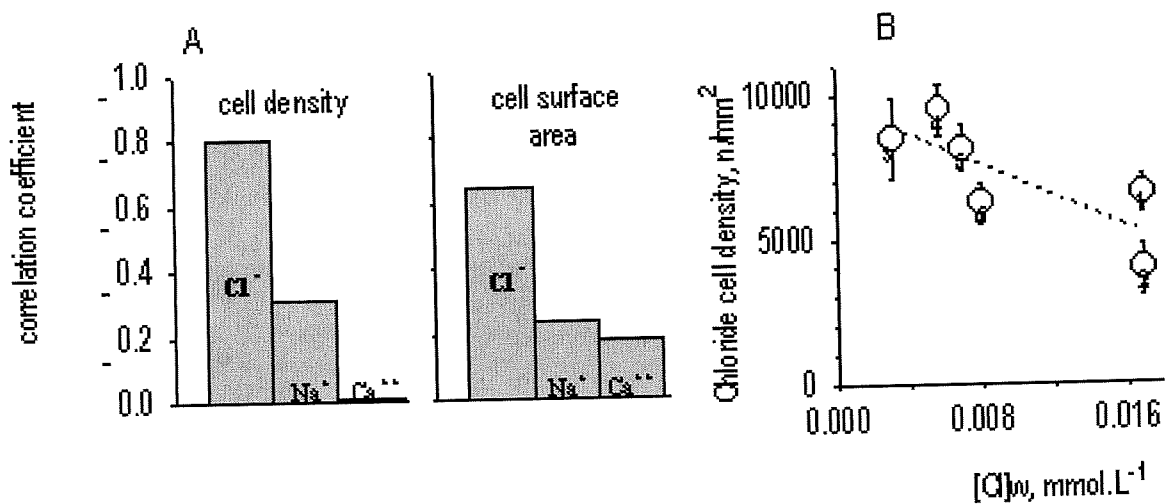


Figure 2: A, Correlation coefficient between chloride cell density and chloride cell surface area of brown trout and water ionic concentration in remote mountain lakes exhibiting a palette of water ionic concentrations. The relations were only considered to be of some adaptive value when a reduction of a given ion stimulated the CC proliferation. The correlation coefficient was only significant as a function of  $[Cl]_w$ . It was lower or absent for all other ions. B, Relationship between chloride cell density and  $[Cl]_w$ ,  $r = 0.88$ .

-Second, they must improve the efficiency of their ionic pumps at the gill level. From laboratory study, it was well known that chloride cells participate to the ionic balance between blood and water. More especially, it was shown that in brown trout a decrease of NaCl in water stimulates their proliferation in low mineralised waters. However, beside this pioneer demonstration, the *in situ* ionic concentration at which this mechanism of adaptation could occur was completely unknown as well as if it was Na, Cl or both Na and Cl that were specifically responsible of this physiological adaptation.

Importantly, note that all data were obtained from fish that were at least 2-4 years old and which were either native of these lakes or stocked as 0+. All animals were caught with gill nets except a series in lake Jorisee (Switzerland).

*Plasma ion analysis.* In fish blood, the main contributors of osmolarity are the Na and Cl ions. Consequently, natremia ([Na]b) and chloremia ([Cl]b) were measured and compared to reference data obtained in the same fish species living in more mineralised waters (Alsatian plain and Vosges mountains, north-eastern France). Results were analysed as a function of water chemistry data.

The results show that *S. trutta* can maintain a normal blood Na concentration  $\geq 110$  mmol·L<sup>-1</sup> in waters where the mineral load is as low as  $\approx 4$  mg·L<sup>-1</sup> but that the blood Cl concentration starts to decrease below 8-10 mg·L<sup>-1</sup>. This [Cl]b response was not directly correlated to the concentrations of Na and Cl in the water but dependent on [Ca]w (Figure 1). When [Ca]w is higher than 30-40  $\mu\text{mol}\cdot\text{L}^{-1}$ , *S. trutta* can maintain a normal chloremia even for [Cl]w as low as 3  $\mu\text{mol}\cdot\text{L}^{-1}$  (see below). This is coherent with literature data on the role of Ca in impermeabilising biological membranes but give new insights into critical limits compatible with brown trout life in remote mountain lakes and/or extremely diluted water solutions. Note that it is in lake Aubé (french Pyrénées) where [Ca]w is only 14-15  $\mu\text{mol}\cdot\text{L}^{-1}$ , and in lake Ovre Neadalsvatn that trouts exhibited the lowest chloremia (70-75 mmol·L<sup>-1</sup> for [Cl]w = 7-9  $\mu\text{mol}\cdot\text{L}^{-1}$ ). Note also, that due to our fish sampling protocol with gill nets, which obviously imposed a severe stress to all fishes, we were unable to say if the low chloremia was the result of the low calcium concentration *per se* or the result of the stress imposed by the test fishing at this low calcium concentration. Nevertheless, the present study demonstrates that for the brown trout *Salmo trutta*, a minimal [Ca]w compatible with a sustainable life is at least 15  $\mu\text{mol}\cdot\text{L}^{-1}$  (the concentration in lake Aubé) and that [Cl]b can be taken as an indicator of stress in low mineralised waters.

*Insights into the adaptation of ion pumping mechanism at the gill level.* This study was performed by analysing the fish gill anatomy by scanning microscopy. All fish gills collected in the Molar lakes were prepared in the field for the anatomical analysis in scanning microscopy. A first global analysis integrated with blood data clearly showed first that the proliferation of chloride cells (characteristic of osmoregulatory problems) in trout gill increases when the mineral load decreases. Three parameters were then specifically analysed. The cell density, the cell surface area and the fractional surface area that is the ratio of the cell surface area per unit of secondary lamellae area. The correlation coefficient between these morpho-anatomical characteristics and the water ionic composition were then calculated in an attempt to discriminate between the various ions able to stimulate the proliferation of chloride cells. The relationships were only considered to be of some adaptive value when a decrease of water ionic concentration was associated to a proliferation or an increase of cellular size of the surface aspects of the chloride cells. Figure 2 shows that the only ion which was systematically associated to an increase of chloride cell density, surface and fractional surface

was the chloride ion. Based on literature data and the present study, we consequently suggest that in these biotopes, [Cl]<sub>w</sub> is the single ion which specifically stimulates the chloride cell proliferation. Together with the calcium, they play a key role in the strategy of adaptation of brown trout in low mineralised waters. Remarkably, the largest proliferation of chloride cell was measured on the gills of brown trouts from Gossenkollesee where [Cl]<sub>w</sub> was only 3  $\mu\text{mol}\cdot\text{L}^{-1}$  ([Ca]<sub>w</sub>  $\approx$  80  $\mu\text{mol}\cdot\text{L}^{-1}$ ). This value appears thus today as the lowest known water [Cl]<sub>w</sub> value compatible with fish life.

Note, in addition that although the problem arising from a low [Cl]<sub>w</sub> can be counterbalanced by a chloride cell proliferation, this physiological adaptation can not replace the deleterious effect of a low [Ca]<sub>w</sub> on the gill epithelium permeability. Indeed, at any [Cl]<sub>w</sub> ranging from 5 to 17  $\mu\text{mol}\cdot\text{L}^{-1}$  the chloremia systematically decreased for [Ca]<sub>w</sub>  $\leq$  20  $\mu\text{mol}\cdot\text{L}^{-1}$ . A high enough [Ca]<sub>w</sub>, is consequently a prerequisite to allow fish life in these extreme environments.

### **Film production:**

#### **“Looking for arctic charr in remote mountain lakes”**

The video-movie that we realised in 1998 and whose aim was to present (i) a test fishing performed by MOLAR scientists within the framework of this program and (ii), with the use of an underwater camera, some aspects of the biotope where the arctic charr is living is commercially available. The film (13 min, color, Pal, Secam, NTSC, betacam, etc) has been produced by the CNRS Audio-Visuel and is distributed in french and in english. The French Ministry of Environment sponsored its distribution. During the MOLAR meeting which was held in Arcachon, it has been freely offered to all participants.

#### **“A protocol for fish sampling in the field”**

This video-movie was recorded in June 1996 during a meeting held in Arcachon. The aim was to unify fish sampling protocol in remote mountain lakes. It was distributed to all persons in charge of fish sampling in the group.

## **IV. List of Publications arising from the project:**

### **Publications**

- R. Mosello, A. Boggero, A. Marchetto, A. Lami, G. A. Tartari, M. Rogora, B. M. Wathne, L. Lien, L.B. Skancke, D. Tait, B. Thaler, N. Rose, R. Harrimann, **J.C. Massabuau**, A. Probst R. Psenner, H. Thies, S. Sommaruga, K.A. Koinig, S. Wogroth, U. Nickus, J. Catalan, L. Camarero, M. Ventura, L. Cruz Pizarro, P. Carillo, M. Villar, J.M. Medina, E. Stuchlik, J. Fott, J. Kopacek, V. Straskrabova, J. Galas, I. Granados, Kudryavtieva Lubov, T.I. Moiseenko, A. Brancelj, G. Muri, A. Gaberscik, A. Barbieri, A. Korhola, S. Sorvari, M. Rautio, J. Virkanen, A.F. Lotter, B. Mueller, B. Steiner, Kraanbuel, M. Gabathuler, K. Hanselmann (1999). The MOLAR PROJECT: atmospheric deposition and lake water chemistry. *J. Limnol.* 58(2) : 88-106.
- Rosseland, B.O., Massabuau, J.-C., Lackner, R, Hofer, R., Grimalt, J. Rognerud, S. and Lien, L. 1999. The ecophysiology and ecotoxicology of fishes as a tool for a monitoring and management strategy for high mountain lakes. Zoology (Urban & Fisher Verlag)
- Massabuau, J.-C. (2000). La fin de l'acide ? *Pour la Science*, Courrier des lecteurs, n° 267, Janvier 2000.

- Grimalt, J.O., Berdie, L., Fernandez, P., Vilanova, R.M., Catalan, J., Psenner, R., Hofer, R., Appleby, Lien, L., Rosseland, B.O., Massabuau, J.-C. et Battarbee, R.W. (1999) Selective trapping of organochlorine compounds in mountain lake of temperate areas. *Nature*. Soumis
- Massabuau et al. Towards limits of life in low mineralised water with trouts. *Nature* (in preparation)

#### **Participations to congress:**

- Rosseland, B.O. L. Lien, B. Morrison, J.-C. Massabuau, R. Hofer, D. Rodriguez, J. Grimalt, T. Moiseenko and Birks, J (1998) AL:PE II project : fish population study. SIL Conference, Irlande, Aout 1998.
- Impact of acid water on fish: physiological effects and population responses. Interfaces in Environmental Chemistry and Toxicology. 8th annual meeting of the Society of Environmental Toxicology and Chemistry., Bordeaux, France. 15-18 Avril 1998.

#### **Organisation of congress:**

- Acid rain : solved or unsolved ? Scientific Session (co-chairman, Prof. Rick Battarbee, University College, London) 8th International Symposium of the Society of Environmental Toxicology and Chemistry (SETAC Europe). 15-19 April 1998.
- Short course : « Ecophysiology in aquatic ecotoxicology ». Short-course in Arcachon A satellite of the 8th International Symposium of the Society of Environmental Toxicology and Chemistry (SETAC Europe). 14 April 1998.
- "Measuring and Modelling the Dynamic Response of Remote Mountain Lake Ecosystem to Environmental Change", 6<sup>th</sup> European meeting "Mountain Lake Research, MOLAR", Arcachon, 3-6 February 1999.
- Workshop : Fish physiology and toxicology in remote mountain lakes. *A satellite workshop of "Measuring and Modelling the Dynamic Response of Remote Mountain Lake Ecosystem to Environmental Change"*, Arcachon, 1-2 February 1999.

#### **Signature of partner**

**Reporting period:** From 1th March 1996 to 28 February 1999

**Partner:** Consejo Superior de Investigaciones Científicas. Department of Environmental Chemistry. Barcelona.

**Principal Investigator:** Joan O. Grimalt

**Scientific Staff:**

Dr. Pilar Fernandez  
Ms. Rosa Vilanova  
Mr. Guillem Carrera  
Ms. Lourdes Berdié  
Ms. Carolina Martinez

**Address:** Department of Environmental Chemistry (CID-CSIC). Jordi Girona, 18. 08034-Barcelona. Catalonia. Spain.

**Telephone:** 34 93 400 61 22

**Fax:** 34 93 204 59 04

**e-mail:** jgoqam@cid.csic.es

## **I. OBJECTIVES FOR THE REPORTING PERIOD**

Field sampling in lakes Redó, Gossenkölle and Øvre Neadalsvatn has been completed.

The analyses of samples of snow, air, water, bulk, wet and dry deposition in all lakes has been completed.

Fish analyses have also been completed.

The results of atmosphere, water, precipitation samples and sediment have been cross-correlated.

The results of the fish pollutants and the hystological, physiological and enzymatic parameters determined by other groups have been cross-correlated.

The composition of trace organic compounds in air, water and fish have been cross-correlated for the elaboration of a model of bioaccumulation and fish intake.

## **II OBJECTIVES FOR THE NEXT PERIOD**

End of project

### III PROBLEMS.

All our tasks in the project were developed without any major problem. All samples were collected and analyses have been completed as scheduled.

### IV MAIN RESULTS ACHIEVED.

#### *Methodology.*

C<sub>18</sub> solid-phase disks have been observed to be useful for the measurement of organochlorine compounds (OC) and polycyclic aromatic hydrocarbons at pg/l in atmospheric precipitation samples with reproducibilities of 5-15% and extraction efficiencies of 80-100%. Quantitation and detection limits of 0.14-3.5 pg/l were achieved from the analysis of 0.25-10 l of water, e.g. bulk precipitation or snow. The use of C<sub>18</sub> disks allows the determination of these organic pollutants in remote areas affording collection and extraction of large numbers of samples with limited instrumentation.

A method for the analysis of trace OC in large numbers of muscle fish samples has been developed. This method provides higher precision than that observed in the most uniform fish populations. Among all sample handling steps, evaporation losses has been observed to constitute the main aspect of recovery decrease. These can be minimized to less than 10% when it is avoided that the extract go to dryness. In any case, the effect of these losses can be compensated by correction by a tetrabromobenzene surrogate.

Sample grounding with sodium sulphate provides significant higher concentrations than freeze-drying. Soxhlet extraction for 18 h is sufficient to draw most OC from the muscle samples, no significant peaks representing measurable concentrations of these compounds have been found by further extraction after this period.

Repeatability and reproducibility is smaller than the dispersion between fishes of similar length and age from the same lake for all compounds except a-HCH.

From the point of view of instrumentation (gas chromatography coupled to mass spectrometry using chemical ionization in the negative ion mode –GC-NICI MS-), the use of ammonia as reagent gas provides lower limits of detection and quantitation than methane for most OC. This lower limits allow the detection and quantitation of species with three and four chlorine substituents in aromatic rings which are difficult to determine at trace levels when methane is used as reagent gas. The use of ammonia as reagent gas also facilitates the quantitation of the DDT derivatives.

The mass spectra obtained with ammonia and methane correspond to the molecular incorporation of thermal electrons rather than true chemical ionization reactions. Despite the differences in fragmentation patterns associated to these two



reagent gases, the use of one or the other does not require changes in the compound-specific ions selected for the selected ion monitoring mode.

In any case, calibration of all OC using straight lines and check for uniform slope values is needed for correct quantitation.

Finally, a method based on HPLC-fluorescence at the excitation/emission wavelength pairs of naphthol (290/335 nm) and pyrenol (345/395 nm) on fish bile samples has been developed. The method has allowed to determine the concentrations of hydroxylated polycyclic aromatic hydrocarbons in fish from the lakes considered in the project. Concentration ranges between 69 and 990 ng/ml bile have been found.

### *Field studies*

High altitude lakes are remote but not pristine environments. All measurements performed on fish, water, air and sediments show that the concentrations of OC and PAH are similar to those found in sites with a moderate degree of contamination which is *a priori* unexpected when considering the long distance of these ecosystems from the pollution sources. The present project has shown that high altitude lakes provide a good case for the study of long-range transport of persistent organic pollutants.

Thus, hexachlorocyclohexanes (HCHs;  $\alpha$ - and  $\gamma$ -isomers), endosulfans ( $\alpha$ -,  $\beta$ -isomers and the sulfate residue), hexachlorobenzene (HCB), DDTs and polychlorobiphenyls (PCBs) were identified and measured in the waters of lakes Redó, Gossenkölle and Øvre Neadalsvatn. High HCH concentrations were found. Those in the lakes from the Alps and Pyrenees (990-2900 pg/l) being in the order of the highest recorded in continental waters. Endosulfans and endosulfan sulfate (120-1150 pg/l) were the second major group of organochlorine contaminants showing a remarkable stability upon atmospheric long-range transport. The concentrations of HCB, DDTs and PCB (4-8, 0.6-16 and 26-110 pg/l, respectively) were low in comparison to other continental waters. HCHs, endosulfans and HCB were essentially found in the dissolved phase. Phase partitioning of the more hydrophobic compounds showed a dependence from temperature and water suspended particles. Comparison between different sampling seasons and water depths showed a remarkable concentration uniformity within lake but major inter-lake differences. Normalization to turnover rates showed higher inter-lake similarity. Preferential accumulation of the less volatile compounds in Gossenkölle and significant increase of baseline contributions of organochlorine compounds and residues in Øvre Neadalsvatn are also evidenced from these turnover rates.

The PCB congener concentrations were also rather uniform both in terms of water depth and seasonality showing steady state conditions. 70% of the variation of the PCB particulate-dissolved phase coefficient ( $K_d$ ) was correlated to temperature and log octanol-water ( $K_{ow}$ ). Lower temperatures and hydrophobicity involved higher association to the particulate phase. This behavior is consistent with the

predominance of plankton among suspended particles following a two compartment model. Thus, temperature dependence seems mainly related to a quick phase transfer mechanism such as surface adsorption to the cell membranes. Log  $K_{ow}$  influence could reflect steric restrictions for the uptake of these compounds upon algal ingestion.

Polycyclic aromatic hydrocarbons (PAH), including alkylated and sulfur derivatives were also found in the suspended particulate matter and the dissolved phase. The PAH patterns in the these two phases were dominated by the low molecular weight compounds (i.e. phenanthrene, fluoranthene and pyrene) in Lakes Redó and Gossenkölle. In Lake Øvre Neådalsvatn, the high molecular weight compounds (i.e. chrysene, benzofluoranthenes, benzo[e]pyrene) were also significant. These PAH patterns showed that their main origin was related to high temperature combustion processes and reflected that were photodegraded due to long range atmospheric transport. The particulate phase PAH composition paralleled those encountered in the superficial sediments and remained constant along the water column indicating that vertical transformation processes were not significant. High molecular weight compounds were mainly associated to the suspended particulate matter, meanwhile low molecular weight compounds were distributed between the two phases. The PAH concentrations (410-570 pg/l in the suspended particulate matter, 270-560 pg/l in the dissolved phase) are one or two orders of magnitude lower than those found in the polluted sites near urban/industrial centers but higher than those reported in the remote Northern North Atlantic. Therefore, the atmospheric transport of PAH to these mountain environments is very significant, despite of their geographical remoteness.

In relation to snow, PAH are found in higher amounts in the Tatra and Caledonian mountains, PCB are higher in the Alps and HCH is highest in the Alps and Pyrenees. The qualitative PAH distributions are dominated by low molecular weight compounds, being phenanthrene the most abundant PAH in all but one site. These compounds also occur predominantly in the gas phase in the atmosphere. Their high abundance in the snowpack witness the occurrence of effective transfer mechanisms from gas to snow flakes. In Starolesnianske (Tatra mountains), a higher contribution of high molecular weight compounds is found. This site exhibits the highest snow PAH and suspended particulate levels. Transformation of the concentration values of these compounds into annual deposition rates and correction for catchment/lake area indicates that in Scandinavia and the Alps a large proportion of PAH incorporation is mediated by snowfallout whereas in the Tatra mountains snow deposition only accounts for a small fraction of the compounds stored in the lake sediments. Among organochlorine compounds, only PCB and HCH have been found above method detection limit in most of the samples. The PCB congener distributions changes significantly between sites, although a predominance of the less chlorinated congeners have generally been observed.

Atmospheric deposition shows a higher content in persistent organic pollutants in wet samples. The deposition fluxes exhibit rather constant values throughout the year.

The study of fish concentrations and sediment inventories (430-2800 meters above sea level, 40-67°N) shows that lake elevation is the major variable determining the accumulation of low volatility OC such as 4,4'-DDE, 4,4'-DDT and penta- to hepta-chlorobiphenyls. These compounds are also significantly correlated with annual average air temperatures. In contrast, volatile OC (sub-cooled liquid vapor pressure  $> 10^{-2.5}$  Pa) do not exhibit any gradient with elevation. The results obtained in the study illustrate that in temperate regions global distillation of OC involves the selective retention of the low volatility compounds at the coldest areas. This fractionation effect is responsible for the accumulation of high concentrations of potentially harmful compounds in high altitude ecosystems. PAH do not show this trend with temperature.

On the other hand, other aspects such as fish age or trophic status are also relevant for the accumulation OC in fish. However, the accumulation trends derived from these factors are smaller than those observed as consequence of temperature effects.

A correlation between levels of lake sediment PAH, hydroxy PAH in fish and antioxidant hormones in fish (namely  $\beta$ -carotene and glutathion disulphide) has been found in the high altitude lakes considered in this study. This is the first case of a correlation identified between markers of environmental stress and a lake pollutant. The analysis of OC and metals have allowed to exclude any trend with these antioxidant hormones in the case of these compounds.

The sedimentary parent PAH mixtures are very uniform irrespective of lake location, lake characteristics and PAH load, corresponding to airborne combustion mixtures refractory to photo-oxidation and chemical degradation. The sedimentary fluxes are lowest in lake Arresjøen (Arctic area),  $6.9 \mu\text{g}/\text{m}^2\text{yr}$ , between  $44\text{-}150 \mu\text{g}/\text{m}^2\text{yr}$  in west and central Europe and very high,  $960\text{-}1700 \mu\text{g}/\text{m}^2\text{yr}$ , in east Europe. Normalization of these values to TOC reflects a uniform pattern in correspondence with continental influence and east-west distribution. This pattern parallels the annual average atmospheric deposition fluxes of sulphate, pointing to combustion particles as the main way of PAH transport into these high altitude lakes. The lowest PAH/TOC ratios are found in the sites more distant from the continent ( $4.6\text{-}4.9 \mu\text{g}/\text{g}$ ), the westernmost locations constitute another group (Iberian Peninsula,  $7.2\text{-}7.8 \mu\text{g}/\text{g}$ ), higher values are found in the Alps and Pyrenees ( $13\text{-}17 \mu\text{g}/\text{g}$ ) and the most polluted lakes are found in the Tatra mountains ( $130 \mu\text{g}/\text{g}$ ).

The historical records of the deposition fluxes of these compounds, determined from radiometrically dated cores, show that both PAH pyrolytic fluxes and concentrations ( $\Sigma = 23$  compounds) increased from uniform background levels ( $5\text{-}30 \mu\text{g m}^{-2} \text{yr}^{-1}$ ,  $20\text{-}100 \text{ng g}^{-1} \text{dw}$ , respectively) at the turn of the century to maximum values in 1960-1980. After these peak values a slight decrease to present day levels has been observed in some lakes, though they are still 3-20 times greater than the pre-industrial period.

Atmospheric PAH inventories were estimated from the vertical integration of sedimentary inventories using  $^{210}\text{Pb}$  to correct for postdepositional transport

processes. This approach consistently reduces variability among lakes from the same region. The results obtained define the lakes in the Tatra mountains and that on Spitsbergen Island as those of highest and lowest atmospheric PAH input, respectively. The other lakes exhibit lower differences although their atmospheric inventory values are consistent with the PAH/TOC values defining the above mentioned regions.

## V. LIST OF PUBLICATIONS ARISING FROM THE PROJECT

P. Fernandez, R. Vilanova and J.O. Grimalt  
PAH distributions in sediments from high mountain lakes.  
*Pol. Arom. Comp.* **9**, 121-128 (1996)

L. Berdié, M. Santiago-Silva, R. Vilanova and J.O. Grimalt\*  
Retention time repeatability as a function of the injection automatism in the analysis of trace organochlorinated compounds with high-resolution gas chromatography.  
*J. Chromatogr. A* **778**, 23-29 (1997)

R. Vilanova, P. Fernandez and J.O. Grimalt  
Atmospheric persistent organic pollutants in high altitude mountain lakes. A preliminary study  
In: *Sea-air exchange: processes and modelling*.  
Edited by J.M. Pacyna, D. Broman and E. Lipiatou. 1998.  
Office for official publications of the European Communities. Luxembourg. 1998. pp. 209-215.

G. Carrera, P. Fernandez, R. Vilanova and J.O. Grimalt  
Analysis of trace polycyclic aromatic hydrocarbons and organochlorine compounds in atmospheric deposition by solid-phase disk extraction  
*J. Chromatogr. A* **823**, 189-196 (1998)

R. Chaler, R. Vilanova, M. Santiago-Silva, P. Fernandez and J.O. Grimalt  
Enhanced sensitivity in the analysis of trace organochlorine compounds by negative ion mass spectrometry using ammonia as reagent gas  
*J. Chromatogr. A* **823**, 73-79 (1998)

L. Berdié and J.O. Grimalt  
Assessment of the sample handling procedures of a man power minimized method for the analysis of organochlorine compounds in large numbers of fish samples  
*J. Chromatogr. A* **823**, 373-380 (1998)

E. Escartin and C. Porte  
Biomonitoring of PAH pollution in high-altitude mountain lakes through the analysis of fish bile  
*Environ. Sci. Technol.*, **33**, 406-409 (1999)

- P. Fernández, R.M. Vilanova and J.O. Grimalt  
Sediment fluxes of polycyclic aromatic hydrocarbons in European high altitude mountain lakes  
*Environ. Sci. Technol.* **33**, 3716-3722 (1999)
- P. Fernandez, R.M. Vilanova, C. Martínez, P. Appleby and J.O. Grimalt  
The historical record of atmospheric pyrolytic pollution over Europe registered in the sedimentary PAH from remote mountain lakes  
*Environ. Sci. Technol.* **34**, 1906-1913 (2000)
- B.O. Rosseland, J.-C. Massabuau, J.O. Grimalt, R. Hofer, R. Lackner, S. Rognerud and L. Lien  
The ecophysiology and ecotoxicology of fishes as a tool for monitoring and management strategy of high mountain lakes and rivers in acidified areas  
*Zoology* **102**, 90-100 (1999/2000)
- G. Carrera, P. Fernández, R.M. Vilanova, and J.O. Grimalt  
Persistent organic pollutants in snow from European high mountain areas  
*Atmos. Environ.*, accepted for publication
- J.O. Grimalt, P. Fernandez, L. Berdie, R.M. Vilanova, J. Catalan, R. Psenner, R. Hofer, P.G. Appleby, B.O. Rosseland, L. Lien, J.C. Massabuau and R.W. Battarbee  
Selective cold trapping of organochlorine compounds in high altitude lakes  
*Nature*, submitted for publication
- L. Berdie, M. Santiago-Silva, R. Vilanova, P. Fernandez and J.O. Grimalt  
Detector linearity in the routine analysis of organochlorinated compounds by GC-ECD and GC-MS  
*Anal. Chem.*, submitted for publication
- R. Vilanova, P. Fernández, C. Martínez and J.O. Grimalt  
Persistent and non-persistent organochlorine pollutants in remote mountain lake waters  
*J. Environ. Qual.*, submitted for publication
- R.M. Vilanova, P. Fernández, C. Martínez and J.O. Grimalt  
Polycyclic aromatic hydrocarbons in remote mountain lake waters  
*Water Res.*, submitted for publication
- R.M. Vilanova, P. Fernández and J.O. Grimalt  
Polychlorinated biphenyl partitioning in the waters of a remote mountain lake  
*Sci. Total Environ.*, submitted for publication
- L. Berdié, J.O. Grimalt, P. Fernandez, R. Vilanova, D. Pastor  
Environmental and physiological aspects determining the composition of organochlorine compounds in fish from high altitude lakes  
*Environ. Sci. Technol.*, in preparation

J.O. Grimalt, R. Vilanova, Fernandez and R. Lackner  
Oxidative stress and polycyclic aromatic hydrocarbon intake in fish from high altitude sites  
*Environ. Sci. Technol.*, in preparation

G. Carrera, P. Fernandez, R. Vilanova and J.O. Grimalt  
Precipitation trends of polycyclic aromatic hydrocarbons in Redo Lake (Pyrenees)  
*Atmos. Environ.*, in preparation

G. Carrera, R. Vilanova, P. Fernandez, J.O. Grimalt, M. Ventura, Ll. Camarero and J. Catalan  
Atmospheric deposition of organochlorinated compounds in Redo Lake (Pyrenees)  
*Atmos Environ.*, in preparation

G. Carrera, P. Fernandez, R. Vilanova and J.O. Grimalt  
Precipitation trends of polycyclic aromatic hydrocarbons in Gossenköllesee Lake (Alps)  
*Atmos. Environ.*, in preparation

G. Carrera, R. Vilanova, P. Fernandez, J.O. Grimalt, M. Ventura, Ll. Camarero and J. Catalan  
Atmospheric deposition of organochlorinated compounds in Redo Lake (Alps)  
*Atmos Environ.*, in preparation

P. Fernandez, R. Vilanova and J.O. Grimalt  
Markers of combustion processes in European high mountain lakes  
*Environ. Sci. Technol.*, in preparation

R. Vilanova, P. Fernandez and J.O. Grimalt  
The composition of organochlorine compounds in atmospheric samples from high altitude lakes  
*Atmos. Environ.*, in preparation

R. Vilanova, P. Fernandez and J.O. Grimalt  
Origin and transformation of airborne polycyclic aromatic hydrocarbons from high mountain lakes  
*Atmos. Environ.*, in preparation

R. Vilanova, P. Fernandez, J.O. Grimalt, M. Ventura, Ll. Camarero and J. Catalan  
Fluxes and reservoirs of organochlorinated compounds in high mountain lakes. I. Lake Redo (Pyrenees)  
*Environ. Sci. Technol.*, in preparation

R. Vilanova, P. Fernandez, J.O. Grimalt, U. Nickus, H. Thies and R. Psenner  
Fluxes and reservoirs of organochlorinated compounds in high mountain lakes. II. Lake Gossenköllesee (Alps)  
*Environ. Sci. Technol.*, in preparation

R. Vilanova, P. Fernandez, C. Martinez, L. Lien and J.O. Grimalt  
Fluxes and reservoirs of organochlorinated compounds in high mountain lakes. III.  
Lake Øvre Neadalsvatn (Scandinavia)  
*Environ. Sci. Technol.*, in preparation

P. Fernandez, R. Vilanova, J.O. Grimalt, M. Ventura, LI. Camarero and J. Catalan  
Deposition fluxes and in-lake distribution of polycyclic aromatic hydrocarbons in high  
mountain sites. I. Lake Redo (Pyrenees)  
*Environ. Sci. Technol.*, in preparation

P. Fernandez, R. Vilanova, J.O. Grimalt, U. Nickus, H. Thies and R. Psenner  
Deposition fluxes and in-lake distribution of polycyclic aromatic hydrocarbons in high  
mountain sites. II. Lake Gossenköllesee (Alps)  
*Environ. Sci. Technol.*, in preparation

P. Fernandez, R. Vilanova, C. Martinez, L. Lien and J.O. Grimalt  
Deposition fluxes and in-lake distribution of polycyclic aromatic hydrocarbons in high  
mountain sites. III. Lake Øvre Neadalsvatn (Scandinavia)  
*Environ. Sci. Technol.*, in preparation

**Signature of partner**

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**date:** 28<sup>th</sup> March 1999

## PART B

### DETAILED REPORT OF THE INDIVIDUAL PARTNERS

Reporting period: 1-3-1996 to 28-2-1999 (Entire period)

Partner: Botanical Institute, University of Bergen

Principal Investigator: H.J.B. Birks

Scientific staff: Einar Heegaard  
John-Arvid Grytnes

Address: Botanical Institute, University of Bergen  
Allégaten 41, N-5007 Bergen, Norway

Telephone: + 47 55 58 33 45  
+ 47 55 58 33 50

Fax: + 47 55 58 96 67

E-Mail: [John.Birks@bot.uib.no](mailto:John.Birks@bot.uib.no)  
[Jon.Grytnes@bot.uib.no](mailto:Jon.Grytnes@bot.uib.no)

#### I. OBJECTIVES FOR THE REPORTING PERIOD:

- Development of the MOLAR primary data-base using ACCESS software.
- Development of an unambiguous site/variable sampling time coding system and series of data-base tables between Bergen, Oslo and London.
- Statistical analysis of data collected during the AL:PE projects that form the basis of part of MOLAR Work Package 3.
- Storage of MOLAR data after analytical quality control.
- Statistical analysis of MOLAR Work Package 3 data

#### II. OBJECTIVES FOR THE NEXT PERIOD:

- The project finished on 28.2.1999.



## PART B

### III. ARE THERE ANY PARTICULAR PROBLEMS? IS YOUR PART OF THE PROJECT ON SCHEDULE?

- No serious problems in connection with the data-base design or structure or with the statistical analyses.
- The absence of data from many MOLAR colleagues created the problem that the data-base design and structure could not be fully tested for Work Packages 1 and 2.

### IV. MAIN RESULTS OBTAINED: *METHODOLOGY, RESULTS, DISCUSSION, CONCLUSIONS* (use other pages as necessary but preferably no more than 2)

The main statistical work by H.J.B. Birks has been on the development of the AL:PE modern diatom-pH calibration data-set, the development of predictive models for lake-water pH using diatoms preserved in lake sediments, and the comparison of diatom pH preferences in high-altitude/high-latitude lakes (AL:PE and MOLAR) and low-altitude (SWAP) lakes. The resulting pH inference model has a root mean square error of prediction (RMSEP) of 0.33 pH units, based on weighted averaging partial least squares. Optima for the major diatom taxa have been estimated by Gaussian logit regression using maximum-likelihood estimation. The results obtained highlight (a) the high quality of the AL:PE diatom data-set as a predictive tool and (b) the uniqueness of high-altitude/ high-latitude lakes in terms of light climate, pH optima, and diatom assemblages.

The main statistical work by John-Arvid Grytnes in conjunction with Einar Heegaard, Roy Thompson, and John Birks has involved regression modelling of the biological and sedimentary variables in the MOLAR Work Package 3 lake sediments in relation to the instrumentally-based climate data for each lake. The modelling has involved principal components analysis of the down-core diatom, chrysophyte cyst, chironomid, and cladoceran data, LOESS regression and smoothing of the climate data using different spans, and linear correlation of the responses (biology, pigments, sedimentary parameters) in relation to five different climatic predictors. The results highlight new statistical problems because of sample temporal autocorrelation and the complex relationships between biological and sedimentary parameters and climate in these highly sensitive high mountain lakes. These problems are currently being assessed in light of recent statistical developments on serial correlation in time series.

### V. List of Publications arising from the project (include copies):

Cameron, N.G., Birks, H.J.B., Jones, V.J. and 13 others. (1999) Surface-sediment and epilithic diatom pH calibration sets for remote European mountain lake (AL:PE project) and their comparison with the Surface Waters Acidification Programme (SWAP) calibration set. *J. Paleolimnology* **22**, 291-317.

Birks, H.J.B. (1998) Numerical tools in fine-resolution paleolimnology-progress, potentialities, and problems. *J. Paleolimnology* **20**, 307-332.

Lotter, A.F., Birks, H.J.B., Hofmann, W. & Marchetto, A. (1997) Modern cladocera, chironomid, diatom, and chrysophyte cyst assemblages as quantitative indicators for the reconstruction of environmental conditions in the Alps I. Climate. *J. Paleolimnology* **18**, 395-420.

Lotter, A.F., Birks, H.J.B., Hofman, W. & Marchetto, A. (1997) Modern cladocera, chironomid, diatom, and chrysophyte cyst assemblages as quantitative indicators for the reconstruction of environmental conditions in the Alps II. Nutrients. *J. Paleolimnology* **19**, 443-463.

Signature of Partner: HJB. Birks

Date: 14.11.00

## PART B

### DETAILED REPORT OF THE INDIVIDUAL PARTNERS

Reporting period: 01.03.96 – 28.02.99

Partner: LFI, Institute of Zoology, University of Bergen

Principal Investigator: Gunnar G. Raddum

Scientific staff: Arne Fjellheim, Øyvind A. Schnell

Address: Institute of Zoology, University of Bergen, N-5007 Bergen, Norway

Telephone: +47 55582236

Fax: +47 55589674

E-Mail: [gunnar.raddum@zoo.uib.no](mailto:gunnar.raddum@zoo.uib.no)

#### I. OBJECTIVES FOR THE REPORTING PERIOD:

Sampling of invertebrates in high mountain lakes at different times and habitats

Sorting of samples and identification of invertebrate species.

Data processing and quality assurance of data base

Reporting and production of manuscripts for international publication at the end of the project

#### II. OBJECTIVES FOR THE NEXT PERIOD:

## PART B

### III. Are there any particular problems? Is your part of the project on schedule?

All work with respect to sampling, processing of samples and identifications of species that we are responsible for, have been carried out in accordance with the proposal for the project.

### IV. MAIN RESULTS OBTAINED: METHODOLOGY, RESULTS, DISCUSSION, CONCLUSIONS (use other pages as necessary but preferably no more than 2)

The processing of qualitative and quantitative invertebrate samples have given an overview of the distribution of invertebrates in high mountain lakes. Species lists and data on seasonal variation have been obtained. The results have been evaluated and manuscripts are prepared for publication.

Important zoo-geographical knowledge of different species have been obtained and new information about the biodiversity in remote mountain lakes of Europe has become available. The effects of altitude (as a proxy for climate), latitude, longitude, water quality and other physical and biological variables for the composition of benthic invertebrates have been evaluated. Altitude (indirectly climate) and pH of the water so far seems to be the most important variables determining the fauna composition (Fjellheim *et al.*, in press). Further statistical treatment, combining results from other workpackages, is finished and analysis integrating different workpackages are carried out. Manuscripts dealing with climatic changes are written based on pooled data from the workpackages. A database dealing with habitat use of different benthic organisms in remote mountain lakes in Europe have been compiled and is available.

A manual has been prepared with the aim to ease chironomid identification and promote a more uniform approach to taxonomy by the different workers within the project (Schnell, 1998a). Also, a proposal for a coding system for European chironomids is published (Schnell *et al.*, 1999).

### V. List of Publications arising from the project (include copies):

Fjellheim, A., A. Boggero, G.A. Halvorsen, A.M. Nocentini, G.G. Raddum, M. Rieradevall & Ø.A. Schnell. Distribution of benthic invertebrates in relation to environmental factors. A study of European remote alpine lake ecosystems. (Verh. Int. Verein. Limnol. 27: in press).

Schnell, Ø.A. 1998 a. Guidelines for the identification of chironomid larvae in the MOLAR project. NIVA report SNO 3710-97. 23 pp.

Schnell, Ø.A. 1998 b. The development of the chironomid fauna in sediment cores from five oligotrophic lakes in Europe (Abstract of oral presentation given at the XXVII SIL Congress in Dublin, August 1998).

Schnell, Ø.A., Rieradevall, M., Granados, I. and Hanssen, O 1999. A chironomid taxa coding system for use in ecological and palaeoecological databases. NIVA report SNO 3710-97

Gunnar G. Raddum and Arne Fjellheim ( in prep.). Abundance and species composition of invertebrates in relation to chemical and physical factors in Lake Øvre Neådalsvatn and Lake Stavsvatn.

Signature of Partner:



Date:25.02.00

**Reporting period: from 1-3-1996 to 28-2-1999**

Partner: Consiglio Nazionale delle Ricerche – Istituto Italiano di Idrobiologia (CNR-III)

Principal Investigator: A. Lami

Scientific staff: R. Mosello, P. Guilizzoni, M. Manca, A.M. Nocentini, A. Pugnetti, A. Boggero, C. Callieri, R. Bertoni, A. Marchetto, G.A. Tartari, L. Corbella, V. Libera, M. Contesini, R. Bettinetti, P. Comoli, M. Gianatti, M. Rogora, M.C. Brizzio, A. Pranzo.

Address: Largo Tonolli, 50, I-28922 Verbania Pallanza, Italy

Telephone: +39-0323-518 300 Fax:: +39-0323-556 513

e-mail: a.lami@iii.to.cnr.it

**I. MAIN OBJECTIVES**

- Data collection in the drainage basin of Lake Paione Superiore (LPS) on: meteorological base parameters, amount of precipitation, chemistry of atmospheric deposition, lake chemistry, microbial pelagic food web including bacteria, autotrophic picoplankton, heterotrophic nanoflagellates, ciliates, phytoplankton, zooplankton;
- sample collection for lake water chemistry analysis on the secondary site, Lake Paione Inferiore (LPI);
- sediment core analysis for pigments and elemental carbon, nitrogen, and sulphur;
- investigation of macroinvertebrates and co-operation with experts to assess the taxonomical benthic refinement;
- organisation of workshop on Analytical Quality Control for chemical analyses;
- participation in specific workshop for method and data harmonisation.

**II. MAIN RESULTS OBTAINED: METHODOLOGY, RESULTS, DISCUSSION, CONCLUSIONS****Workpackage 1*****Collection of volume of precipitation and meteorological data*** (A. Lami, V. Libera)

Since July 1996 an automatic weather station (AWS) has been installed on LPS. This equipment has provided data on temperature, solar radiation, wind direction and speed, amount of precipitation.

With the aim of collecting all the meteorological data relevant to our geographical area, we are also collecting data from other high altitude AWS in co-operation with the Meteorological Service of the Piedmont Region. The station will be kept working beyond the contract duration through the financial support from the local authority, Regione Piemonte, and the data will be available for scientific purpose.

These data will help to construct a more complete set of meteorological information relevant to the work involved in the MOLAR Workpackage 1 and 3. These activities have been performed in collaboration with Dr R. Thompson, Univ. of Edinburgh, Edinburgh, UK and Dr. D. Livingstone, EAWAG, Zurich, CH.

***Chemistry of atmospheric deposition*** (R. Mosello, A. Marchetto, M. Rogora)

Atmospheric deposition was sampled at the station of Graniga, located at 1080 m a.s.l., in the same valley where lakes Paione Superiore and Inferiore (2269 and 2002 m a.s.l.) are located. Samplings and chemical analyses were performed weekly. The volume of precipitation and the main chemical characteristics evaluated during the contract period are summarised in table 1.

Tab. 1 – Volume of precipitation and main chemical characteristics of the atmospheric deposition collected at Graniga station.

	Volume mm	pH range	NH <sub>4</sub> <sup>+</sup> median(μeq l <sup>-1</sup> )	H <sup>+</sup> median(μeq l <sup>-1</sup> )	SO <sub>4</sub> <sup>=</sup> median(μeq l <sup>-1</sup> )	NO <sub>3</sub> <sup>-</sup> median(μeq l <sup>-1</sup> )
1996	1853	3.5-6.75	35	23	36	32
1997	1610	3.87-6.56	33	15	31	37
1998	1251	3.82-6.93	50	20	48	43

### Lake chemistry (R. Mosello, A. Marchetto, M. Rogora)

The LPS sampling was performed monthly or biweekly from July 1996 to December 1998. In LPI we took only outflow samples. Values of total ionic concentrations between 122-185 and 192-236 μeq l<sup>-1</sup> and of conductivity 8-12 and 11-13 μS cm<sup>-1</sup> at 20°C are measured in LPS and the surface values in LPI, respectively. Figure 1 shows the trends, observed over the last 8 years, of pH, alkalinity, sulphate and total inorganic nitrogen (TIN) for the two lakes. The main difference lies in their alkalinity values, which range between 0 - 10 μeq l<sup>-1</sup> in LPS and between 20 - 40 μeq l<sup>-1</sup> in LPI. Therefore, pH is between 5.2-6.3 in LPS, while in LPI the range is 6.1-6.8. Alkalinity and pH values show well-defined seasonal variations. The lowest values are measured at the snowmelt (June-July) when large amounts of pollutants (especially nitrate and sulphate) reach the lakes, and maximum values at the end of the summer and during the snow cover. Minimum summer values of nitrate correspond to maximum phytoplankton uptake. Figure 1 clearly shows a significant increase in pH (particularly in LPS) and a decrease in sulphate and TIN corresponding to the same long-term trends observed in atmospheric depositions.

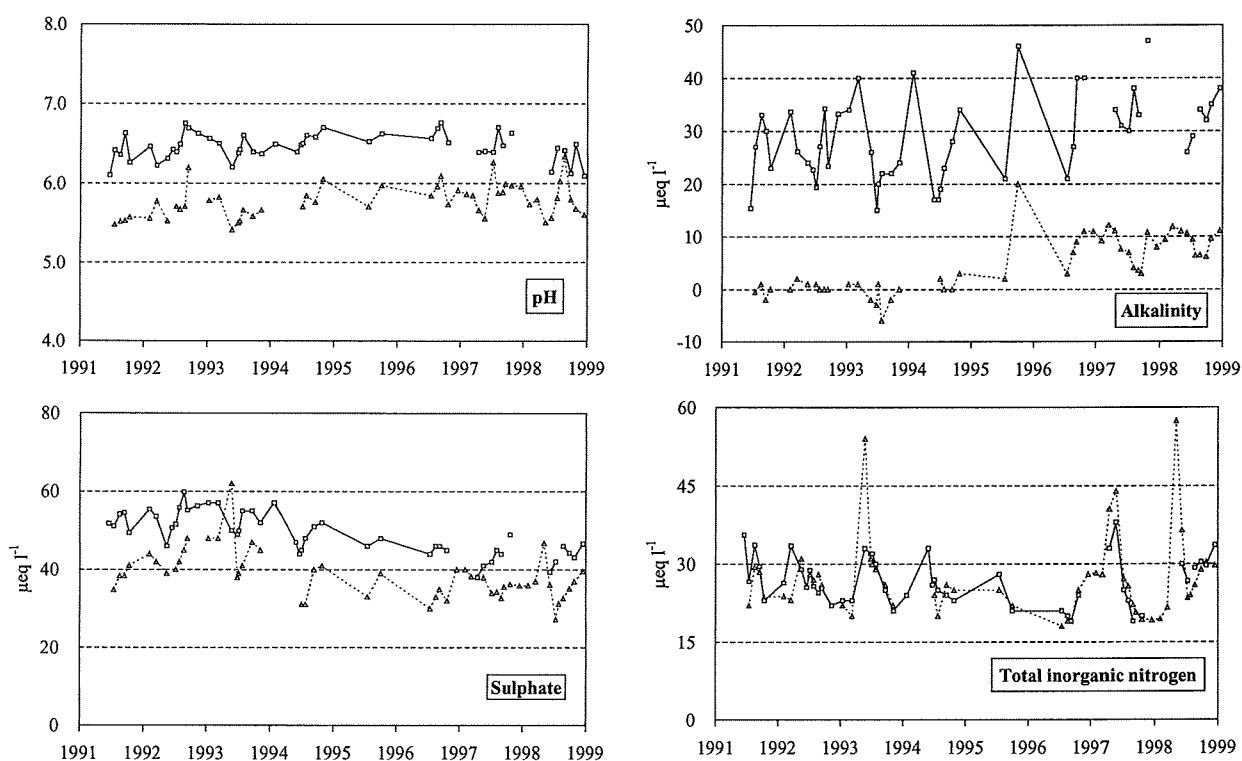


Fig. 1 - Trends of pH, alkalinity, sulphate and total inorganic nitrogen in lakes Paione Superiore (dashed line) and Inferiore (solid line).

### Microbial (pelagic) Food Webs - 1<sup>st</sup> Level

*Organic carbon and microbial food web assemblages in an oligotrophic alpine lake.* (C. Callieri and R. Bertoni)

Picoplankton, both autotrophic (APP) and heterotrophic (HPP), ciliates and heterotrophic nanoflagellates (HNF) were counted and their biovolume measured monthly over a 3 year period in Lake Paione Superiore (LPS), a high mountain lake in the Italian alpine region. Analyses of organic carbon, particulate and dissolved, were performed at the same time. APP were negligible and picocyanobacteria

almost absent. HPP showed seasonal variations, with low numbers in winter/spring and maxima of nearly  $106 \text{ cell ml}^{-1}$  in August/September, corresponding to  $60 \mu\text{g C l}^{-1}$ . Free-living, non-pigmented flagellates showed a density range from  $104 \text{ l}^{-1}$  to  $106 \text{ l}^{-1}$  with a prevalence of cells  $<3 \mu\text{m}$ . Their carbon ranged between  $0.1\text{--}9 \mu\text{g C l}^{-1}$ . Ciliate numbers ranged from 0.02 to  $11103 \text{ l}^{-1}$ . For much of the year different species of *Urotricha* were found. Conversely, *Strombidium* appeared during the ice-free period and *Halteria grandinella* under the ice, indicating a strict dependence on temperature. Carbon in the microbial loop of LPS (near the bottom) was mainly confined to bacteria (73%), with 20% in HNF and only 7% in ciliates. Total organic carbon (TOC) concentration, measured after the removal of net plankton, ranged from 0.26 to  $1.77 \text{ mg C l}^{-1}$  with a prevalence of the dissolved form (87% av.). The average particulate organic carbon (POC) concentration was  $0.24 \text{ mg C l}^{-1}$ . All the components of the microbial loop showed a decline under the ice-cover. Bacterial carbon concentration was three times lower under the ice than in the ice-free season ( $7.9\text{--}24.4 \mu\text{g C l}^{-1}$ , respectively); protozoa carbon too declined under the ice-cover ( $3.1\text{--}5.8 \mu\text{g C l}^{-1}$  for HNF and  $0.4\text{--}1.7 \mu\text{g C l}^{-1}$  for ciliates in the ice-cover and ice-free periods, respectively). The drop in the microbial-loop carbon occurring in late summer may be related to the presence of a *Daphnia* population peak. At that moment, the structure of the microbial loop is transformed by a top-down control of *Daphnia*.

*Biomass and species structure of the phytoplankton of an high mountain lake* (A. Pugnetti and R. Bettinetti)

A three whole-year study (1996-1998) on the composition and dynamics of phytoplankton community of the high mountain lake, acid sensitive Lago Paione Superiore (LPS) was carried out. The data were analyzed and compared with those gathered during the years 1991-1993. The phytoplankton was made up by nanoplanktonic unicellular algae, the only exception being the colonial *Dinobryon sertularia*. Just four species, belonging to Chrysophyceae (*Chromulina* sp., *Dinobryon sertularia* and *Mallomonas alveolata*) and to Dinophyceae (*Gymnodinium* sp.) were important as biomass and density, and they were always present throughout the year. The prevalence of potentially mixotrophic species suggests an adaptive strategy to the low environmental concentrations of inorganic carbon and phosphorus. The seasonal variations of the total biomass were similar to those observed in the previous years. The total number of species has increased; this could be related with the recent increase of the pH and of the alkalinity.

*Zooplankton* (M. Manca and P. Comoli)

We report here the results of a three year study on the zooplankton of Lago Paione Superiore, an acid sensitive lake above the tree line in the Italian Alps. The research was carried out within MOLAR, an EC-founded Project on "Measuring and Modelling the dynamic response of remote mountain lakes ecosystems to environmental change". This study comes after a series of investigations on the effects of acidification, in which we documented the changes occurred with decreasing water pHs, by comparing the recent situation with that in the literature of the 40s, and reconstructed the beginning of anthropogenic disturbance through an analysis of the past cladocera assemblages archived in the lake sediments. A characteristic pattern in seasonal periodicity is a transition from a community dominated by small zooplankton (August) to a community where the large particle-feeder *Daphnia longispina* dominates. This is a typical pattern observed in fishless, copepod-cladocera lakes. Regardless from which food is able to exploit, *Daphnia* population of Lago Paione Superiore is composed by well-fed organisms, visually rich in lipids, able to produce more than one generation/year of parthenogenetic females at density levels which are rather high in an oligotrophic high mountain lake.

*Carbon partitioning in the food web of a high mountain lake: from bacteria to zooplankton* (C. Callieri, A. Pugnetti and M. Manca)

The organisms of the microbial loop in Lake Paione Superiore (LPS), a high mountain lake in the Italian Alpine region, were studied together with phytoplankton and zooplankton for three successive years. The biomass of bacteria, HNF (heterotrophic nanoflagellates), ciliates and phytoplankton, as mean carbon concentration in the three years, was 30 and  $37 \mu\text{g C l}^{-1}$  near the surface (SUR) and the bottom (BOT) respectively. Under the ice-cover the mean biomass carbon decreased especially at the BOT, whereas at SUR the decrease was less evident due to the maintenance of higher phytoplankton biomass (mixotrophic flagellates). In LPS ~50% of the carbon was confined in bacteria, 20% in protozoa and 30% in phytoplankton. The ratio Autotrophs/Heterotrophs was lower than 1 (mean: 0.97 at SUR and 0.58 at BOT) thus indicating a system with a predominance of the heterotrophs. This might be the result of light inhibition of algal growth coupled to a production of dissolved carbon, utilized by bacteria. During late summer the peak of *Daphnia longispina*, the main component of the zooplankton of LPS, increased the carbon content in the lake to a total of 158 and  $300 \mu\text{g C l}^{-1}$  in 1997 and 1998 respectively. At the late

summer peaks, zooplankton represented from 78 to 89% of the total carbon of the pelagic communities. Furthermore, the presence of *Daphnia* could be responsible for a decrease in the biomass carbon of a variety of organisms (algae, protozoa and bacteria). It may be possible that this is an instance of zooplankton grazing on algae, protozoa and also bacteria, as *Daphnia* has very broad niches and may eat pico-, nanoplankton and small ciliates. In the oligotrophic LPS, a diet which also includes protozoa could give *Daphnia* a further chance of survival, as ciliates are an important source of fatty acids and sterols.

*Macroinvertebrates* (A.M. Nocentini, A. Boggero)

Qualitative "kick samples" were taken during the ice-free period in LPS at 3 littoral, 2 inlets and 2 outlets (100 and 200 m downstream) stations, using a net with a 225 µm mesh aperture. The depth level considered was about 50-100 cm and littoral sampling stations were selected taking account of differences in substratum. When the inlets were completely dry; only littoral and outlet samples were taken.

The macrobenthos of the littoral community is prevalently composed of Insecta, particularly Diptera Chironomidae, which represent more than 90%. Second in importance are Oligochaeta, while Plecoptera (Nemouridae and Leuctridae), Trichoptera (Limnephilidae and Rhyacophilidae) and Coleoptera (Dytiscidae) are quite well represented. Hydracarina and Turbellaria are less frequent. Other groups, such as Culicidae, Empididae, Limoniidae, Simuliidae and Tipulidae, are negligible. The profundal community is qualitatively and quantitatively poorer, composed as it is almost exclusively by Chironomids, while Oligochaets are present only in two cores out of six.

### Workpackage 3

*Pigment analysis* (A. Lami, A. Marchetto, P. Guilizzoni)

Eight sediment cores (SAAN1, HAGE2; LEDV4, GKS3, OVNE5, TERI6, REDO1 and CIM1) were collected by site-operator and sent to our Institute for plant pigment, carbon nitrogen and sulphur determinations. The identification and quantification of the specific carotenoids of algae was performed by High Pressure Liquid Chromatography (HPLC) as described by the MOLAR method Manual and ca. 900 samples was measured. The same number of samples was analysed for carbon, nitrogen and sulphur content. The sediment remaining after the pigment extraction was transferred to the laboratory responsible for zooplankton remains analysis. All the data were transferred to the MOLAR database.

A special meeting among the specialists for the determination of the Chrysophytes cysts was organised in Pallanza by A. Marchetto. The main objective was to refine the cysts taxonomy in order to produce a comparable analysis of the different cores collected in the WP3.

A comprehensive presentation of the results in addition to the special volume in Journal of Paleolimnology, will be edited by A. Lami, A. Korhola, & N. Cameron in Journal of Limnology.

### III. PRESENTATION OF RESULTS

In 1996 we participated in the 1<sup>st</sup> MOLAR Workshop, held in Prague, Czech Republic.

We organised a Workshop in Pallanza, 5-7 June 1996, for AQC and the harmonisation of methods of chemical analysis of surface lake water samples and atmospheric deposition.

R. Mosello, in co-operation with B. Wathne, NIVA, is leading the intercalibration exercises for lake water and atmospheric deposition analysis within the MOLAR project. During 1996 two exercises were performed, dealing with surface water (June) and atmospheric deposition (November).

A. Marchetto was involved in the Diatom intercalibration exercise and organised in Pallanza a meeting among the Chrysophytes cysts specialists.

A. Lami attended the ALPFORUM in Chamonix, 10-13 September 1996, presenting a poster on "Limnological research on High Altitude lakes". This Forum was organised by Pôle Européen Universitaire et Scientifique, Grenoble, in the framework of the "Convenzione delle Alpi".

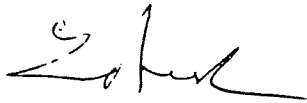
C. Callieri, in collaboration with the V. Straskrabova group, provided comparative data on bacterioplankton countings and attended the Workshop on microbial loop held in C. Budejovice in May 1996.

A special volume of the "Journal of Limnology", Vol. 58 (2), edited by V. Straskrabova, C. Callieri and J. Fott with the title "Pelagic Food web in mountain lakes (MOUNTAIN LAKES RESEARCH PROGRAM)", was published with the aim to collect the papers derived from the studies done in the WP1 on the pelagic food web.



A meeting of the MOLAR chemistry group held in Pallanza from 11 to 13 November 1998.  
A special volume of the "Journal of Limnology", edited by A. Lami, A. Khorola and N. Cameron with the title "Paleolimnology, climate variability and ecosystem dynamics at remote european alpine lakes (MOUNTAIN LAKES RESEARCH programme, MOLAR)", is in press.  
Results of the our research within the MOLAR project were presented during two congresses, S.It.E. (Società Italiana di Ecologia), held in Naples from 11 to 14 September 1996, and A.I.O.L. (Associazione Italiana Oceanologia e Limnologia), held at Portonovo (AN), from 28 to 30 September 1998.

Signature of Partner:

A handwritten signature in black ink, appearing to read 'A. Lami', written over a light blue horizontal line.

Dr. A. Lami

**DETAILED REPORT OF THE INDIVIDUAL PARTNERS**

Reporting period: 01/03/96 to 28/02/99

Partner: University of Liverpool, GB (ULIV)

Principal Investigator: Professor P G Appleby

Scientific staff: Dr C M G van den Berg  
Professor J A Dearing  
Mr A Koulikov  
Dr C Colombo  
Dr E Fischer  
Dr B Lange  
Dr Hu Yuchan

Address: University of Liverpool  
P.O.Box 147  
Liverpool  
L69 3BX  
Great Britain

Telephone: +44 151 794 4020

Fax: +44 151 794 4061 E-Mail: appleby@liverpool.ac.uk

**I. OBJECTIVES FOR THE PERIOD OF THE PROJECT:**

1. To develop procedures for measuring fallout Pb210 in rainwater samples and to use the methods to measure atmospheric fluxes of Pb210 at the principal WP2 sites.
2. To collect soil cores from the principal WP2 sites and to prepare them for radiometric analyses to determine long-term atmospheric fluxes of Pb210 and Cs137.
3. To develop procedures for measuring Pb210 and Cs137 in the water columns of lakes and their distribution between the particulate and soluble phases, and to use the methods to determine concentrations and fluxes in the water columns of the principal WP2 sites.
4. To determine trace metal concentrations and their speciation in the water columns of the principal WP2 sites.
5. To determine trace metal records in sediment cores from some of the WP2 sites.
6. To date by Pb210, Cs137 and Am241 sediment cores from most of the WP2 and WP3 sites.
7. To investigate the possibility of using fallout Pb210 and Cs137 as tracers in studying the take-up of trace metals in lake biota.
8. To carry out magnetic analyses on sediment cores from the WP3 sites.
9. To develop and test models for the transfer of fallout radionuclides and trace metals through the WP2 catchment/lake systems.

## II. REMAINING OBJECTIVES:

1. To finalise estimates of the atmospheric fluxes of  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$  and  $^7\text{Be}$  at each site using rainfall data and records in soil in cores,
2. To finalise calculations of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  transport parameters for the water columns of the main WP2 sites and to evaluate models of the transport of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  to the bottom sediments.
3. To carry out a systematic comparison of radionuclides and trace metals in rainwater, lake water and bottom sediments.
4. To refine and evaluate models of the transport of atmospherically delivered pollutants through alpine catchment/lake systems and the value of radionuclides as tracers for interpreting sediment records.

## III. Were there any particular problems ? Was your part of the project completed on schedule ?

The methods used to measure fallout radionuclides in rainfall and in the water column were relatively new and some development work was necessary. Uncertainties in total precipitation, particularly during the winter months when it was mainly in the form of snow, led to some difficulty in calculating radionuclide fluxes directly from rainfall. These appear to have been solved following a careful analysis of rainfall data from the different types of collectors. In the water column studies the main problem experienced was in the development of a suitable range of filters for analysing the fraction of radionuclides attached to particulates. In order to obtain information about the size range we used  $1\ \mu\text{m}$  and  $0.45\ \mu\text{m}$  in series. In the initial two tests the  $0.45\ \mu\text{m}$  filters proved unsatisfactory, but a suitable type was eventually found. In spite of their novelty, and the logistical difficulties, the methods used have however proved satisfactory overall, the results appear to be good, and the project was completed on schedule.

## IV. MAIN RESULTS OBTAINED: *METHODOLOGY, RESULTS, DISCUSSION, CONCLUSIONS*

### 1. Atmospheric Deposition of Radionuclides

#### Methods

Radioactive fallout ( $^{210}\text{Pb}$  and  $^7\text{Be}$ ) has been measured in rainwater samples collected from Gossenkollesee, Redo, Øvre Neadalsvatn, Lochnagar, Jorisee and Starolesnianske. Radionuclides were removed from the sample by coprecipitation with manganese dioxide. The precipitate was separated from the supernatant liquid by filtration, dried and the activities determined by gamma spectrometry. Yields were determined using standard solutions prepared from a certified Amersham  $^{210}\text{Pb}$  standard.

Soil cores were collected from sites adjacent to Gossenkollesee, Redo, Øvre Neadalsvatn, Lochnagar, Jorisee and Starolesnianske. Dried subsamples have been analysed for fallout  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$  and  $^{241}\text{Am}$  by gamma spectrometry to determine the fallout inventories.

#### Results

Concentrations in rainwater showed large fluctuations of timescales of 2-4 weeks, but mean annual values are very uniform on a regional basis and in line with predictions. At sites near the Atlantic seabord (Redo, Øvre Neadalsvatn, Lochnagar) mean annual  $^{210}\text{Pb}$  concentrations all lay in the range  $66\text{-}84\ \text{Bq}\ \text{kl}^{-1}$  with variations in flux being largely controlled by variations in rainfall. Concentrations at sites from central Europe (Gossenkollesee, Starolesnianske) were significantly higher ( $146\text{-}173\ \text{Bq}\ \text{kl}^{-1}$ ) reflecting the global west/east increase within land masses.

In spite of the anticipated difficulties (limited suitable core sites, the impact of snow cover), the soil core results appear to quite good. From the  $^{210}\text{Pb}$  inventories we can calculate the mean flux over c.30 years. At most sites these are comparable with the short-term values from direct measurements, confirming the constant nature of the  $^{210}\text{Pb}$  flux. The one exception is Redo where the soil core measurements appear to record the long-term influence of Saharan dust inputs. The data on  $^{137}\text{Cs}$  will

allow us to reconstruct the record of  $^{137}\text{Cs}$  deposition. At some sites there were very substantial inputs from the 1986 Chernobyl accident, in addition to the inputs from global fallout from the atmospheric testing of nuclear weapons.

## Discussion

Measurements of the  $^{210}\text{Pb}$  flux in Europe (from both soil cores and direct precipitation) show that at a local level there is a strong correlation between fallout and rainfall. Higher fallout levels in Central Europe compared to those in Great Britain reflect the usual west to east increase within continents, presumably due to a build up of  $^{222}\text{Rn}$  concentrations in the atmosphere as the prevailing winds transport air masses over the land surface. These results will be integrated into those from earlier studies to generate a model for estimating radionuclide fluxes at all European sites, enhancing their value as a tracer for pollution studies.

## 2. Radionuclides in the Water Column

### Methods

Particulate and dissolved  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  were measured in the water columns of Gossenkollesee, Redo and Øvre Neadalsvatn using an INFILTREX II water sampler. The particulate fraction was determined using 1  $\mu\text{m}$  and 0.45  $\mu\text{m}$  filters in series. The filters were dried and weighed to determine the suspended sediment concentrations and analysed for  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  by gamma spectrometry. The soluble fraction was determined using exchange columns with appropriate extraction materials. These were removed in four separate sections, dried and analysed for  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$ , again by gamma spectrometry. Fluxes of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  through the water column have been measured via concentrations on samples collected in sediment traps. Measurements have also been carried out on plankton and fish.

### Results and discussion

Although some of the data still needs to be analysed in detail, the main results are now clear.  $^{210}\text{Pb}$  concentrations in the water column are  $\sim 2\text{-}5 \text{ Bq kL}^{-1}$ , representing a c.40 times dilution of the rain water. There is a clear seasonal influence due to the influence of ice cover, and this is presently being modelled.  $^{137}\text{Cs}$  concentrations are in the range  $\sim 0.5\text{-}4 \text{ Bq kL}^{-1}$ . Since there has been no atmospheric fallout of  $^{137}\text{Cs}$  since 1986, the source must be either catchment runoff or remobilisation.

## 3. Metal speciation in the water column

### Methods

Trace metal concentrations and their speciation have been determined in water column samples from Gossenkollesee, Redo and Øvre Neadalsvatn using anodic (ASV) and cathodic stripping voltammetry (CSV) in the Liverpool University Oceanography laboratory. Analyses have been carried out on both filtered (0.4  $\mu\text{m}$  and 0.1  $\mu\text{m}$ ) and unfiltered, samples. Methods to determine the concentrations of Pb and Cd in lake waters using a mercury film electrode by ASV, selenium by CSV, and the chemical speciation of Pb by ligand competition with detection by CSV, were developed specifically for lakewaters.

### Results and discussion

Concentrations of Pb, Cd, Ni, Co have been determined at all three sites and in all fractions, and are in the ranges: Pb 0.3-1 nM, Cd 0.07-0.2 nM, Ni 1.5-3 nM, Co 0.2-0.6 nM. High Pb concentrations in the surface samples from Redo in summer are attributed to atmospheric inputs. Initial results suggest that these trace metals are mainly in the soluble phase. The speciation data indicate that lead occurs predominantly complexed by organic matter in the water column of the lake. Enhanced concentrations in some species were recorded at mid-depths, possibly due to biological factors. Systematic comparisons between trace metals and radionuclides are presently being carried out.

#### 4. Sediment Dating

##### Methods

Cores from Lochnagar (NAG8), Ovre Neadalsvatn (OVNE4&7), Saanajarvi (SJ96/1), Gossenkollesee (GKS2), Jorisee (JORI3), Hagelsee (HAG96-1), Nizne Terianske (TERI7), Jezero Ledvicah (LEDV5), Redo (RCM2), Cimera (CIM97-1) have been analysed for the radionuclides  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  by gamma spectrometry. Sediment chronologies have been calculated by  $^{210}\text{Pb}$  using an appropriate model and validated where possible by  $^{137}\text{Cs}$  and/or  $^{241}\text{Am}$ .

##### Results

This work has been completed and the results submitted to the MOLAR data base.

#### 5. Mineral magnetic analyses

##### Methods

Cores from all WP3 sites were analysed for a range of mineral isothermal magnetic properties, including magnetic susceptibility and a range of hysteresis loop parameters. All the data sets have been interpreted in terms of dominant sources and origins of the magnetic minerals, ranging from a strong pollution signal in several of the lakes to detrital and authigenic signals in others.

##### Results

This work has been completed and the results submitted to the MOLAR data base.

#### V. List of Publications arising from the project:

- Aldrich, A.P., van den Berg, CMG, Thies, H., Nickus, U (2000): The redox speciation of iron in two lakes. *Limnol. Oceanogr.* submitted
- Appleby, P.G., A O Koulikov, L Camarero, M Ventura. "The input and transmission of fallout radionuclides through Redo, a high mountain lake in the Spanish Pyrenees" (In preparation).
- Brancelj, Anton, Milijan Šiško, Gregor Muri, Christian Kamenik, Peter Appleby, Andrea Lami, Ewan Shilland, Neil L. Rose, Stephen J Brooks, John A. Dearing. "Lake Jezero v Ledvici (NW Slovenia) - impacts of earthquakes and climate change to the lake ecosystem". (Submitted for publication).
- Brancelj, Anton, Milijan Šiško, Andrea Lami, Peter Appleby, Irena Rejec-Brancelj, Darko Ogrin. "Changes in the Trophic Level in an Alpine Lake Jezero V Ledvicah (NW Slovenia) induced by Earthquakes and Climate Change". (Submitted for publication)
- Fischer, E. and CMG van den Berg, 1999. Anodic stripping voltammetry of lead and cadmium using a mercury film electrode and thiocyanate. *Analytica Chimica Acta*, 385: 273-280.
- Kamenik, Christian, Karin A. Koinig, Roland Schmidt, Peter G. Appleby, John A. Dearing, Andrea Lami, Roy Thompson, Roland Psenner. "800 years of environmental changes in a high alpine lake (Gossenköllesee, Tyrol) inferred from sediment records". (Submitted for publication)
- Koinig, Karin A., Christian Kamenik, Roland Schmidt, Anna Agusti-Panareda, Peter Appleby, Jan Fott, Andrea Lami, Neil Rose, Øyvind A. Schnell, Richard Tessadri, Roy Thompson, Roland Psenner. "Palaeoenvironmental changes in an alpine lake (Gossenköllesee, Austria) over the last 200 years – the influence of air temperature on biological parameters". (Submitted for publication).
- Korhola, A., S. Sorvari, M. Rautio, P. G. Appleby, J. A. Dearing, Y. Hu, N. Rose, A. Lami & N. G. Cameron. "A multi-proxy analysis of climate impacts on recent development of subarctic Lake Saanajärvi in Finnish Lapland". (Submitted for publication)
- Lange, B; van den Berg, CMG (2000) Determination of selenium by catalytic cathodic stripping voltammetry. *Analytica Chimica Acta*, in proof.
- Lotter, A.F., P. G. Appleby, J. A. Dearing, J.-A. Grytnes, W. Hofman, C Kamenik, A. Lami, D.M. Livingstone, C. Ohlendorf, N. Rose, M. Sturm & R. Thompson. "The record of the last 200 years in the sediments of Hagelseewli (2339 m asl), a high elevation lake in the Swiss Alps". (Submitted for publication)
- Šporka, F., E. Štefková, P. Bitušik, P. G. Appleby, J. A. Dearing, A. Lami, N. Rose, & N. E. Shilland. "The paleolimnological analysis of sediments from high mountain lake Nižné Terianske pleso in High Tatras (Slovakia)". (Submitted for publication)

Signature of Partner:



Date:

24/5/00

## PART B

### DETAILED REPORT OF THE INDIVIDUAL PARTNERS

Reporting period: 1. March 1996 to 28. February 1999

Partner: Swiss Federal Institute for Environmental Science and Technology (EAWAG)

Principal Investigator: PD Dr A.F. Lotter

Scientific staff: Drs G. Goudsmit, W. Hofmann, B. Müller, G. Lemcke, DM Livingstone, C. Ohlendorf, M. Sturm

Address: EAWAG  
CH-8600 Dübendorf  
Switzerland

Telephone: +41-31-631 4923

Fax: +41-31-332 2059

E-Mail: [lotter@sgi.unibe.ch](mailto:lotter@sgi.unibe.ch)

#### I. OBJECTIVES FOR THE REPORTING PERIOD:

During the reporting period the major objectives of the Swiss contribution to the MOLAR WP3 were:

- i) the sampling and the measurements of water-column biology, physics and chemistry, and water-column sediment fluxes at Hagelseewli
- ii) to elaborate stratigraphical biological and physical sediment analyses
- iii) to measure on-site meteorology at Hagelseewli
- iv) to establish empirical relationships between surface air temperatures and epilimnetic water temperatures in lakes at different altitudes
- v) to apply lake models in a preliminary test run
- vi) to assess the data quality of the meteorological data from all MOLAR WP3 AWS stations
- vii) to explore climatic influences on the break-up of lake ice

#### II. OBJECTIVES FOR THE NEXT PERIOD:

III. Are there any particular problems? Is your part of the project on schedule?

- The project was finished on schedule.

IV. MAIN RESULTS OBTAINED: *METHODOLOGY, RESULTS, DISCUSSION, CONCLUSIONS*  
(use other pages as necessary but preferably no more than 2)

The response of the physical and chemical limnology of Hagelseewli (2339 m a.s.l.) to local meteorological forcing was investigated from 1996 to 1998 using an automatic weather station, thermistor chains, water samples and sediment traps. On-site meteorological measurements revealed the paramount importance of local topographic shading for the limnology of the lake. A high cliff to the south diminishes incident radiation by 15% to 90%, resulting in a long period of ice cover. Hence, the spring and summer seasons are extremely condensed, allowing only about 2 months per year for mixing, oxygen uptake, nutrient inflow, water exchange and phytoplankton growth. Regular measurements of water temperature, chemistry and diatom composition show that Hagelseewli responds very rapidly to changes in nutrient concentrations and light conditions. This response is restricted mainly to an extremely short productivity pulse, which takes place as soon as the lake is completely free of ice. Ice-free conditions are indicated by the occurrence of planktonic diatoms. In contrast to most low-altitude lakes, maximum productivity occurs in the middle of the water column (6-9 m), where first light and then soluble reactive phosphorus (SRP), are the limiting factors. During the period of thawing, large amounts of ammonium enter the lake. Nevertheless, allochthonous nutrient input is not important because SRP, the limiting nutrient for algal growth, originates from the sediments. Water chemistry data and data from sediment traps show that, although autochthonous calcite precipitation does occur, the calcite crystals are redissolved completely in the bottom waters during the extended period of ice cover. Thus, the most important factor for changes in the nutrient budget, primary production and preservation of calcite is the bottom water oxygen status, which is governed by the occurrence of an ice-free period. We hypothesise that the length of the ice-free period is of minor importance for the generation of particles, which could be archived in the sedimentary record as climate proxy indicators. These are mainly produced during peak primary production which only lasts for a few days and then decreases again to very low levels. Therefore, considering the question what kind of climatic signal Hagelseewli may record, we presume that the mere occurrence of an ice-free period, rather than its duration, is archived in the sedimentary record.

Biostratigraphies such as pollen, diatoms, and chironomids were elaborated. The diagrams have been zoned using a combination of optimal zonation with a broken-stick model to assess the significant number of biozones (see Figs. 1-3). The cladoceran analyses showed that the concentration of chydorids as well as of planktonic cladocerans was extremely low.

Thermistor measurements conducted in a Hagelseewli and a series of neighbouring lakes during the summer season showed that the short-term structure of summer lake surface water temperature (LSWT) in a suite of lakes at different altitudes is essentially the same as that of air temperature over a large altitudinal gradient. LSWTs tend to exceed corresponding air temperatures by 3-5 K. They decrease approximately linearly with altitude, allowing an LSWT "lapse rate" to be defined that is slightly greater than that of air temperature. Diel variations in LSWT are large, implying that individual manual water temperature measurements are unlikely to be representative. Local factors such as topographic shading, partial ice cover and meltwater inflows affect LSWTs, but not air temperatures, possibly resulting in severe distortion of the relationship between the two. Hagelseewli gives a particularly good example of this. Several implications for palaeolimnological studies directed at palaeoclimate reconstruction result.

(i) Palaeolimnologically reconstructed LSWTs are likely to be significantly higher than the air temperatures prevailing at the altitude of the lake. (ii) Lakes used in palaeoclimate reconstruction studies should be selected to minimise local effects distorting the summer air-water temperature relationship. (iii) If at all avoidable, palaeolimnological temperature calibration studies should not be based on single manual water temperature measurements. (iv) Consideration should be given to calibrating palaeolimnological temperature inference models directly in terms of air temperature rather than water temperature. (v) The primary climate effect on the aquatic biota of high-altitude lakes (above about 2200 - 2500 m a.s.l. in the Alps) may be mediated by ice cover, and therefore be related more to air temperatures prevailing before freeze-up and during thawing than to the temperatures (air or water) prevailing during the open-water period.

An investigation of the timing of break-up of various lakes in the Northern Hemisphere showed that the effects of the North Atlantic Oscillation and other large-scale climatic phenomena can be quite easily detected. Because spring break-up triggers many ecologically important physical, chemical and biological processes, the detection of large-scale climate forcing signals in the timing of break-up implies that the ecology of individual lakes may be linked to climate on a very large scale. This is an important result in view of the dominant role played by ice cover in controlling physical, chemical and biological processes in the MOLAR lakes.

A model was developed to simulate the effect of local topography on solar radiation incident on mountain lakes. This model was applied successfully to Hagelseewli and other MOLAR lakes. Physical modelling of the water column was successful during the open-water phase, but the modelling of ice cover presents problems.

A contribution was made to the reconstruction of air temperatures at MOLAR sites over the last 200 years. The applicability of lapse rates obtained from Alpine meteorological stations to the MOLAR sites in the Alpine region was investigated, based on the measured AWS data from the MOLAR sites. With respect to Hagelseewli, the air temperature was able to be reconstructed back to 1961 based on air temperature measurements at Jungfrauoch, and back to 1755 based on the long Basle air temperature series.





HAG96-1 Diatoms  
 Analysis: A:F. Lotter

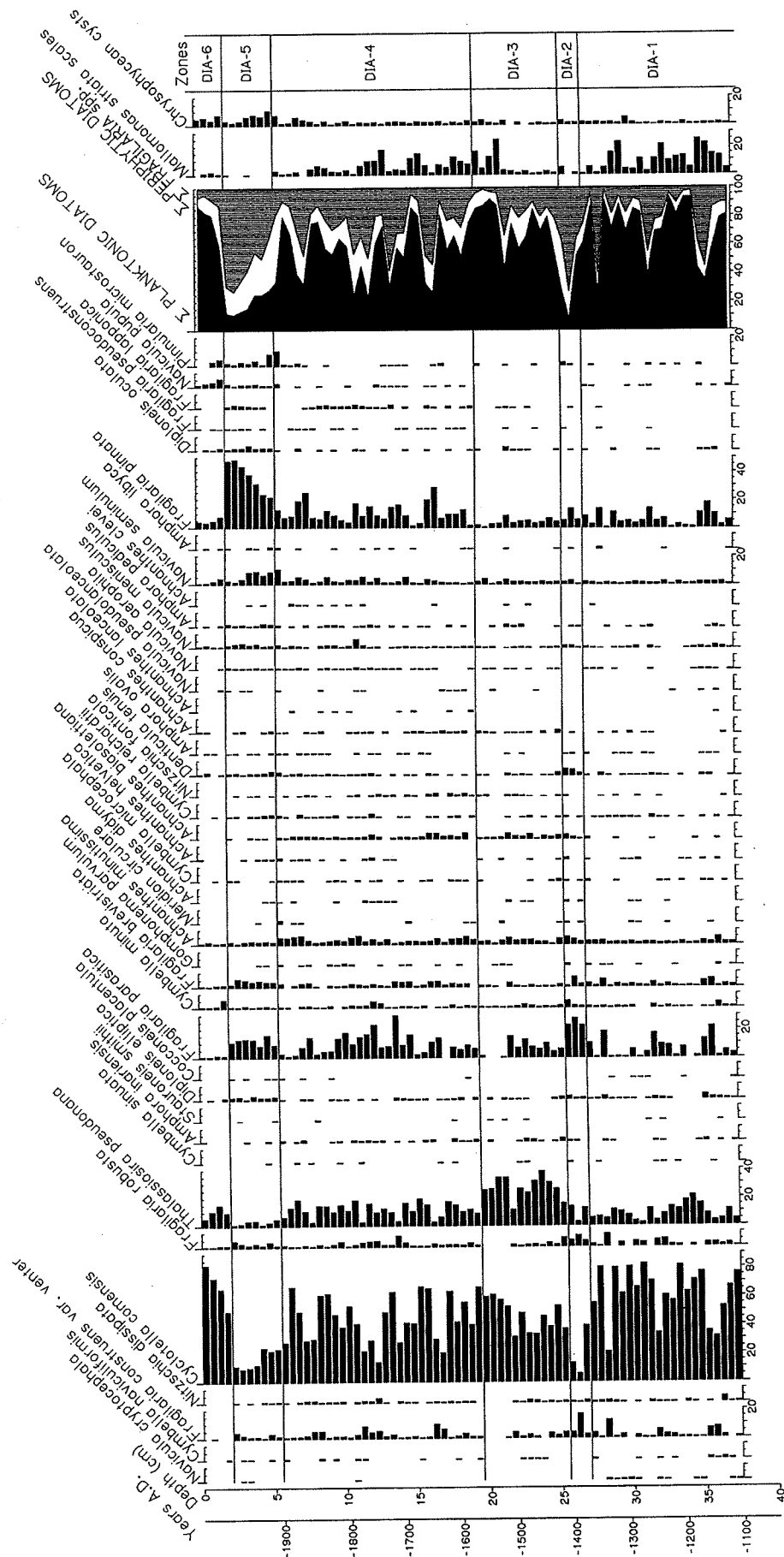


Figure 2. Diatom stratigraphy of Hagelsewli core HAG96-1.

HAG96-4 Chironomids

Analysis: W. Hofmann

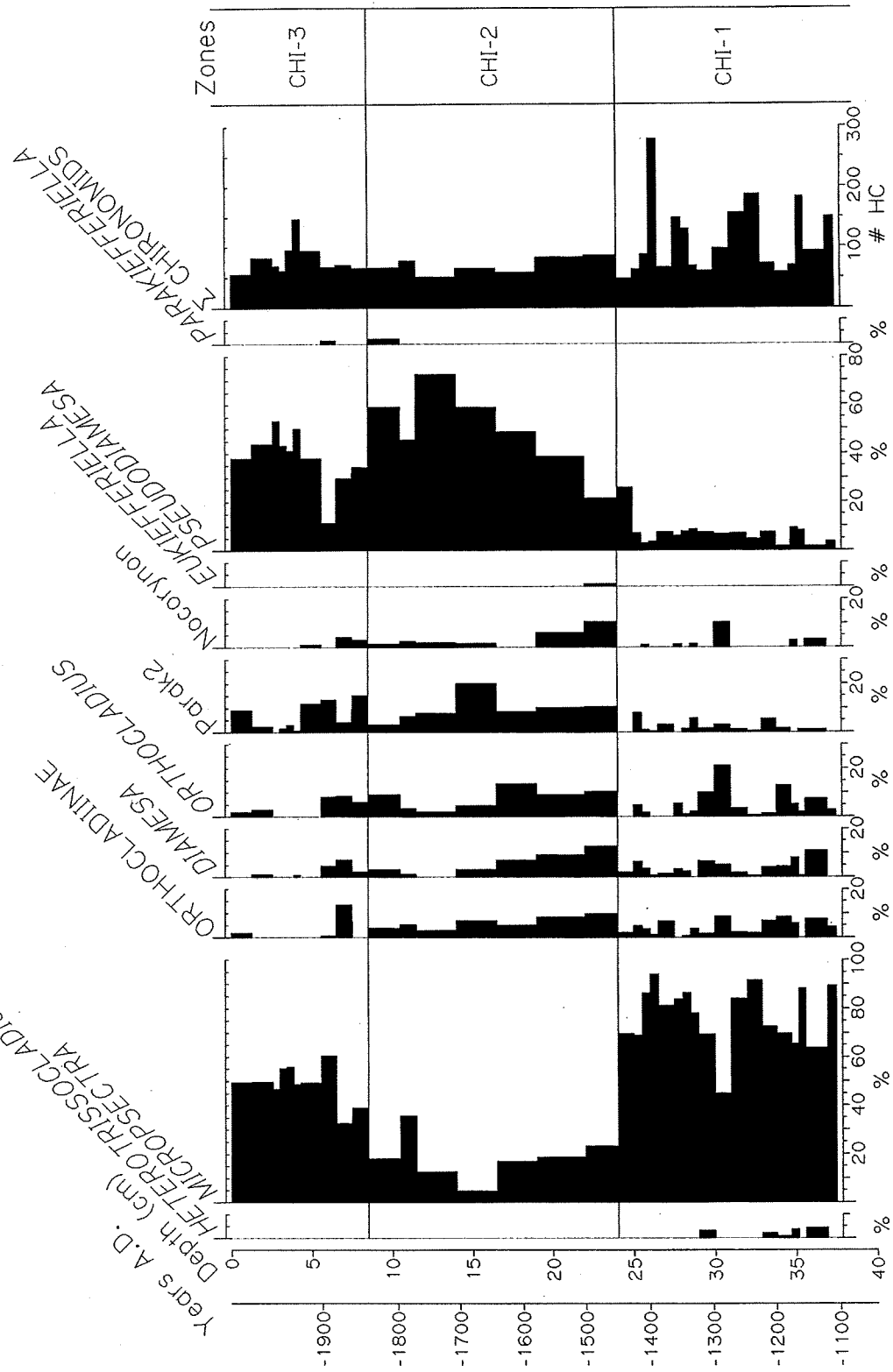


Figure 3. Chironomid stratigraphy of core Hagelseewli HAG96-4, expressed in depths of core HAG96-1.

V. List of Publications arising from the project (include copies):

- Agusti-Paraneda, A., R. Thompson and D.M. Livingstone (1999). Reconstructing climatic variations at high elevation lake sites in Europe during the instrumental period. *Verh. Internat. Verein. Limnol.*, **27** (in press).
- Bigler, C. (1998). Verbreitung von Diatomeen im Oberflächensediment eines alpinen Sees im Berner Oberland (Hagelseewli 2339 m ü. .M.). Diplomarbeit, phil.-nat. Fakultät, Universität Bern. 79 pp.
- Goudsmit, G.-H., G. Lemcke, D.M. Livingstone, A.F. Lotter, B. Müller and M. Sturm (1999). Hagelseewli: a fascinating mountain lake - suitable for palaeoclimate studies? *Verh. Internat. Verein. Limnol.*, **27** (in press).
- Livingstone, D.M. (1997). Break-up dates of Alpine lakes as proxy data for local and regional mean surface air temperatures. *Clim. Change*, **37**(2), 407-439.
- Livingstone, D.M. (1998). Das Auftauen des St. Moritzer Sees: Ein Indikator für überregionale Lufttemperatur und globalen Vulkanismus. *EAWAG Jahresbericht 1997*, 41-42.
- Livingstone, D.M. (1999). Large-scale climatic forcing detected in historical observations of lake ice break-up. *Verh. Internat. Verein. Limnol.*, **27** (in press)
- Livingstone, D.M. (1999) Ice break-up on southern Lake Baikal and its relationship to local and regional air temperatures in Siberia and to the North Atlantic Oscillation. *Limnol. Oceanogr.* (submitted)
- Livingstone, D.M. and A.F. Lotter (1998). The relationship between air and water temperatures in lakes of the Swiss Plateau: a case study with palaeolimnological implications. *J. Paleolimnol.*, **19**(2), 181-198.
- Livingstone, D. M., A.F. Lotter and I.R. Walker (1999). The decrease in summer surface water temperature with altitude in Swiss Alpine lakes: a comparison with air temperature lapse rates. *Arctic, Antarctic and Alpine Res.* **31**, 341-352
- Lotter, A.F. and Bigler, C. Do diatoms in the Swiss Alps reflect the length of ice-cover? *Aquatic Sciences*, in press.
- Lotter, A.F., P. Appleby, J.A. Dearing, J.-A. Grytnes, W. Hofmann, C. Kamenik, A. Lami, D.M. Livingstone, C. Ohlendorf, N. Rose, M. Sturm and R. Thompson. The record of the last 200 years in the sediments of Hagelseewli (2339 m asl), a high-elevation lake in the Swiss Alps. *Journal of Paleolimnology*, submitted.
- Ohlendorf, C., Bigler, C., Goudsmit, G.H., Lemcke, G., Livingstone, D.M., Lotter, A.F., Müller, B. and Sturm, M. Causes and effects of long periods of ice cover on a remote high Alpine lake. *Journal of Limnology*, submitted.
- Van der Knaap, W.O., J.F.N. van Leeuwen, A. Fankhauser and B. Ammann. Palynostratigraphy of the last centuries in Switzerland based on 23 lake and mire deposits: chronostratigraphic pollen markers, regional patterns, and local histories. *Review of Palaeobotany and Palynology* **108**, 85-142.

Signature of Partner:

Date: 15-5-2000

## PART B

### DETAILED REPORT OF THE INDIVIDUAL PARTNERS

Reporting period: March 1, 1996 - February 28, 1999

Partner: Charles University of Prague, Faculty of Science, Department of Hydrobiology, Czech Republic

Principal Investigator: Dr. Jan Fott

Scientific staff: Dr. Evzen Stuchlik, Dr. Martin Cerny, Dr. Miroslava Prazakova, Dr. Veronika Sacherova,  
Martin Blazo, Otakar Strunecky

Address: Vinicna 7, 128 44 Prague 2, Czech Republic

Telephone: +420 2 2195 3251

Fax: +420 2 2491 9704

E-Mail: fott@cesnet.cz

#### I. OBJECTIVES FOR THE REPORTING PERIOD:

##### a/ Field work:

Field work (sampling for water chemistry, phytoplankton, zooplankton, and profiling) at the site 15.1 Starolesnianske Pleso (WP1 and WP2, site operator Evzen Stuchlik) and 15.2 Terianske Pleso (WP3). Sampling surface sediment of a set of Tatra lakes. Operating precipitation collectors in the catchment of Starolesnianske Pleso (bulk collectors) and at Skalnate Pleso (WADOS collector, bulk collector, horizontal collector). Sampling soils and snow at Starolesnianske Pleso.

##### b/ Laboratory work:

- (i) analysing phytoplankton and zooplankton from the sites O.Neadalsvatn, Stavsvatn, Lochnagar, Gossenköllesee, Starolesnianske and Terianske Pleso, analysing phytoplankton from the site Dlugi Staw, analysing zooplankton from the site Jörisee.
- (ii) chemical analyses of lakewater, rainwater, snow and soil from the sites Starolesnianske Pleso, Terianske Pleso and from the weather station Skalnate Pleso.
- (iii) analysing remains of Cladocera from the WP3 cores Terianske Pleso and Gossenköllesee and from surface sediments of Tatra lakes.

##### c/ Meetings and organisational activities

-The first meeting of the MOLAR project was held in Prague from 12<sup>th</sup> to 15<sup>th</sup> March, 1996.  
-Evzen Stuchlik organised a WP2 workshop at the Hydrobiological Station of the Charles University (Blatna, January 1999). Later on, experts in MAGIC modelling Richard Wright from NIVA, Oslo and Chris Curtis from UCL, London, stayed at the Hydrobiological station several days calibrating the model for Starolesnianske Pleso.

Martin Cerny has compiled the MOLAR homepage ( <http://www.natur.cuni.cz/~pah/molar/> ) which was being gradually improved.

Jan Fott participated as one of the guest editors of a special volume of the *Journal of Limnology* which was devoted to pelagic food webs in mountain lakes - Straskrbova et al. (eds.), 1999.

MAIN RESULTS OBTAINED: *METHODOLOGY, RESULTS, DISCUSSION, CONCLUSIONS*  
(use other pages as necessary but preferably no more than 2)

METHODOLOGY (list of techniques newly employed in the project)

### Field equipment:

- 2 aluminium boats were transported to the sites (the last stage with use of a helicopter) together with two large aluminium containers for storage of equipment.
- 4 bulk collectors for sampling precipitation (type NILU) were installed in the catchment of the lake Starolesnianske.
- A precipitation collector (type WADOS) for measurement of wet only precipitation was installed at the site Skalnate Pleso, where it is under permanent control at the local meteorological station.

### Laboratory equipment and instrumentation

- fluorometer Turner TD-700 for routine determinations of chlorophyll-a in vertical profiles
- spectrophotometer ATI-Unicam, UV2-100 + SuperSipper (calibration of chlorophyll-a measurements, determination of Al)
- system for robotization of conductometry, potentiometry and titrations - titration manager TIM900, two burettes ABU900, conductometer CDM210 (all Radiometer Analytical), balances Sartorius P-150 - (pH, Alkalinity, K20, Fluoride)
- A method for fast measurement of microscopical objects (phytoplankton, zooplankton) was acquired, using a digital calliper in connection with a drawing tube of a microscope. Data were sent directly into an Excel sheet. The system was used also for counting phytoplankton and zooplankton.
- Methodological aspects of the integrated study on pelagic food webs in the MOLAR lakes (parts: Phytoplankton, Zooplankton) were described and discussed by Straskrabova et al. (1999).

## RESULTS

### Water Chemistry

Data gathered by analyses of lakewater, rainwater and snow from the sites 15.1 Starolesnianske pleso, 15.2 Terianske pleso and from the weather station Skalnate pleso were used by the MOLAR water chemistry group (1999) in an overview of the ionic composition of lakewaters and precipitations in alpine areas of Europe. In the paper main processes controlling the composition and ionic ratio of deposition and lakewater is discussed as well. Kopacek et al. (1998) dealt with the aspect of reversal in lakewater chemistry following the reduction of sulphur and nitrogen emissions in Central Europe. In a later study (Kopacek et al., 2000) the trophic status of alpine lakes is discussed. More detailed work dealing with Tatra lakes is under progress.

### Plankton

Data on phytoplankton and zooplankton abundance & biomass were used together with data assessing other groups consisting the pelagic food web: bacteria, autotrophic phytoplankton, heterotrophic nanoflagellates, ciliates (Straskrabova et al. 1999a, 2000; Straskrabova et al. submitted). The comparison of the lakes under study according to their food web structure is given by the Final Report of Straskrabova (IH ASCR). Seasonal maxima of phytoplankton biomass indicated trophic status of the lakes, ranging from ultraoligotrophy

(Dluga Staw, PHYmax < 5 µg.l<sup>-1</sup> C to oligotrophy (most of the lakes) and mesotrophy (Starolesnianske Pleso, PHYmax = 2500 µg.l<sup>-1</sup> C. Lakes altered by acidification lie on the both sides of the trophic scale (Dluga Staw, Starolesnianske Pleso).

Seasonality and depth distribution of phytoplankton were studied in three alpine lakes of the High Tatra Mountains: Nizne Terianske pleso, Dluga Staw and Starolesnianske pleso (Fott et al., 1999). The lakes differ in size, depth, nutrient status (phosphorus) and acidification status (pH, alkalinity, calcium). The highest biomass was found in the small, shallow, phosphorus - rich and acidified lake Starolesnianske. An extremely low phytoplankton biomass was found in the medium sized Dluga Staw, which is very poor in phosphorus and which is a transition lake between the acidified and bicarbonate ones. The lake Nizne Terianske is a standard deep, oligotrophic high mountain lake by most of its characters, phytoplankton included.

Most of phytoplankton of the three lakes are flagellates. Seasonal variation in the amount of chlorophyll per unit biovolume was observed in the lakes Nizne Terianske and Starolesnianske, brought about apparently by changes of the underwater light climate. Although the dominance of the major phytoplankton taxa changed throughout the year, no distinct pattern of seasonal periodicity was found in any of the three lakes.

Large pelagic zooplankton (Crustacea) prevail over small (Rotatoria) in all the MOLAR lakes. Typical representatives of pelagic Crustacea belong to five groups; only one species of each group occurs in any particular lake. The groups are: (i) copepods of the genus *Cyclops* (mostly *C. abyssorum*), (ii) copepods of the family Diaptomidae (*Arctodiaptomus alpinus* or *Eudiaptomus gracilis*, *E. graciloides*, *Mixodiaptomus laciniatus*, *Diaptomus cyaneus*), (iii) cladoceran genus *Daphnia* (*D. pulex*-group or *D. longispina*), (iv) cladoceran *Holopedium gibberum*, (v) cladoceran *Bosmina longispina* (incl. the var. *obtusirostris*).

Based on the occurrence of large pelagic zooplankton the MOLAR lakes can be divided in two main groups

- A. The northern maritime lakes (British Isles and Fennoscandia) – all with *Holopedium gibberum* and *Bosmina longispina*
- B. The continental high-mountain lakes of the Tatras and the Alps (with *Cyclops abyssorum taticus*) and the high-mountain lakes of the Iberian Peninsula. *Holopedium* and *Bosmina* are absent, although their presence at some sites would be zoogeographically possible. In the Tatras & the Alps *Cyclops abyssorum taticus* may be accompanied by *Arctodiaptomus alpinus*. Two MOLAR lakes in the Tatras lost their original pelagic zooplankton, presumably due to anthropogenic acidification.

The presence of large *Daphnia* species (*D. pulex*-group or *D. longispina*) in high proportion to other components indicates the absence of fish, although not all the fishless MOLAR lakes are inhabited by them. The copepod *Mixodiaptomus laciniatus* inhabits the two lakes lying on the extremes of the South – North axis (la Caldera, Chuna).

#### Sediment Cladocera

Cladoceran remains from two cores (Gossenköllesee, Nizne Terianske Pleso) were identified and counted in the Prague laboratory. The Gossenköllesee dataset was used for the study on the influence of climatic variation in the last 200 years on the biological sediment record (Koinig et al., submitted). The Terianske dataset is still being evaluated.

Surface sediments of 30 lakes in the Tatra mountains from altitudes 1089-2145 m were analysed for cladoceran remains. Ten species of the family Chydoridae were found, from which three (*Chydorus sphaericus*, *Alona affinis*, *Acroperus harpae*) were the most abundant. *Chydorus* was the only species present in lakes above the tree line – with the two exceptions of lakes of relatively high alkalinity. This finding limits the possibility of use Chydorid cladocerans for indication of climate variations to lakes below the tree line, in most of the Tatra sites.



List of Publications arising from the project:

Fott J., Blazo M., Stuchlik E., Strunecky O., 1999: Phytoplankton in three Tatra mountain lakes of different acidification status.- *Journal of Limnology*, 58: 107-116.

Koinig K.A, Kamenik C., Schmidt R., Agusti-Panareda A., Appleby P., Fott J., Lami A., Rose N., Schnell O.A., Tessadri R., Thompson R., Psenner R.: Palaeoenvironmental changes in the alpine lake (Gossenköllesee, Austria) over the past 200 years / the influence of air temperature on biological parameters.- submitted to *Journal of Paleolimnology*.

Kopacek J., Stuchlik E., Fott J., Vesely J., Hejzlar J., 1998: Reversibility of acidification of mountain lakes after reduction of nitrogen and sulfur emissions in Central Europe.- *Limnology & Oceanography*, 43: 357-361.

Kopacek J, Stuchlik E, Straskrabova V., Psenakova P., 2000: Factors governing nutrient status of mountain lakes in the Tatra Mountains. - *Freshwater Biology* 43, 369-383.

MOLAR Water Chemistry Group, 1999: The MOLAR project: atmospheric deposition and lake water chemistry.- *Journal of Limnology*, 58: 88-106.

Straskrabova V., Simek K., Macek M., Hartman P, Fott, J., Blazo M., 2000: Pelagic food webs and microbial loop in clear-water mountain lakes sensitive to acidification.- *Verh. int. Ver. Limnol.*, 27 (in press).

Straskrabova, V., Callieri C., Cruz-Pizarro L., Fott J., Hartman P., Macek M., Nedoma J., Simek K., 1999a: Investigations on microbial food webs in mountain lakes - aims and methods. In: *Pelagic food webs in mountain lakes*.- *Journal of Limnology*, 58: 77-87.

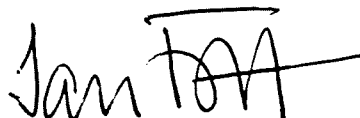
Straskrabova, V., Callieri C., Fott J. (eds.), 1999b: *Pelagic food webs in mountain lakes (Mountain Lakes Research Program)*.- *Journal of Limnology*, 58 (2), p.77-222.

Straskrabova V., Fott J., Nedoma J., Vrba J.: Microbial pelagic food webs in low-alkalinity lakes – forested and alpine catchments. - submitted to: *Silva Gabreta (Vimperk)*.

Psenakova P., Stuchlik E., Fott J. & Sacherova V.: Morphometric parameters of the Starolesnianske lake, the High Tatra Mountains, Slovakia.- submitted to: *Geograficky casopis (Bratislava)*.

Signature of Partner:

Jan Fott



**DETAILED REPORT OF THE INDIVIDUAL PARTNERS**

Reporting period: March 1, 1996 - February 28, 1999

Partner: HBI ASCR - Hydrobiological Institute, Academy of Sciences of the Czech Republic

Principal Investigator: Viera Straškrabová

Scientific staff: Petr Hartman, Josef Hejzlar, Jirí Kopáček, Miroslav Macek, Karel Murtinger,  
Jirí Nedoma, Karel Šimek, Jaroslav Vrba

Address: Na sádkách 7, C. Budejovice, CZ 37005, Czech Republic

Telephone: 420 38 7775819

Fax: 420 38 5300248

E-Mail: verastr@hbu.cas.cz

**I. OBJECTIVES FOR THE REPORTING PERIOD:**

*Chemistry (WP1, 2 and 3)*

- Participation of chemical lab into all intercalibration experiments, harmonization of methods
- Chemistry of lake water and rains – monitoring total phosphorus and dissolved reactive P, organic nitrogen, ammonia N, organic carbon and silica in lake profile of Nizne Terianske pleso (Tatra, SK) and in lake water and precipitation at Starolesnianske pleso (Tatra, SK) for 19 months
- Sampling of sediments in the lakes of Tatra Mts for nutrient, organic matter and metal analyses.

*Microbiology and pelagic food webs (WP 1)*

- Coordination of pelagic food web studies
- Construction of project database on pelagic food web results
- Elaboration of sampling and laboratory protocols for microbial food webs studies 1<sup>st</sup> level (abundances and biomass) and 2<sup>nd</sup> level (fluxes – primary production and exudation, bacterial uptake, bacterial production, elimination of bacteria)
- Analyzing bacteria, picocyanobacteria, heterotrophic flagellates and ciliates (1st level microbiology) in 9 lakes (from Norway, United Kingdom, Switzerland, Italy, Poland, Slovakia, Russia) during two ice-free seasons
- Measuring microbial processes (2nd level) in 3 lakes (in Norway, Slovakia and Poland).
- Summarization of microbial food webs results from 12 lakes
- Dissemination of results on pelagic food webs at international conferences and in publications

**II. Are there any particular problems ?**

No particular problems, construction of database and final summarizing of pelagic food web results was delayed by late delivery of data on several components of pelagic food web (in responsibility of other partners).

### III. MAIN RESULTS OBTAINED:

*Sediments* - sediment cores were sampled from 23 lakes in Tatra Mts and layers 0-1 cm, 1-5 cm and 5-10 cm analyzed (pH, C, N, P, Na, K, Ca, Mg, Al, Fe, Mn), data delivered to responsible WP coordinators. Adsorption isotherms of phosphorus were measured. Data were used for constructing MAGIC model by the responsible WP coordinators.

*Chemical analyses* - Starolesnianské Pleso (Work Package 1, 2, 3): (i) lake water 34 samples per year, surface layer, total P, soluble reactive P, organic N, ammonia N, organic C and Si analyzed from samples delivered by site operators, (ii) bulk and wet-only precipitation in similar frequency, the same analyses except of Si. - Nižné Terianské Pleso (Work Package 3): 7 samplings per year in 10 layers, the same analyses as in Starolesnianské Pleso, samples delivered by site operators. Results were delivered to site operators who included them into project chemical database and delivered them to the responsible WP coordinators.

*Protocole for pelagic food webs* – for sampling, field measurements and for laboratory elaboration of pelagic food webs 1<sup>st</sup> and 2<sup>nd</sup> level protocole was elaborated before the first ice-free season and included in MOLAR Manual. Experienced partners were specified who are able to perform analyses of 1<sup>st</sup> level data and measurements of 2<sup>nd</sup> level and methodical workshop for them was organized before the first sampling season (May 1996) in Ceske Budejovice.

*Intercalibration of microbial biomass* - one sample from Redo Lake was analyzed for bacterial biomass by 6 partners. The differences between partners were in similar range as the variability of results in subsamples by the same partner. Intercalibration of bacterial and heterotrophic flagellate biomass from all samples from Lago Paione Superiore has been done regularly in parallel with one partner for the whole season.

*Microbial biomass* - “1st level microbiology” (Work Package 1) in preserved samples delivered by site operators, from 9 lakes (Øvre Neådalsvatn, Stavsvatn, Chuna, Starolesnianské, Nižné Terianské, Džugi Staw, Lochnagar, Lago Paione Superiore, Jörisee), 8 - 16 times per two ice-free seasons, in 1 to 3 depths, abundances and volumes of bacteria, heterotrophic and autotrophic flagellates, picocyanobacteria and ciliates analyzed. Ciliates in Džugi Staw and Lago Paione Superiore, bacteria in Jörisee analyzed by other partners.

*Microbial processes* - “2nd level microbiology” (Work Package 1) measured in expeditions to the lakes Starolesnianské Pleso (3 depths, 4 measurements in June and September), Øvre Neådalsvatn (5 depths, 2 measurements in July), Džugi Staw (4 depths, 1 measurement in September), primary production by phytoplankton, exudation and bacterial uptake of exudates, bacterial production by thymidine and leucine method, bacterial elimination using fluorescently labelled bacteria.

*Coordination of pelagic food web measurements.* All data on pelagic food webs were delivered to HBI and included to database. The database was completed in 1999. During project meetings in Barcelona (1997), Bled (1998) and Arcachon (1999) special workshops of experienced partners on pelagic food webs were organized and methodical progress discussed.

*Summarization of pelagic food web studies* was discussed in the workshop of experienced partners organized by HBI and III-CNR in November 1998 in Pallanza. Special issue of Journal of Limnology devoted to MOLAR pelagic food webs was prepared and appeared in December 1999.

*Dissemination of results.* Organization of MOLAR and mountain lake ecology session at SIL (International Society for Limnology) Congress in Dublin, presentation of pelagic food webs results at Lake99 in Copenhagen May 1999, publications.

### CONCLUSIONS

- 84 glacial lakes in Tatra Mountains (Slovak and Polish), sampled in September 1993 and 1994 were elaborated with respect to their nutritional status (N, P, C, chlorophyll-a, bacteria). Parameters, which might determine nutritional status were tested: elevation, water acidity, catchment vegetation. Concentrations of organic carbon, organic nitrogen, chlorophyll-a and bacterial numbers were tightly correlated with total phosphorus content. Their levels were highest in forest lakes, then decreased in alpine lakes with decreasing amount of catchment vegetation and soil cover, and were the lowest in lakes situated in bare rocks. The above pattern was further modified by lake water

acidity. In alpine lakes with pH between 5 and 6, concentration of total P, organic C and chlorophyll were lower than in more or less acid alpine lakes, and zooplankton was absent. Nitrate concentrations followed an inverse trend to total P: lowest values in forest lakes, then increased with increasing amount of catchment vegetation. Not the elevation, but vegetation cover in catchment was crucial factor determining nutrient status.

- Data on biomass of different components of pelagic food webs from 4 North European lakes in a west-east transect (Lochnagar, Stavsvatn, Øvre Neådalsvatn, Chuna), from 3 Tatra lakes (Starolesnianské and Nižné Terianské pleso, Długi Staw) and from 1 lake in the Alps (Gossenköllesee) were summarized (Table 1). In lakes with the highest total biomasses (above  $100 \mu\text{g l}^{-1} \text{C}$ ), total organic C concentrations were the highest (1 to  $2.3 \text{ mg l}^{-1}$ ), the biomasses of phytoplankton also were high (Starolesnianské, Chuna and one value in Stavsvatn) and the ratio of autotrophic to heterotrophic microbial biomass was above 10 or more. The lowest pelagic biomass found in Długi Staw roughly corresponded to 5% of its total organic C concentration, whereas the highest biomasses found in Starolesnianské and Chuna lakes reached 20% of total organic C. Picocyanobacteria were almost absent in the lakes studied. In both the extreme lakes (Starolesnianské and Długi) zooplankton is almost absent and the top trophic link in these lakes were heterotrophic and mixotrophic flagellates and ciliates. No relation of total biomass or their particular components to pH or alkalinity was found.

Table 1. Pelagic biomass, ranges of average column values during one sampling season in  $\mu\text{g l}^{-1} \text{C}$ , and ratios: aut/het. micr. - phytoplankton to bacteria+protists, phy/zoo - phytoplankton to zooplankton.

Lake	phytoplankton	bacteria	protists	aut/het.micr.	phy/zoo
Lochnagar	3 - 10	18 - 20	0 - 0.5	0.6 - 0.7	-
Stavsvatn	14 - 195	4 - 20	0 - 0.6	0.9 - 10	0.5 - 0.7
Øv. Neådalsvatn	8 - 13	6 - 12	0.2 - 0.8	0.6 - 1.7	1.2 - 2.6
Chuna	57 - 83	2.5 - 3.3	0.2 - 0.4	18 - 24	1.0 - 1.3
Starolesnianské	334 - 450	11 - 17	0 - 14	13 - 26	334 - 450
Niž. Terianské	17 - 33	6 - 29	0 - 3.1	0.6 - 5.7	2.3 - 5.8
Długi Staw	2 - 5	2 - 11	0 - 0.01	0.2 - 2.6	24 - 53
Gossenköllesee	44 - 64	8 - 14	5 - 13	2.2 - 3.4	1.4 - 18

- Primary production, exudation and bacterial utilization of algal products was measured in three lakes (Table 2). Total production (i.e. particular production of phytoplankton, bacterial utilization and dissolved exudates) was more than by one order lower than in lowland lakes and reservoirs, but the percentages of exudation and bacterial utilization were significantly higher (22-87% and 8-36%, respectively). The percentage of extracellular release (including part immediately utilized by bacteria) is increasing with decreasing total production, and the exudation in the ultraoligotrophic lake Długi even surpasses particulate production. Both the data in preceding paragraph and the data on exudation and their utilization by bacteria showed that in oligotrophic mountain lakes, the share of bacteria compared to other components increases, both in terms of biomass and in terms of carbon fluxes. It is not yet clear whether the main factor is trophic, alkalinity or acidity, and what is the proportion of allochthonous carbon compared to autochthonous production.

Table 2 Primary production, exudation and bacterial utilization of algal products in mountain lakes.

lake	date	total production $\mu\text{g l}^{-1} \text{h}^{-1} \text{C}$	particulate prod. $\mu\text{g l}^{-1} \text{h}^{-1} \text{C}$	bact. in partic. %	exudation in tot. %
Starolesnianské	June 17, 97	2.08	0.92	21	55.6
Starolesnianské	June 20, 97	2.4	1.22	8	48.4
Sarolesnianské	Septemb. 3, 97	4.28	3.53	6.8	21.7
Starolesnianské	Septemb. 6, 97	10.98	8.41	7.2	25.4
Dlugi Staw	Septemb. 9, 97	0.1025	0.010	198	86.9
Ovre Neadalsv.	July 20, 97	0.131	0.087	24.8	34.2
Ovre Neadalsv.	July 22, 97	0.128	0.069	29.8	50

IV. List of Publications arising from the project:

- Kopáček, J., Stuchlík, E., Straškrabová, V., Pšenáková, P., 2000: Factors governing nutrient status of mountain lakes in the Tatra Mountains. *Freshwater Biology* 43: 369-383.
- Straškrabová, V., Šimek, K., Macek, M., Hartman, P., Fott, J., Blažo, M., 2000: Pelagic food webs and microbial loop in low alkalinity mountain lakes. *Verh. Internat. Verein. Limnol.* 27, in print.
- Straškrabová, V., Šimek, K., Nedoma, J., 1999: Importance of pelagic bacteria in lakes and reservoirs of different trophic – implications for long-term monitoring. (Extended abstract). In: *Lake 99, Sustainable Lake Management, 8<sup>th</sup> Internat. Conf. on the Conservation and Management of Lakes*, 17-21 May 1999, Copenhagen-Denmark, Book of Abstracts, Vol. II, S7-5, 4 pages.
- Straškrabová, V., Callieri, C., Carrillo, P., Cruz-Pizarro, L., Fott, J., Hartman, P., Macek, M., Medina-Sánchez, J.M., Nedoma, J., Šimek, K., 1999: Investigations on pelagic food webs in mountain lakes - aims and methods. – In: V. Straškrabová, C. Callieri, J. Fott (guest eds), *Pelagic food web in mountain lakes. Mountain Lakes Research Program, J. Limnol.* 58: 77-87.
- Barbieri, A., Veronesi, M., Simona, M., Malusardi, S., Straškrabová, V., 1999: Limnological survey in eight high mountain lakes located in Lago Maggiore watershed (Switzerland). – In: V. Straškrabová, C. Callieri, J. Fott (guest eds), *Pelagic food web in mountain lakes. Mountain Lakes Research Program, J. Limnol.* 58: 179-192.
- Simona, M., Barbieri, A., Veronesi, M., Malusardi, S., Straškrabová, V., 1999: Seasonal dynamics of plankton in a mountain lake in the southern Alps (Laghetto Inferiore, Switzerland). – In: V. Straškrabová, C. Callieri, J. Fott (guest eds), *Pelagic food web in mountain lakes. Mountain Lakes Research Program, J. Limnol.* 58: 169-178.

Signature of Partner:



Date: March 31, 2000

## PART B

### DETAILED REPORT OF THE INDIVIDUAL PARTNERS

Reporting period: March 1, 1996-February 28, 1999

Partner: IZ SAS - Institute of Zoology, Slovak Academy of Sciences, Bratislava, Slovakia

Principal Investigator: Dr. Ferdinand Šporka

Scientific staff: Dr. Elena Štefková, Dr. Il'ja Krno, Dr. Peter Bitušik

Address: Dúbravská cesta 9, SK-842 06 Bratislava, Slovakia

Telephone: +421-7-5930 2609

Fax: +421-7-5930 2646

E-Mail: [sporka@savba.sk](mailto:sporka@savba.sk)

#### I. OBJECTIVES FOR THE REPORTING PERIOD:

- Participation of site 15.1 Starolesnianske pleso (WP1), by sampling and determining chironomids and epilithic diatoms.
- Installation and measuring meteorological data and water surface temperature of lake 15.2 Nizne Terianske pleso (NTER), by Automatic Weather Station (2 seasons)
- Core sampling from NTER, installation sediment traps
- Sampling and analysing epilithic diatoms and littoral chironomids from Nizne Terianske pleso (WP3) two ice free seasons.
- From NTER 4 cores were taken, which were sent to responsible laboratories, excludes diatoms and chironomids.
- Dissemination of our results from sediments at international conferences and in publications

#### II. Are there any particular problems ?

No particular problems, final summarising our results were finished in time.

### III. MAIN RESULTS OBTAINED: METHODOLOGY, RESULTS, DISCUSSION, CONCLUSIONS (use other pages as necessary but preferably no more than 2)

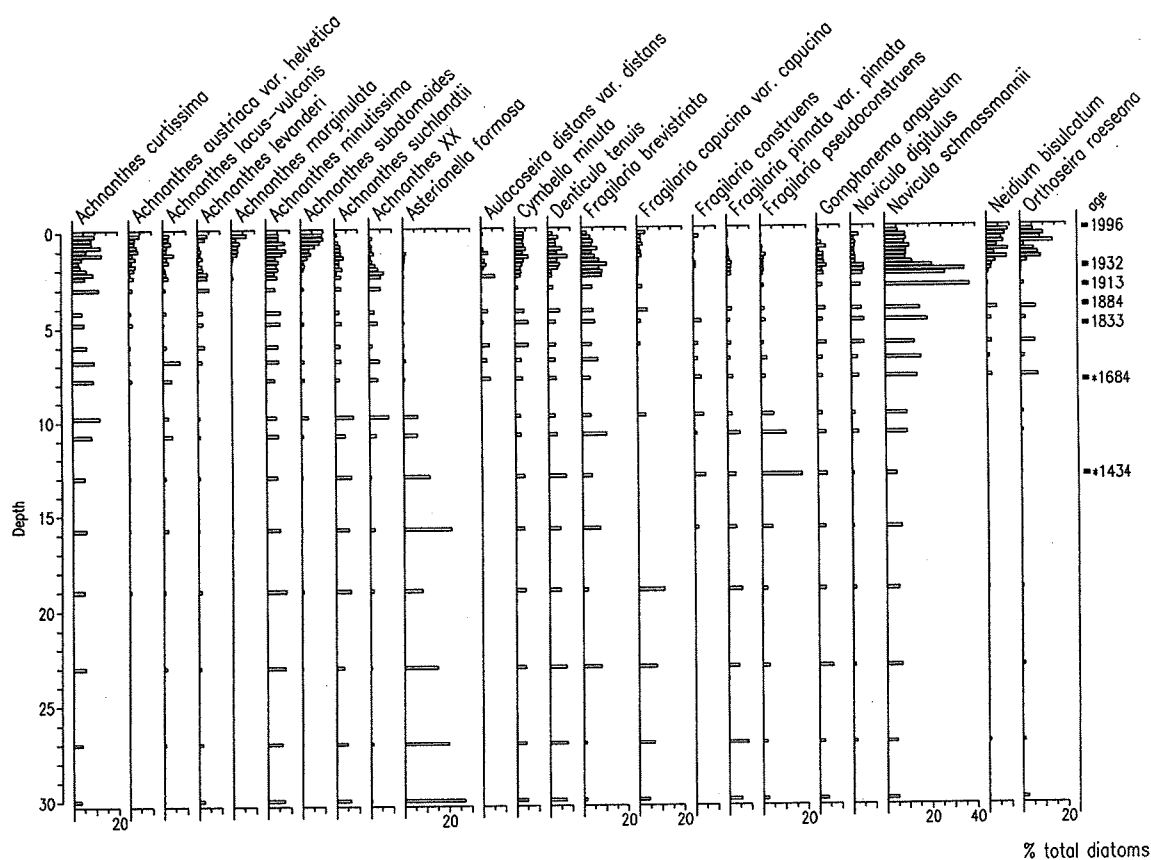
#### Diatoms

26 levels from the Nižné Terianske pleso core "TERI 7" have been analyzed for diatoms and chrysophytes. A total of 99 taxa representing 25 genera were recorded, of these 23 taxa had abundance greater than 5 %, 10 species greater than 10 %. A summary percentage diatom diagram illustrates the most important changes (Fig. 1). Diatom analysis of the entire core shows the differences in assemblages in various part of the sediment core. The taxa that occur at high percentage through the core include planctonic and non-planctonic diatoms, as well as benthic species. The assemblages in the upper part of the core are different from the bottom part. In the upper 3 cm there are increases in many diatom taxa, previously absent or rare in the core e.g. *Achnanthes marginulata*, *A. subatomoides*, *A. levanderi*, *A. austriaca* v. *helvetica*, *Orthoseira roeseana*, *Navicula digitulus*, *N. schmassmannii* and *Stauroneis anceps*. In the bottom part of the core were dominant e.g. *Asterionella formosa* (in upper part absented), *Denticula tenuis* and *Fragilaria capucina*.

Four sediment trap samples have been analysed for diatoms and chrysophytes. 65 diatom taxa were found there with dominant species of *Orthoseira roeseana* and more species of *Achnanthes*.

Epilithic diatoms from Nižné Terianske pleso were taken too. Together 56 taxa were identified from it. Most common species were *Achnanthes minutissima*, *Cymbella minuta*, *Denticula tenuis* and *Navicula gallica* var. *perpusilla*.

Fig. 1 Summary diatom diagram (species occurring at >5%)

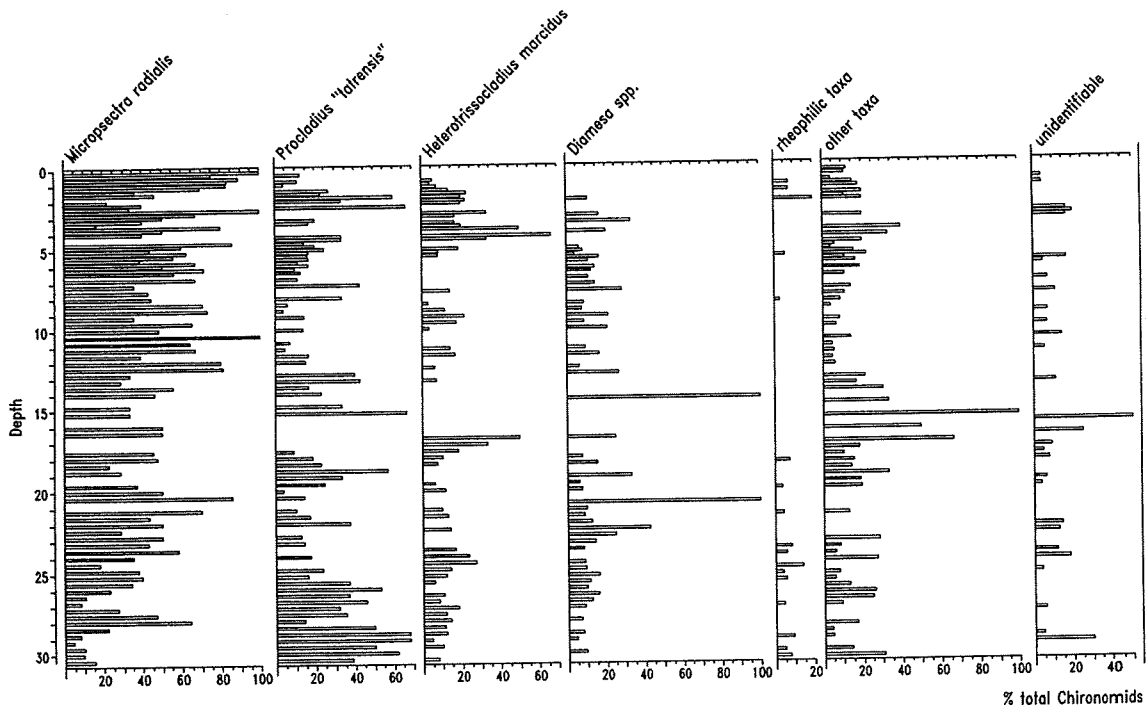


### Chironomids

From sub-fossil chironomid remains (head capsules) eleven chironomid taxa were identified. The subfossil record was dominated by *Micropsectra radialis* followed by *Procladius* sp., *Diamesa* spp. and *Heterotrissoclebidus* cf. *marcidus* (Fig. 2). Three more or less clear changes in the relationship between the dominant taxa were recognised. The first two ones take place between 19.4 - 18.6 cm and 17.8 and 13.8cm, respectively. They can not be connected with atmospheric pollution and could be rather caused by climatic oscillations.

The top of the core showed generally decreasing of the absolute head capsules number from the 5.0 - 4.8 cm. The irregular occurrence of *Diamesa* and often changes in the relative abundance of *M. radialis* were connected with this event. *Diamesa* was not found above 2.0 cm. These findings together with subfossil diatom and cladoceran data suggest that high deposition in the Tatra region may have had an effect on communities in the lake despite of the high buffer capacity and stable pH of the lakewater.

Fig. 2 Summary chironomids diagram



### AWS

Meteorological data collection from AWS, situated at Nizne Terianske lake collected 10 parameters (wind direction and speed, solar energy, radiation- incident and reflected, pressure, temperature air and water, humidity and precipitation) with problems cause with battery failure. The logging started at May 31 and stopped completely at October 2 but with three breaking, cause maybe cut off any sensors. Maximum air temperatures recorded in 1998 were 20.77°C (August 3) and maximum surface water temperatures were 11.6°C (August 16). The maximum wind speed was 19,24m.s<sup>-1</sup>, and maximum daily precipitations were 51.6mm (September 14).

### V. List of Publications arising from the project (include copies):

Wathne, B.; Lien, L.; Skancke, L. B.; Rose, N.; Harriman, R.; Mosello, R.; Boggero, A.; Marchetto, A.; Lami, A.; Tartari, G. A.; Rogora, M.; Tait, D.; Thaler, B.; Massabuau, J. C.; Psenner, R.; Thies, H.; Sommaruga-Wögrath, S.; Koinig, K. A.; Nickus, U.; Catalan, J.; Camarero, L.; Ventura, M.; Cruz Pizzaro, L.; Carillo, P.; Villar, M.; Medina, J. M.; Stuchlík, E.; Fott, J.; Strunecký, O.;

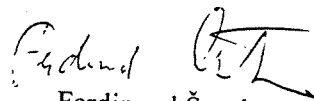


Kopáček, J.; Straškrabová, V.; Šporka, F.; Bitušík, P.; Galas, J.; Granados, I.; Moiseenko, T. I.; Kudryavtjeva L.; Brancelj, A.; Muri, G.; Gaberscik, A.; Barbieri, A.; Korhola, A.; Sorvari, S.; Rautio, M.; Virkanen, J.; Lotter, A. F.; Müller, B.; Steiner, B.; Krähenbühl, U.; Gabathuler, M., and Hanselmann, K. The MOLAR Project: atmospheric deposition and lake water chemistry. *J. Limnol.* 1999; 58:88-106.

Bitušík, P., Kubovčík, K., 1999. Sub-fossil chironomids (Diptera: Chironomidae) from the sediments of the Nižné Terianske pleso (High Tatra Mts., Slovakia). *Dipterologica bohemoslovaca* 9: 11 - 20.

Cameron, N. G., Birks, H. J. B., Jones, V.J., Berge, F., Catalan, J., Flower, R.J., Garcia J., Kawecka, B., Koinig, K.A., Marchetto, A., Sánchez-Castillo, P., Schmidt, R., Šiško, M., Solovieva, N., Štefková, E. & Toro, M. 1999. Surface-sediment and epilithic diatom pH calibration sets for remote European mountain lakes (AL:PE Project) and their comparison with the Surface Waters Acidification Programme (SWAP). *J. of Paleolimnol.* 22: 291-317.

Signature of Partner:

  
Ferdinand Šporka

Date: 24.2.1999

## DETAILED REPORT OF THE INDIVIDUAL PARTNERS

Reporting period: June 1996- March 1999

Partner: Institute of Freshwater Biology, Polish Academy of Sciences

Scientific staff: Prof. Barbara Kawecka  
Dr Andrzej Kownacki  
Dr Elżbieta Dumnicka  
Dr Joanna Galas  
Dr Anna Jachner  
Dr Krzysztof Wiąckowski  
Dr Marek Kot

Address: Institute of Freshwater Biology, Polish Academy of Sciences  
31-016 Sławkowska 17, Krakow, Poland

Telephone: +48 12 4222115

Fax: +48 12 4222115

E-Mail: Galas@zbow.pan.krakow.pl

The lake Długi Staw Dasienicowy (Tatra Mts, Poland) is situated above timber line, at an altitude 1783 m. It has maximum depth 10.6 m, ice free period fluctuates between nine to seven months (September/ October - May/ July). Its catchment area is formed by granitoids covered by moraine with primitive and podsollic soils. The vegetation cover is alpine meadow and bare rocks. The lake is supplied with water from melting snow and precipitation. The lake bottom is covered by bare rocks and stones, between them are small patches of mud and fine particles sediments. The middle part of the bottom is covered by moss *Warnsdorfia exannulata*.

The lake Długi Staw is fishless.

Water samples for chemical analyses were taken 11 times a year, precipitation samples were collected weekly in the Meteorology Station located at the Hala Gasienicowa, close to the lake area, but at the lower altitude of 1507 m. During the ice free period the epilithic diatoms, zooplankton, ciliates and macroinvertebrates were investigated.

pH of the precipitation was acidic, in 70% of all measured samples pH values were between 4.0 and 4.5.

Progressive decreasing trends for pH values and S-SO<sub>4</sub> concentration were observed (Fig.1), which suggests the influence of others parameters on acidification of the precipitation. The nitrogen content especially as N-NH<sub>4</sub> was elevated.

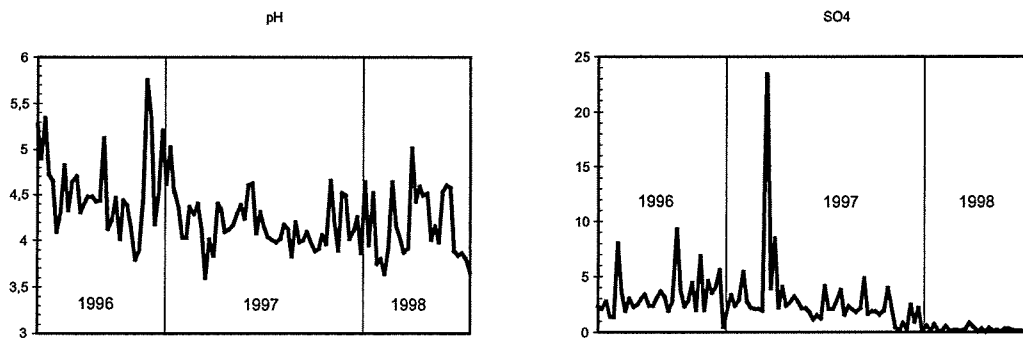


Fig. 1 Trends of pH and SO<sub>4</sub> the precipitation collected from the Hala Gasienicowa.

The lake water has good buffering capacity: the Ca<sup>+2</sup> concentration is 1.1 - 2.25 mg dm<sup>-3</sup> and Mg<sup>+2</sup> is 0.04 - 0.26 mg dm<sup>-3</sup>. Despite that buffering capacity the lake is acidified: pH values for 1996, 1997 and 1998 were 4.56, 4.98 and 5.39 respectively. The lowest value of pH of the lake water was observed during heavy rainfall and the snowmelt. The concentrations of NO<sub>3</sub>-N are high, mean values for the three investigated lakes are: 0.4, 0.6 and 0.7 mg dm<sup>-3</sup>. These high values of nitrate were observed since the beginning of the 90-ties, also in other studied Tatra lakes.

Flora and fauna of Dlugi Staw is very poor in term of both the number of taxons and individuals.

Diatom communities were very scarce, 115 taxons were found. The epilithic flora was dominated by *Achnanthes marginulata*, a non-alpine species, also *A. minutissima* and *Cymbella minuta*. These diatom communities are characteristic for oligotrophic and slightly acidic high mountain lakes.

The structure of epilithic communities of Dlugi Staw did not exhibit bigger changes during the last years, which indicates relative stability in the environmental conditions in this lake. Some ciliates found in Dlugi Staw belong to the group typical for lake plankton such as small

Prostomatida (Urotrichia) and Oligotrichia (Halteria). They are the species feeding on nanoplankton or more or less omnivorous forms. The specialised species feeding on bacteria (Cyclidium and Scuticociliatida) were scarce, because of the lack of available food. The observed density of ciliates was lower than 0.2 ind. ml<sup>-2</sup>, which indicates highly oligotrophic conditions in the lake. It results from low nutrient concentrations, short vegetation period and short time of water retention in the lake.

The crustacean zooplankton community in the studied lake was very poor, it consisted of only seven species, which have been noted in that lake for a long time. The dominant species is *Chydorus sphaericus*, which number was up to 800 ind. m<sup>-3</sup> (October 1997), the second very abundant species was *Alonella excisa* (Cladocera) (Tab.1). The only copepods noted in the studied lake were *Diacyclops bicuspidatus*.

Dlugi Staw	1996	1997	1998
<i>Chydorus sphaericus</i>	36	253	83
<i>Alonella excisa</i>	36	172	19
<i>Acanthocyclops vernalis</i>		47	
<i>Diacyclops bicuspidatus</i>	1		4

Tab. 1. Mean density (ind. m<sup>-2</sup>) of zooplankton species found in the profundal of Dlugi Staw.

The phytoplankton biomass, which is the main zooplankton food source, is extremely low (chlorophyll a - 0.01 µg dm<sup>-3</sup>). This value is typical for Tatra waters - very poor in nutrients and low pH.

In the profundal of Dlugi Staw lake Nematoda dominated, they ranged between 64% in 1996 to 33% in 1998 out of the whole benthos (Tab. 2). The second dominant was Chironomidae (36% - 33%) represented by five taxa; two of them (*Procladius sp.* and *Heterotrissocladius marcidus*) were found only in the lake profundal. Oligochaeta constituted only a few percent of the profundal benthos, they were represented by three taxa. The only species of Coleoptera noted in that lake habitat was *Agabus solieri*, well known from many other high Tatra lakes. The fauna density fluctuated during the year: the lowest number was observed at the beginning of the season (VI, VII - 600- 4000 ind. m<sup>-2</sup>), the highest number was found in the fall (IX, X - 5800 - 19500 ind. m<sup>-2</sup>).

Bigger diversity was noted in the lake littoral (Tab. 3). Oligochaeta dominated there (95%-41%), mostly *Cognettia spp.* This amfibiothic species is very characteristic for slightly acidic habitats. Also *Cernosvitoviella* (mostly *C. tatrensis*) was very abundant in the lake littoral, this species is characteristic for Tatra waters. The most abundant was *Micropsectra coracina* (Chironomidae).

	1996	1997	1998
NEMATODA	5773	5373	299
OLIGOCHAETA	199	431	200
DIPTERA			
Chironomidae	2886	2255	398
COLEOPTERA	100	50	0
TOTAL	8958	8109	897

Tab. 2. Mean density (ind. m<sup>2</sup>) of makrobenthos in the profundal zone of the Dlugi Staw lake.

	1996	1997	1998
NEMATODA	2	2	2
OLIGOCHAETA	35	145	116
PLECOPTERA	4		
TRICHPTERA	1	1	
DIPTERA			
Chironomidae	50	4	1
COLEOPTERA	2	1	1
TOTAL	94	153	120

Tab. 3. Average number of makrobenthos in the littoral zone of the Dlugi Staw lake

Species living in the profundal zone have life cycles well adapted to the severe environmental conditions (long ice-cover period, periodical decline of pH). However, at the same time lack of competition enabled them to reach relatively high densities. In the littoral, which is periodically drying zone, community with amphibious taxa like *Cognettia*, Diptera Limonidae or *Smittia* sp. was present.

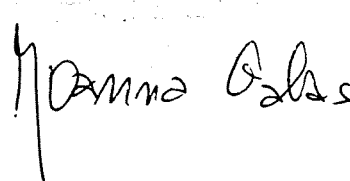
List of Publications arising from the project:

The MOLAR Water Chemistry Group. 1999. The MOLAR Project: atmospheric deposition and lake water chemistry . *J. Limnol.*, 58: 88-106.

Kownacki A., J. Galas, E. Dumnicka, S. Mielewczyk. Macroinvertebrate communities in permanent and temporary high mountain lakes (Tatra Mts). (in press - *Annales de Limnologie*)

Signature of Partner:

Date: 10.04.2000



**DETAILED REPORT OF THE INDIVIDUAL PARTNERS**

Reporting period: March 1 1996 - February 28 1999

Partner: National Institute for Biology  
Laboratory for freshwater and terrestrial ecosystems research ( NIB)

Principal Investigator: Anton Brancelj

Scientific staff: Alenka Gaberščik, Olga Berčič-Urbanc, Milijan Šiško, Gregor Muri,  
Andreja Jerebic

Address: Večna pot 111, 1000 Ljubljana, Slovenia

Telephone: +386 61 123 33 88

Fax: +386 61 123 5038

E-Mail: [anton.brancelj@uni-lj.si](mailto:anton.brancelj@uni-lj.si)

**I. OBJECTIVES FOR THE REPORTING PERIOD:**

- 1.) Water column sampling
- 2.) Sampling of contemporary diatoms and Cladocera in littoral zone
- 4.) Contemporary zooplankton and phytoplankton (diatoms)
- 5.) Sediment traps (SCP, diatoms and cladocerans remains)
- 6.) Sediment core diatoms and cladocera from lake Ledvica
- 7.) Sediment core cladocera from lake Redo
- 8.) Meteorological data collection

## II. Are there any particular problems ?

All planned activities were finished according to the schedule agreed at the beginning of the project. Fieldwork was finished in the middle of summer in 1998 but we prolonged the sampling (water chemistry) and measurements (meteorology) with the same frequency into 1999. We left automatic weather station (AWS) in operation for the next four years. In 1998 we have problems for one month with solar sensor but it was repaired. Due to improper manipulation of data logger we lost data for one month (in May 1998). During winter time wind direction sensor was blocked by ice for few days.

Both in 1997 and 1998 we had problems with considerable oscillation of water level. There was extremely high water level in summer and extremely low in autumn. Differences were more than 2,5 m. As a result we could not collect representative benthos samples.

## III. MAIN RESULTS OBTAINED:

### Water column analyses

From spring 1996 till autumn 1998 water column was sampled 23 times. Ruttner bottle (volume 3.5 litres) was used. Samples were collected with 2.5 m intervals from the surface to the bottom at the deepest part of the lake. Temperature, oxygen and conductivity were measured on the spot. The rest of parameters (nutrients and major ions) were determined in the laboratory within 24 hours after sampling. UV-VIS spectrophotometer was used for most of laboratory analyses.

Five samplings were done during ice cover. Thickness of the ice varied between 20 and 80 cm and duration of the ice-cover was about 7 month (November to May).

Most of chemical parameters in the water column have considerable oscillations from one sampling date to another, while average annual values show relatively stabile conditions. Most of oscillations have origin in intensive precipitation (about 1800 mm of rain). Water has alkaline reaction (in 1996 pH = 7.87, in 1997 pH = 7.75, in 1998 pH = 7.93). Alkalinity and conductivity were high (1996: 1462  $\mu\text{eqv l}^{-1}$ , 151  $\mu\text{S cm}^{-1}$ ; 1997: 1415  $\mu\text{eqv l}^{-1}$ , 181  $\mu\text{S cm}^{-1}$ ; 1998: 1593  $\mu\text{eqv l}^{-1}$ , 184  $\mu\text{S cm}^{-1}$ ). The lake is oligotrophic, also values of total phosphorus and total nitrogen are relatively high ( $P_{\text{tot}}$ : 1996: 20.5  $\mu\text{g l}^{-1}$ , 1997: 30.70  $\mu\text{g l}^{-1}$ , 1998: 26.33  $\mu\text{g l}^{-1}$ ;  $N_{\text{tot}}$ : 1996: 1.02  $\text{g l}^{-1}$ , 1997: 0.95  $\text{g l}^{-1}$ , 1998: 1.37  $\text{g l}^{-1}$ ).

The main source of oscillations between two consecutive samplings is intensive diffuse inflow of rain water. The lake is on limestone geology with well developed carstic phenomena. Measurements made in June 1999 showed that inflow is as high as 0.8  $\text{m}^3 \text{s}^{-1}$  and after heavy rain water in the lake could theoretically be exchanged within 3 – 4 days.

### Sampling of contemporary diatoms and Cladocera in littoral zone

In a period of three years sampling of biota in the littoral zone (five samplings) there were difficulties because of intensive water level oscillations (up to 2.5 m). A result was relatively poor benthic flora and fauna and no representative semi-quantitative samples could be obtained there. Qualitative analyses of both groups get the same species composition in all three years. In Cladocera there were three species present in the littoral zone. *Chydorus sphaericus* and *Alona affinis* were common. The third species, *Alona rectangula* was rare and represented less than 10 % of littoral zone Cladocera.

Analyses of diatom samples from the transect has been collected in Sept. 1996 showed that the most common diatom species was *Acanthos minutissima*. The species occupied the interval from surface to the depth of 12,5 m. Eighteen diatom species were identified in transect samples which were relatively abundant. There was a clear difference between epilithic community (occupying interval between 0 and 10 m -rocky bottom) and epithelic community (between 12,5 and 15 m of depth - soft bottom). Similar pattern was observed in Cladocera. *Chydorus sphaericus* was limited to the upper littoral zone (mainly between 2.5 and 7.5 m), whilst *Alona affinis* prevailed below a depth of 7.5 m.

#### Contemporary zooplankton and phytoplankton (diatoms)

Samples for analyses of contemporary zooplankton species composition, its biomass and chlorophyll concentrations were collected at the same dates as water-column chemistry. Phytoplankton in lake Jezero v Ledvici was present all the time in very low concentration (expressed as  $\mu\text{g l}^{-1}$  of Chl), with maximum concentration of  $0.55 \mu\text{g l}^{-1}$  (as mean volume weighted value). Values above  $1 \mu\text{g l}^{-1}$  were exceptional and were recorded only in the near-the-bottom strata (maximum recorded was  $1.4 \mu\text{g l}^{-1}$ ). Year to year mean concentrations could oscillated up to 50 % and have been probably related to precipitation. There were no diatoms in the plankton.

Macrozooplankton was represented by three taxa (*Arctodiaptomus alpinus*, *Cyclops abyssorum tartricus* and *Daphnia longispina*). In zooplankton was observed oscillation of biomass during the course of three years. Maximum value of a standing crop of zooplankton biomass was recorded in 1997 ( $0.19 \text{ g m}^{-3}$ ), slightly less in 1997 ( $0.18 \text{ g m}^{-3}$ ). In 1998 the value of maximum biomass was  $0.11 \text{ g m}^{-3}$ .

#### Sediment traps (SCP, diatoms and Cladocera remains)

Sediment traps were emptied at the same dates as water column samples were collected. There were four tubes (70 cm high) with total area of  $172 \text{ cm}^2$  and were positioned at the depth of 12 m in the middle of the lake. There were no diatom remains in the trap and number of remains of *Daphnia* increased in autumn period only. Number of SCP in the trap was analysed in our laboratory. Number of particles varied from year to year. In 1997 a cumulative number of particles was four times higher compared those in 1998 (about  $2500 \text{ SCP cm}^{-2} \text{ y}^{-1}$  and about  $600 \text{ SCP cm}^{-2} \text{ y}^{-1}$  respectively).

#### Sediment core diatoms and cladocera from the lake Ledvica

Five cores were taken at the deepest part of the lake in August 1996 using a gravity corer. On the lakeshore, four cores (labelled LEDV2 to LEDV5) were immediately cut into 2 mm thin slices. From each slice, sub-samples for different analyses (physical sediment properties, dating, pigments, SCP, organic pollutants, cladoceran, chironomid and diatom remains) were collected. Core LEDV4 was used for the analysis of pigments, C, N and S concentrations, DW, LOI, and cladoceran and diatom remains. Core LEDV5 was used for  $^{210}\text{Pb}$  dating. An additional sixth core (LEDV6) was taken for the visual analysis of the vertical cross-section of the sediment to record changes in colour and structure.

In total 40 diatom taxa and 4 cladoceran taxa were found in the sediment core from the lake. There is no change in species distribution but there are quantitative changes. Particularly in upper-most part of the core number of remains of both groups increase. Other analyses (DW, LOI, pigments, sedimentation rate) of the sediment indicate that top-most 16 cm were effected



by some external event. As the most probable there are earthquakes that hit the lake several times (1890, 1942 and 1976, slump in 1915). From 1942 onward (corresponding to the depth of 12 cm in the sediment) number of diatom remains increases but those of Cladocera start to oscillate. In the top 2.5 cm of the sediment number of diatom remains is increasing and has the highest value per unit. In Cladocera, the situation is opposite - their number decrease and values are low comparing other part of the core. In Cladocera in the upper 12 cm of the core is a co-dominance of *Chydorus sphaericus* and *Alona affinis*, whilst bellow the depth of 12 cm remains of *A. affinis* are rare. Remains of *Daphnia longispina* are present in all sections of the core in low numbers. Their abundance increases in the topmost 12 cm.

Both, diatoms and Cladocera, reacted to increased eutrophication, which followed earthquakes, with increased abundance. Abundance of both groups dropped several years after the event. From 1960 onward there is a constant increase of number of diatom remains and decrease those of Cladocera. In the same period, there is a tendency of average annual temperature increase to.

The whole data set of diatoms and Cladocera remains from lake Jezero v Ledvici was sent to central data base of MOLAR project in Bergen.

#### Sediment core Cladocera from the lake Redo

The same procedure used for analyses of the Cladocera in the sediment from Jezero v Ledvici was used for Lake Redo. Analyses were finished in autumn 1998. In total, 7 species were determined. *Megafenestra aurita*, *Daphnia pulicaria*, *Chydorus sphaericus* and *Alona affinis* were the most dominant species in Redo sediment. *M. aurita* was common in the top-most 10 cm of the sediment. Interval between 10 and 20 cm of the depth is characterised with remains of *A. affinis* and *C. sphaericus*. *D. pulicaria* has bimodal distribution being the most common in the top-most 5 cm and bellow 15 cm. The whole data set of Cladocera remains from lake Redo was sent to central data base of MOLAR project in Bergen.

#### Meteorological data collection

A Delta-T automatic weather station (AWS) started to operate in Oct. 1 1996. Air temperature, solar and net radiation, air pressure, relative humidity, precipitation, wind speed and wind direction were measured every 30 min. In the period from Oct. 1996 to Oct. 1998 without serious problems, except in May 1998 when we lost data for one month period. In 1998 we have to replace solar radiation sensor because old one get wet. Data were collected from the data logger in 2 - 6 month intervals.

During the period of observation, daily mean air temperatures at the AWS varied between  $-15.0^{\circ}\text{C}$  and  $+19.3^{\circ}\text{C}$ . From Oct. 1996 to Oct. 1998 there was a tendency of increasing of summer temperature comparing those with previous years (maximum value:  $24.5^{\circ}\text{C}$  in Aug. 1998;  $20.2^{\circ}\text{C}$  in Sept. 1997; mean month  $12.8^{\circ}\text{C}$  in Aug. 1998 and  $11.6^{\circ}\text{C}$  in Aug. 1997) and decreasing of minimum winter temperature ( $-14.5^{\circ}\text{C}$  in Feb. 1998;  $-11.7^{\circ}\text{C}$  in Feb. 1997). Amount of precipitation (rain only) was the same (about 1800 mm) in both years with maximum of 512 mm in Nov. 1997 and 532 mm in Oct 1998.

The whole set of meteorological data was sent to central data base of MOLAR project in Bergen. We continue to collect meteorological data in the years 1999 and 2000.

*Data from sediment analyses, water column chemistry and meteorology are in details presented in three papers, submitted for Journal of Limnology (ex. Memorie dell'Istituto Italiano di Idrobiologia) and Journal of Palaeolimnology (see List of publications).*

#### IV. List of Publications arising from the project

- Brancelj, A., Kosi, G., Šiško, M., 1997. Distribution of algae and crustacea (Copepoda & Cladocera) in mountain lakes in Slovenia with different trophic levels. *Periodicum Biologorum*: 99(1):87-96.
- Brancelj, A., Gorjanc, N., Jačimović, R., Jeran, Zvonka, Urbanc-Berčič, Olga, 1999. Analysis of sediment from Lovrenška jezera (lakes) in Pohorje = Analiza sedimenta iz Lovrenškega jezera na Pohorju. *Geogr. zb.*, 1999, št. 39, str. 7-28.
- Brancelj, A., Šiško, M., Lami, A., Appleby, P., Livingstone, D. M., Rejec-Brancelj, I., Ogrin, D., (in print). Changes in the trophic level of an alpine lake, Jezero v Ledvici (NW Slovenia), induced by earthquakes and climate change. *J. Limnol.*
- Brancelj, Šiško, M., Muri, G., Kamenik, C., Appleby, P., Lami, A., Shilland, E., Rose, N. L., Brooks, S. J., Dearing, J. A., (submitted). Lake Jezero v Ledvici (NW Slovenia) - impacts of earthquakes and climate change to the lake ecosystem. *J. Paleolimnol.*
- Cameron, N. G., Briks, H. J. B., Jones, V. J., Berge, F., Catalan, J., Flower, R. J., Garcia, J., Kawecka, B., Koinig, K. A., Marchetto, A., Sanchez-Castillo, P., Schmidt, R., Šiško, M., Solovieva, N., Štefkova, E., Toro, 1999. M. Surface-sediment and epilithic diatom pH calibration sets for remote European mountain lakes (AL:PE Project) and their comparison with the Surface Waters Acidification Programme (SWAP) calibration set. *J. Paleolimnol.* 22:291-317.
- Catalan, J., Ventura, M., Camarero, L., Granados, I., Thies, H., Lotter, A., Lien, L., Korhola, A., Barbieri, A., Stuchlik, E., Brancelj, A. (submitted). Seasonal variability in remote mountain lakes: implications for climatic signals in their sediment record. *J. Paleolimnol.*
- Gaberščik, A., Urbanc-Berčič, O., Brancelj, A., Šiško, M., 1997: Mountain lakes - remote, but endangered. In: Roš M. (editor). Proceedings of the 1<sup>st</sup> international conference on environmental restoration; 1997 July 6-9; Ljubljana. Ljubljana IAWQ specialist group on environmental restoration, 1997: 452-6
- Gaberščik, A., Urbanc-Berčič, O., Brancelj, A., Šiško, M., 1998. Seasonal dynamic of main trophic parameters in three alpine lakes in the Triglav national park (Slovenia). In: Abstracts. Kinneret: Kinneret Limnological Laboratory.
- Mazej, Z., Gaberščik, A., 1998. Macrophytes in different types of lakes: species composition and species vitality. V: Monteiro, Ana (ed.) Vasconcelos, Teresa (ed.), Catarino, Luis (ed.). Management and ecology of aquatic weeds: proceedings of the 10th EWRS international symposium on aquatic weeds, Lisbon 21-25 September 1998. Lisbon: European Weed Research Society.
- Mazej, Z., Gaberščik, A., 1999. Species composition and vitality of macrophytes in different types of lakes. *Acta Biologica Slovenica.* 42:43-52.
- Muri, G., Čermelj, B., Faganeli, J., Brancelj, A., 1999. Comparison between black carbon distribution in alpine lacustrine and coastal marine sediments. V: Ninth Annual V.M. Goldschmidt Conference : Harvard University, Cambridge, Massachusetts, August 22-27, 1999, str. 205.
- Urbanc, J., Brancelj, A., 1999. Karst groundwater connections in the valley of Seven Triglav Lakes. V: International Workshop on Karst Hydrology and Karst Water Management,

Ljubljana, Slovenia, November 4-6, 1999: groundwater pollution in Karst : preserving water quality in Karst systems : book of abstracts. Ljubljana: Institut Jožef Stefan, 1999, str. 47-48.

Urbanc-Berčič, O., Brancelj, A., Šiško, M., 1998. Carbonaceous particles from sediment traps in mountain lakes of the Triglav National Park, Slovenia. In: International conference on Water quality management in national parks and other protected areas: second announcement : under the auspice of the Croatian government : Primošten, 20-23 may 1998.

Signature of Partner:



Dr. Anton BRANCELJ

Date: April 10 2000

**DETAILED REPORT OF THE PARTNER 22**

Reporting period: 1.03.98 - 28.02.99

Partner: Institute of North Industrial Ecology Problems of Kola Science Centre

Principal Investigator: Prof. Tatyana Moiseenko

Scientific staff: Dr. Lubov Kudravtseva (analytical works, hydrochemistry), Dr. Vladimir Dauvalter (sedimentology), Dr. Anatoly Lukin, Julia Sharova (ichthyology), Dr. Boris Ilyashuk (invertebrate), Dr. Ludmila Kagan (diatoms), Dr. Oksana Vandysh (zooplankton), Andrey Sharov (phytoplankton), Sergey Sandimirov (meteorology, hydrology), Elena Ilyashuk (chironomids).

Address: 14 Fersman Street, Apatity, Murmansk region, 184200, Russia.

Telephone: 7-81555-74964, 7-81555-79786

Fax: 47 789 14 117

E-mail: tatyana@inep.ksc.ru

**I. OBJECTIVES FOR THE REPORTING PERIOD:**

Intensive monitoring of lake - Chuna side under the program WP -1. Research of a chemical composition of atmospheric precipitation, water chemistry, condition of biological communities - phyto -, zooplankton, fishes in north-east of Europe.

**II. OBJECTIVES FOR THE NEXT PERIOD:**

Generalization of results and reporting. Estimation of influence of atmospheric transmission on water quality of lakes of northern Europe and their biodiversity. Geochemical and paleoecological reconstruction of climate changes and environment in north of Europe.

III. Are there any particular problems ? Is your part of the project on schedule ?

#### IV. MAIN RESULTS OBTAINED

The combination of conditions of high arctic latitude with altitude causes the importance Chuna-site for the European project - understanding of pollutants transmission and early exchanges in ecosystems. Methodology of research within the framework of manual on WP -1.

Chemistry of deposits. In 1998 the pH of deposits in Chuna site vary from 4.87 to 4.99 in a winter period and 4.12-5.72 in a summer period. The dominant anion is sulphate: 0.37-0.87 mg/l in snow samples and 0.9-4.1 mg/l in rain. The concentration of nitrate in deposits much below and changes from 0.036 up to 0.230 mgN/l. Thus, the main parameters of deposits from Chuna site in 1998 insignificantly differ from deposits 1997.

Water chemistry. The pH of Chuna lake waters changes in an interval 5.97-6.39, alkalinity in summer period 1998 changes from 15 to 21  $\mu\text{eqv/l}$ . The dominant cation is Ca (0.8-1mg/l), the dominant anion is  $\text{SO}_4$  (1.4-2.03 mg/l). These parameters correspond noticed in 1996-1997.

The definition Ni, Cu, Mn, Sr, Al, Fe was carried out by Graphite Atomic Absorption Spectroscopy. The contents of Ni = 0.5-3.4  $\mu\text{g/l}$ , Cu = 0.3-1.6  $\mu\text{g/l}$ , Cd = 0.05-0.1  $\mu\text{g/l}$ . The high level of Ni and Cu was noticed in a surface layer in June after a snowmelt time. It can be as a result of watershed inputs, where these elements get due to activity of the enterprise. The contents Al in water of Chuna lake changed from 4 up to 60  $\mu\text{g/l}$ , Fe - from 2 up to 14  $\mu\text{g/l}$ . The content of Cr = 0.008-0.01  $\mu\text{g/l}$ , Pb = 0.013-0.017  $\mu\text{g/l}$  (were determined by ICP MS).

Phytoplankton. The phytoplankton samples were taken in the beginning of summer (9th July) and beginning of autumn (5th September). The diversity of the phytoplankton was sufficiently low, number of species was 5-9 in the different samples (Fig. 1). The composition of phytoplankton at 9th July was typical for this season. The value of plankton algae more in hypolimnion (278  $\text{mm}^3/\text{m}^3$ ) in compare with epilimnion (46  $\text{mm}^3/\text{m}^3$ ). The dominated algae were *Cryptomonas marsonnii*, *Peridinium aciculiferum*, *Cosmarium sp.* and *Stephanodiscus alpinus* (9th July). In the samples of September the diatom algae were absent. The samples were dominated by green algae *Elacatotrix gelatinosa* and *Oocystis sp.* (5th September). The total volume of phytoplankton was 47  $\text{mm}^3/\text{m}^3$ .

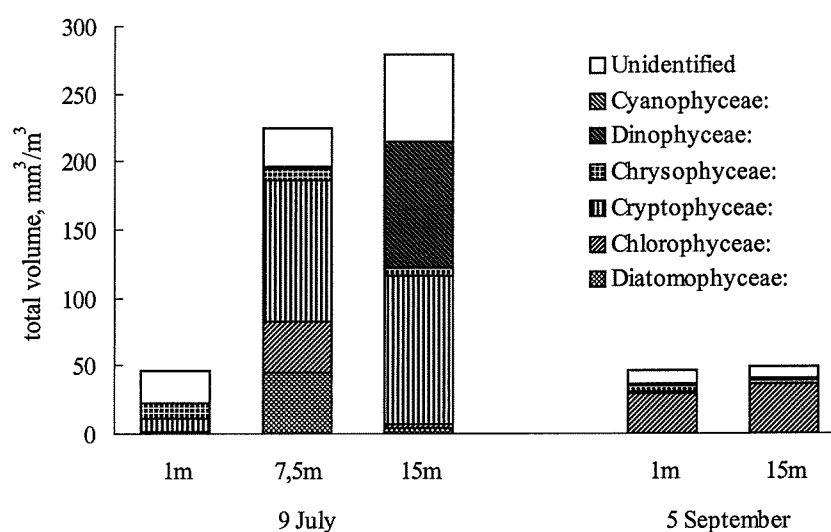


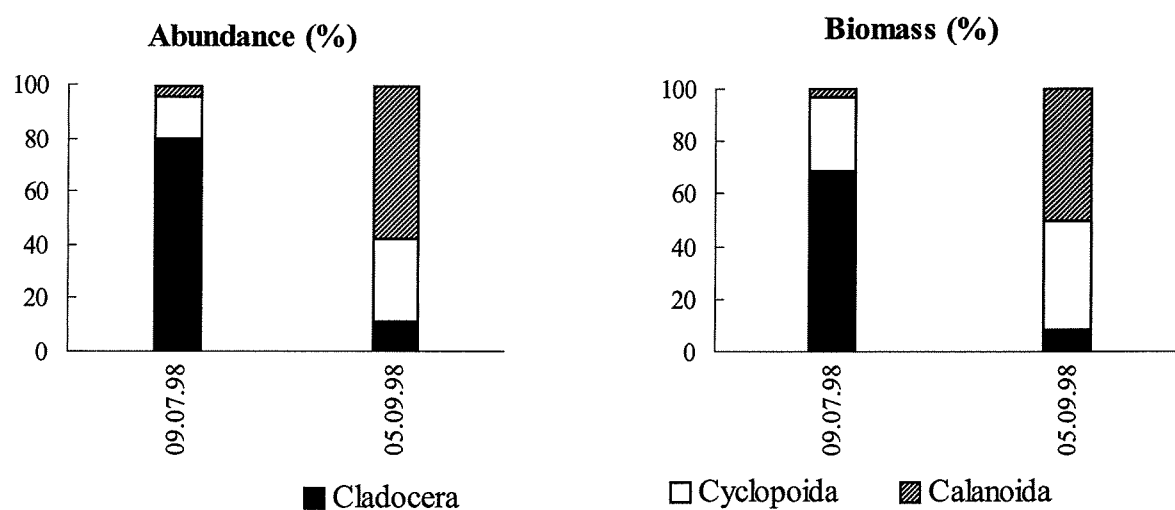
Fig. 1. Phytoplankton composition of the Cuna lake in 1998.

Zooplankton. Zooplankton species composition, number of individuals in sample, number of individuals  $\times 10^3 \text{ m}^{-3}$  and biomass (mg wet weight  $\text{m}^{-3}$ ) in Chuna lake during study period are given in Table 1.

**Table 1.** Zooplankton taxa recorded from samples in the reported period

	N in sample	N $\text{ind} \times 10^3$ $\text{m}^{-3}$	B mg w. w. $\text{m}^{-3}$	N in sample	N $\text{ind} \times 10^3$ $\text{m}^{-3}$	B mg w. w. $\text{m}^{-3}$
Sampling date	09.07.	09.07.	09.07	05.09	05.09	05.09
Depth, m	0-14	0-14	0-14	0-14	0-14	0-14
<b>Rotatoria</b>	30	0.07	0	17	0.04	0
<i>Kellicottia longispina</i>	30	0.07	0	17	0.04	0
<b>Cladocera</b>	7052	16.01	701.1	259	0.58	26
<i>Alonopsis elongata</i>	1	0.002	0.1	2	0.004	0.2
<i>Bosmina obtusirostris</i>	466	1.06	23.80	150	0.34	9.9
<i>Bythotrephes longimanus</i>	-	-	-	2	0.004	3.7
<i>Holopedium gibberum</i>	6585	14.95	677.2	105	0.24	12.2
<b>Copepoda</b>	1755	3.98	316.3	2081	4.72	292.1
<i>Cyclops scutifer</i>	1380	3.13	284.8	731	1.66	132.1
<i>Eudiaptomus gracilis</i>	375	0.85	31.5	1350	3.06	160
<b>Total</b>	<b>8837</b>	<b>20.06</b>	<b>1017.4</b>	<b>2357</b>	<b>5.34</b>	<b>318.1</b>

In the current study 1998 a total of 7 zooplankton species (Rotatoria - 1, Cladocera - 4, Copepoda - 2) were recorded in the investigated lake (Table 1). The dominant and common species have been: in July *Bosmina obtusirostris*, *Holopedium gibberum*, *Cyclops scutifer*, in September - *Cyclops scutifer* and *Eudiaptomus gracilis*. Highest abundance ( $20.06 \text{ ind} \times 10^3 \text{ m}^{-3}$ ) and biomass ( $1017.4 \text{ mg w.w. m}^{-3}$ ) during period of observations 1996-1998 was recorded in July 9th 1998. Cladocera prevailed in July 9th (>79% of total abundance and 69% of total biomass). Cyclopoida (31% of total abundance and 41% of total biomass) and Calanoida (57% of total abundance and 50% of total biomass) were a dominant groups in September (Fig. 2).



**Fig. 2.** Relative mean of basic groups of zooplankton in total abundance (%) and in total biomass (%) in monitored lake in 1998

Abundance ( $\text{ind} \times 10^3 \text{ m}^{-3}$ ) and biomass ( $\text{mg w.w. m}^{-3}$ ) calculations showed differences between months. It is obvious that changes in zooplankton community structure associated mainly with a

seasonal variations of relative abundance of planktonic crustacean (*Bosmina obtusirostris*, *Holopedium gibberum*, *Cyclops scutifer*, *Eudiaptomus gracilis*).

Species of broad ecological requirements, which are capable to survive under low pH and low temperature (*Holopedium gibberum*, *Bosmina obtusirostris*, *Eudiaptomus gracilis*) were found.

Invertebrates. A total of 27 taxa were recorded in the Chuna lake from kick and grab samples during 1998. A total of 11 species of chironomids were identified in samples from different zones of the Chuna lake.

The acidification value of the Chuna Lake was characterized as mesoacidic using the acidification index by Raddum et al. (1988) and Fjellheim and Raddum (1990). The mean acidification index was higher in September (0.40) than in August (0.33).

Subfossil chironomid remains were analyzed in 12 samples from sediment core (12 cm). A total of 618 chironomid head capsules and 22 taxa were found. The four most important species (in order of abundance) were *Micropsectra insignilobus*, *Stictochironomus spp.*, *Paratanytarsus penicillatus* and *Heterotrissocladius marcidus* (Fig. 3). The declines in *M. insignilobus*, *Stictochironomus spp.* and abrupt increases in *P. penicillatus* and *H. marcidus* were noted in sediments dated to recent decades. The diatom stratigraphy and chemical sediment analysis from the Chuna lake indicated gradual acidification and pollution by heavy metals of the lake during the past decades (Moiseenko et al., 1997). The declines in *Micropsectra*-species and the increases in other Tanytarsina are consistent with the other acidification studies (Walker et al., 1985; Dermott et al., 1986; Schnell, Willassen, 1996; Guilizzoni et al., 1996).

Fish. In 1998 the population of brown trout consisted of 50 individuals. The amount of age groups had increased in population. Fish of 5 (4+) age prevailed. The population was presented by brown trout from age of 2 (1+) years old up to age of 7 (6+) years old, while in 1997 fish at the age of 1+ and 6+ were absent. The catch was dominated by female in ratio 1:2.3. The analysis of growth rate of brown trout showed up decrease one in 1998 in compare with 1996-1997 when the growth rate was considerably better. Age and length distribution are presented in Fig. 4 a, b.

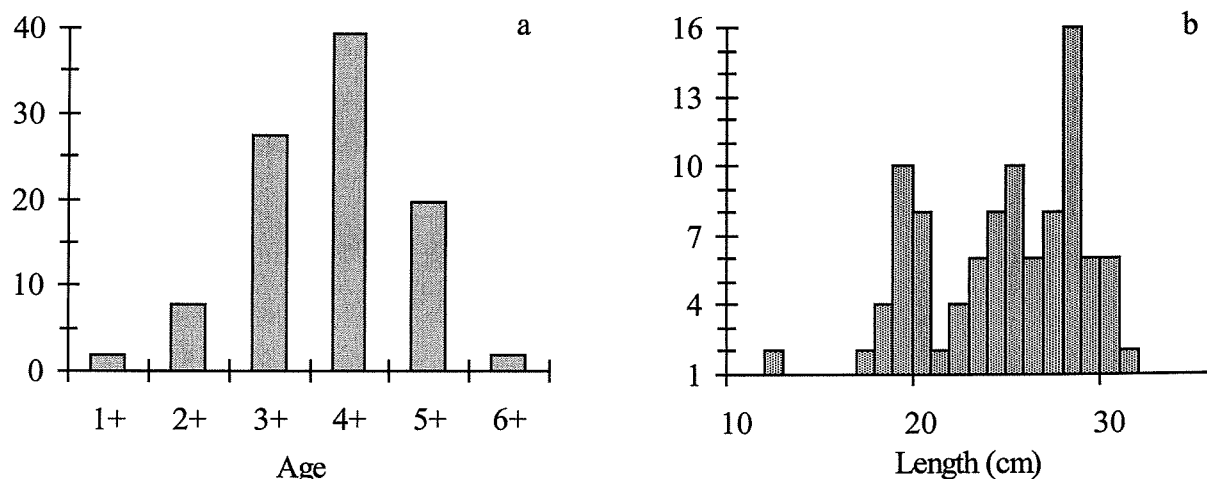


Fig.4. Distribution (%) of age (a) and length (b) of brown trout (*Salmo trutta L.*) in Chuna Lake in 1998.

## **DISCUSSION and CONCLUSIONS**

The results of monitoring in 1998 have shown, that a condition of the Chuna lake ecosystem for three years it is enough stable.

Despite of variability of climatic conditions in these years, distinct trends is not revealed. Precipitation of anthropogeneous sulphur - 0.3 g/m<sup>2</sup> year, pH of deposits - 4.1-5.7.

Seasonal fluctuation of water composition are typical as of all northern lakes. In the spring in snowmelt period (May - June) pH values of water are lowest, and the sulphate contents raise. It specifies, that the major factor of acidification is the sulphate influx from the watersheds. Dynamics of nutrient elements is laid to the typical scheme: increase them in freeze-up period and decrease in vegetation period.

In the summer species dominated - algae *Cryptomonas marsonnii*, *Peridinium aciculiferum*, *Cosmarium sp.* and *Stephanodiscus alpinus*.

Number and biomass of zooplankton in comparison with other arctic lakes are high - up to 20.06 ind × 10<sup>3</sup> m<sup>-3</sup> and 1017.4 mg w.w. m<sup>-3</sup>, respectively. The maximum was in period of opened water. The dominant and common species of zooplankton have been: in July *Bosmina obtusirostris*, *Holopedium gibberum*, *Cyclops scutifer*, in September - *Cyclops scutifer* and *Eudiaptomus gracilis*.

The received monitoring data testify to relative stability of lake in relation to short-term variations of climate and environment.

The more interesting information is received on the basis of the paleoecological data. In 1997 the analysis of geochemical composition and diatoms of sediment core, in 1998 Chironomids composition in the sediment core was completed. The significant changes of all three components are noticed from the layer 4-5 cm, appropriate to industrial development of the European North. According to results of diatoms research, the changes in the layer 8-9 cm connected with industrial activity of the Central Europe are revealed.

V. List of publications arising from the project (include copies):

- Moiseenko T.I., Dauvalter V.A., Kagan L.Ya. 1997. Mountain lakes as indicator of air pollution. *Water Resources*, V. 24, No. 5. - P. 556-564.
- Moiseenko T.I., Dauvalter V., Kagan L.Y. Mountain lakes of Russian Subarctic as air pollution markers // *Issues in Environmental Pollution*, Denver, Colorado, USA, 23-26 August, 1998. - Denver, Colorado, USA, 1998. - Abstract 3.04.

Signature of Partner:

Tatjana Moiseenko



Date: 28<sup>th</sup> February 1999



## **DETAILED REPORT OF THE INDIVIDUAL PARTNERS**

### **MOLAR FINAL REPORT**

Reporting period: **March 97 – February 1999**

Partner: **Laboratorio Studi Ambientali (LSA), Sezione Protezione Aria e Acqua (SPAA),  
Dipartimento del Territorio (DT), Cantone Ticino TI), Switzerland (23)**

**Principal Investigator: Dr. Alberto Barbieri**

**Scientific Staff: Marco Simona, Mauro Veronesi, Giovanni Kappenberger, Manuela Simoni  
Vassalli and Paola Lanfranchi Da Rold**

**Address: Laboratorio Studi Ambientali  
SPAA  
Riva Paradiso, 15  
CH – 6900 Paradiso-Lugano  
Switzerland**

**Tel Nr. +41 91 993 13 01**

**Fax Nr. +41 91 993 12 68**

**E-mail: alberto.barbieri@ti.ch**

### **OBJECTIVES FOR THE REPORTING PERIOD**

- **Sampling campaign, data evaluation and final report**

**Laboratorio Studi Ambientali  
Sezione Protezione Aria e Acqua  
Riva Paradiso 15 - 6900 Paradiso**

*12/4/2000 Barbieri*

## Laghetto Inferiore (Central Southern Alps), Cantone Ticino, Switzerland

### Recent trends in chemistry and mass budget

From 1996, Laghetto Inferiore (LI) has been included in the Mountain Lakes Research (MOLAR) program. LI, situated at 2074 m a.s.l., has a watershed mainly composed of crystalline silicic rocks, a maximum depth of 33 m and a theoretical renewal time of 41 days (Tab.1). The watershed includes a second lake, Laghetto Superiore (LS), located at 2128 m a.s.l. The surface water pH of LI is around 6.6; while alkalinity is about  $30 \mu\text{eq l}^{-1}$ , increasing to  $90 \mu\text{eq l}^{-1}$  at the maximum depth (Tab.2).

Calculated inputs from atmospheric deposition and the main tributary streams, were compared with changes in the lake concentration, and outflow fluxes on a monthly basis (Tab.3).

Weathering ranged between  $90\text{-}130 \text{ meq m}^{-2}$  of alkalinity using a mass budget approach of which 50% was consumed by the actual ( $\text{H}^+$ ) and potential ( $\text{NH}_4^+$ ) atmospheric acidity (Fig.1.). Chemical trends over the period 1985-1998 show an increase in alkalinity and a decrease in sulphate, due to a reduction in the deposition of atmospheric acidity, and a decrease in nitrate, probably because of increased lake productivity (Fig.2).

### Seasonal dynamics of plankton

The pelagic populations in Laghetto Inferiore (southern Swiss Alps) were studied between 1996 and 1998 during the ice-free period (Tab.4). Investigations revealed a considerable number of phytoplankton (Fig.3) species but few zooplankton species. The vertical distribution of the main species of algae shows a marked vertical stratification, with higher biomass concentrations in the deep zone (Fig.4). Along this profile, species in the same taxonomic class tend to be distributed at different depths, according to their specific light requirements. During the study period no clear seasonal succession of populations was observed, also because of the influence of precipitation on the biological cycles. On the whole there was a good correspondence between the biomass values of phytoplankton and those of chlorophyll *a*, both on integral samples of the whole water column and on the vertical profile. This result might be especially useful in the context of further campaigns for monitoring this water body.

### Regionalisation: Limnological survey in eight high mountain

Eight high mountain lakes located above 2000 m a.s.l. in the watershed of Lago Maggiore, with alkalinity between  $10$  and  $100 \mu\text{eq l}^{-1}$ , were studied during summer 1997 (Tab. 5). The survey revealed that some of the lakes had a saline density gradient which might hinder the mixing of water and restrict the oxygenation in hypolimnion. Following acidification, aluminium was present in some lakes in the form of  $\text{Al}(\text{OH})_2^+$ , with pH around 5.9, and as  $\text{Al}(\text{OH})_4^-$ , with pH around 6.6 (Fig.5). The negative correlation observed between pH and nitrate concentrations (Fig.6) seems to be linked to vegetal activity. In fact, acidity in soil and water, combined with the presence of aluminium, can partially inhibit the metabolism of plants and algae, and reduce the assimilation of  $\text{NO}_3^-$ .

Major biological differences emerged among the lakes, both at the level of plankton composition and biomass, and in seasonal dynamics (Tab.6). Dinophyceans and chlorophyceans predominated quantitatively in the lakes with low pH and alkalinity values, whereas diatoms were present in the lakes with higher values of these parameters.

The phytoplankton biodiversity index showed a considerable variation from lake to lake (Tab.7). Higher alkalinity and salinity was not coupled to a higher biocenosis diversity and one or two species tend to dominate the others.

Tab. 1: Geographic and morphometric characteristics of lakes and watersheds

		Laghetto Inferiore	Laghetto Superiore
Longitude		08°35'38"	08°35'08"
Latitude		46°28'37"	46°28'36"
Altitude	m	2074	2128
Altitude max watershed	m	2648	2648
Lake area (a)	km <sup>2</sup>	0.0484626	0.080038
Watershed area (b)	km <sup>2</sup>	1.78 (1)	1.22
b/a rate		36	15
Maximum depth	m	33	29
Mean depth	m	10.6	12.7
Volume	m <sup>3</sup> 10 <sup>6</sup>	0.511465	1.01404
Mean precipitation (prec)	mm y-1	2416	2416
Precipitation surplus	mm y-1	2000 (2)	2000
Mean residence time	days	51	150
Origin		glacial circle	glacial circle
Soil cover	<i>bedrock</i>	86%	88%
	<i>pasture</i>	7%	6%
	<i>lake</i>	7%	6%

(1) includes the watershed of Laghetto Superiore

(2) net waterflux through the soil

Tab. 2: Weighted mean values of temperature, pH, oxygen (mg l<sup>-1</sup>), conductivity (µS cm<sup>-1</sup>), ion concentrations (µeq l<sup>-1</sup>), reactive phosphorus and silica (µg l<sup>-1</sup>), particulated phosphorus and nitrogen (µg l<sup>-1</sup>), total phosphorus and nitrogen (µg l<sup>-1</sup>) of Laghetto Inferiore (1996-1999).

	16.7.96	18.10.96	18.3.97	9.10.97	19.2.98	22.7.98	15.2.99
<b>Temperature</b>	7.18	4.54	3.01	7.39	3.18	6.28	3.09
<b>Dissolved oxygen</b>	10.00	9.54	9.38	9.25	-	9.04	8.38
<b>pH</b>	6.34	6.21	6.39	6.39	6.26	6.43	6.26
<b>Conductivity, 20°C</b>	12.3	13.8	14.2	11.1	12.4	11.1	12.2
<b>Calcium</b>	60.2	74.6	76.7	67.8	72.6	60.72	81.1
<b>Magnesium</b>	7.2	8.8	9.2	9.2	9.5	8.0	10.1
<b>Sodium</b>	13.0	13.6	13.2	12.2	15.1	12.0	17.2
<b>Potassium</b>	10.3	11.5	11.5	11.0	12.3	10.5	12.7
<b>Alkalinity</b>	32.1	46.9	47.0	33.0	39.6	33.3	45.3
<b>Sulphate</b>	39.6	43.1	46.5	39.4	43.3	37.6	44.3
<b>Chloride</b>	2.9	2.5	2.3	1.9	3.2	3.1	2.8
<b>Ammonium</b>	1.2	2.9	0.4	0.3	0.1	1.9	0.1
<b>Nitrite</b>	0.1	0.2	0.0	0.1	0.0	0.1	0.1
<b>Nitrate</b>	15.5	16.2	17.4	14.7	16.5	16.6	19.7
<b>Anions</b>	90.2	109.0	115.0	89.1	104.2	90.7	112.1
<b>Cations</b>	91.9	111.5	114.2	100.5	111.7	93.0	122.7
<b>Particulated nitrogen</b>	13	20	14	21	30	13	-
<b>Total nitrogen</b>	252	356	-	364	-	392	-
<b>Reactive phosphorus</b>	1.8	1.4	2.1	0.5	-	0.6	-
<b>Particulated phosphorus</b>	1.5	0.9	2.0	1.9	1.3	0.9	-
<b>Total phosphorus</b>	2.8	4.6	-	10.4	-	0.6	-
<b>Reactive silica</b>	648	713	802	628	740	664	860

Tab. 3: Fluxes balance of Laghetto Superiore (LS) and Laghetto Inferiore (LI); ions (meq m<sup>-2</sup> y<sup>-1</sup>)  
silica (mmole m<sup>-2</sup> y<sup>-1</sup>)

	Inputs		Output		Output - Input	
	Rain	Snow	LS	LI	LS	LI
Acidity	13.1	5.8	1	1	-18	-18
Calcium	14.7	1.0	113	128	97	113
Magnesium	4.0	0.0	15	16	11	12
Sodium	4.5	0.0	21	25	17	20
Potassium	1.0	0.0	19	24	18	23
Ammonium	27.4	2.9	6	7	-24	-24
Alkalinity	0.6	0.0	53	65	52	64
Sulphate	35.9	3.9	70	85	30	45
Nitrate	23.1	4.9	32	35	4	7
Chloride	3.9	0.0	6	7	2	3
Cations	64.8	9.7	175	200	101	125
Anions	63.5	8.8	161	191	88	119
Reactive silica	0.0	0.0	18	21	18	21

Fig. 1: Mass balance (a) and fluxes (b) of ions in the LS and LI catchments.

LS input: atmospheric load to the watershed of LS; it does not include weathering.

LI input: includes LS output and atmospheric loads to the watershed of LI; it does not include weathering of LI watershed.

LS and LI output: loads leaving the lakes through the outlets.

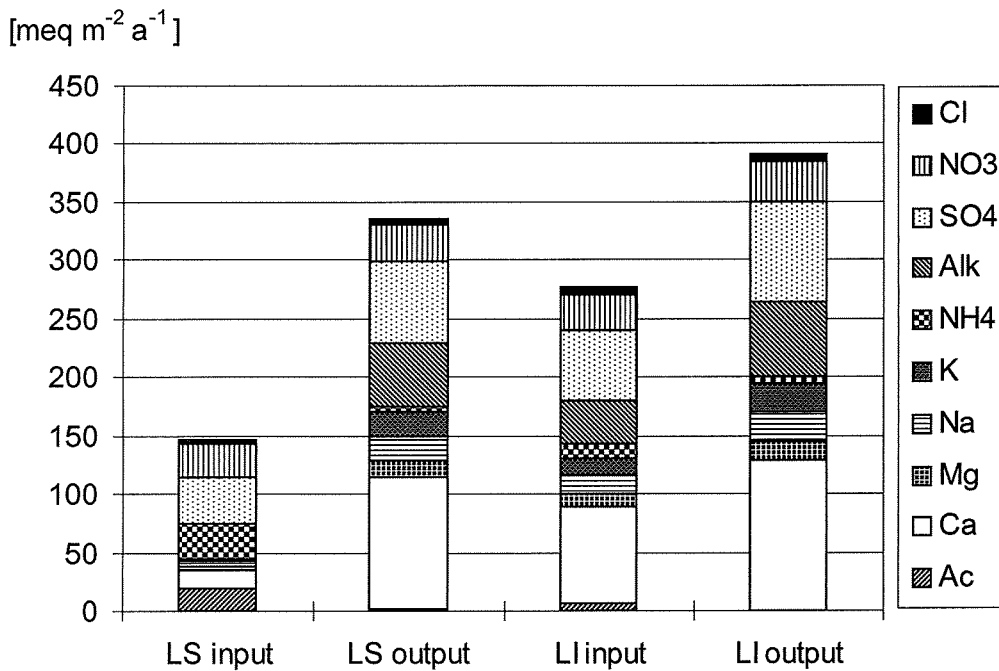
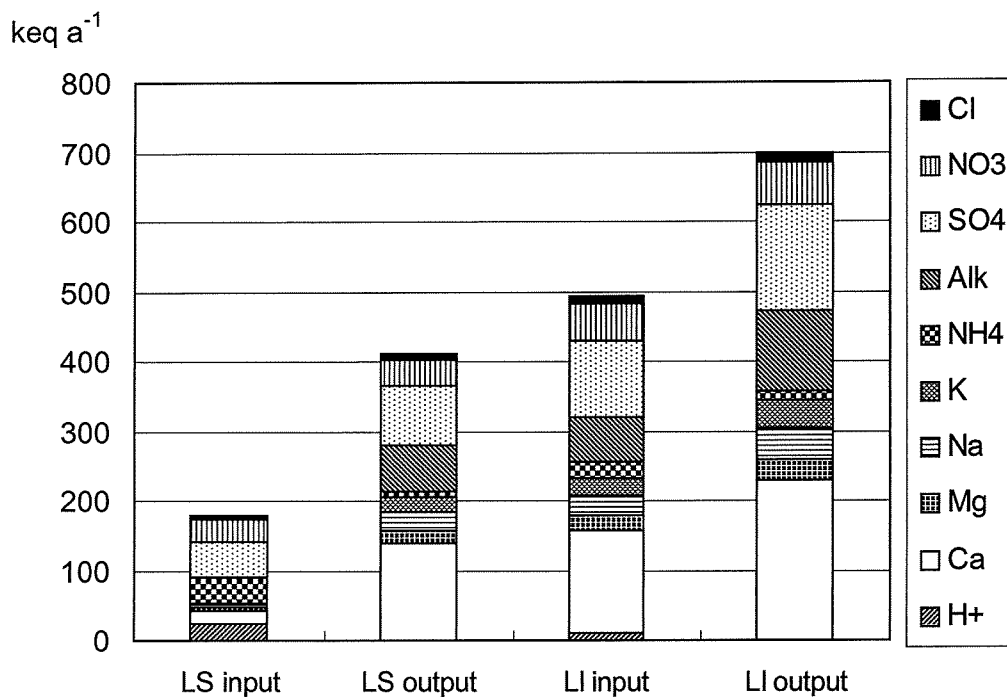
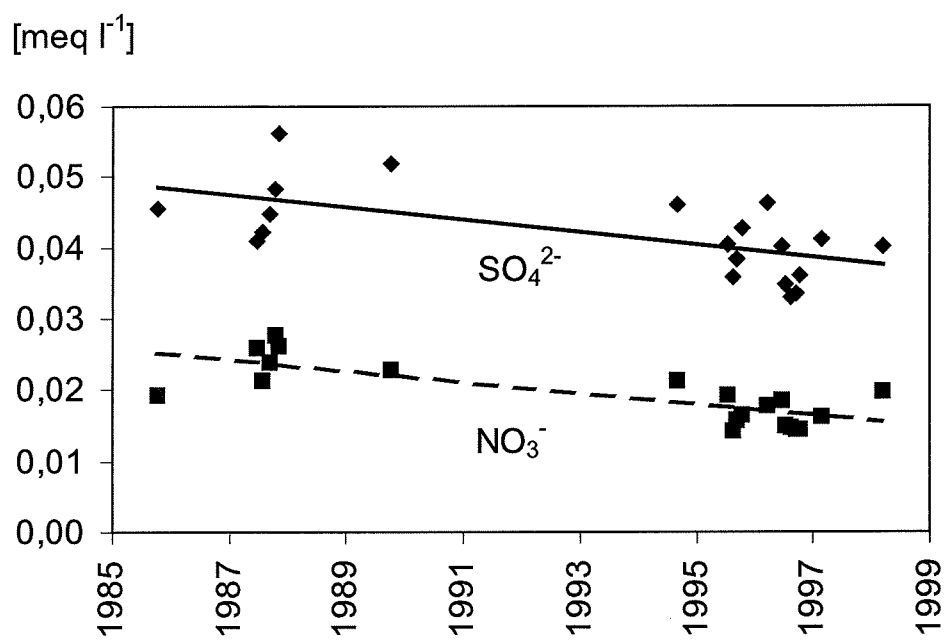
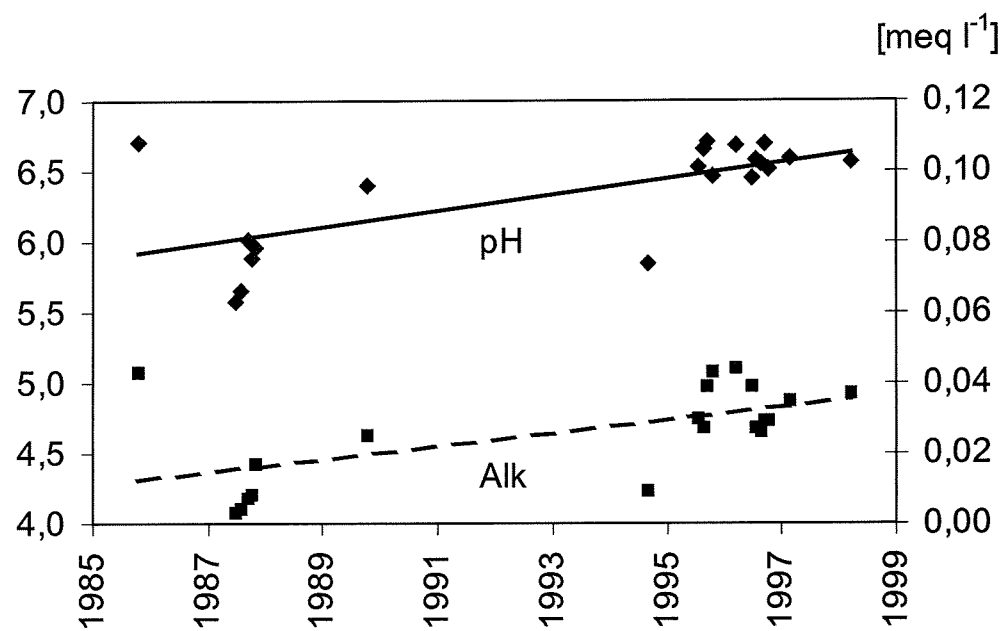


Fig. 2: Trends of pH, alkalinity, sulphate and nitrate in Laghetto Inferiore (-0.4 m depth)



Tab. 4: Plankton taxa found in Laghetto Inferiore

<b>Cyanophyceae</b>	<b>Dinophyceae</b>	<b>Conjugatophyceae</b>	<b>Rotifera</b>
<i>Dactylococcopsis</i>	<i>Gymnodinium (large)</i>	<i>Closterium</i>	<i>Keratella hiemalis</i>
<i>Phormidium</i>	<i>Gymnodinium (small)</i>	<i>Cosmarium</i>	<i>Polyarthra vulgaris-dolichoptera</i>
<b>Chrysophyceae</b>	<i>Peridinium cunningtonii</i>	<i>Mougeotia cfr. transeani</i>	<i>Synchaeta sp.</i>
<i>Dinobryon divergens</i>	<i>Peridinium - cysts</i>	<i>Staurastrum</i>	<b>Copepoda</b>
<i>Chrysophyceae (cysts)</i>	<i>Dinophyceae (various)</i>	<i>Arthrodesmus octocornis</i>	<i>Cyclops abyssorum taticus</i>
<i>Mallomonas cfr. areolata</i>	<b>Chlorophyceae</b>	<i>Gonatozygon pilosum</i>	<b>Cladocera</b>
<i>Chromulinales</i>	<i>Oedogonium</i>	<b>Cryptophyceae</b>	<i>Acroperus harpae</i>
<b>Bacillariophyceae</b>	<i>Chlamydomonas</i>	<i>Cryptomonas</i>	
<i>Surirella</i>	<i>Coenocystis</i>	<i>Rhodomonas</i>	
<i>Fragilaria</i>	<i>Elakatothrix</i>	<i>Tribonema</i>	
<i>Achnantes</i>	<i>Oocystis</i>	<b>nanoplankton</b>	
<i>Navicula</i>	<i>Sphaerocystis</i>	flagellates	
	<i>Tetraëdron</i>	not flagellates	
	<i>Planktosphaeria</i>		

Figure 3 Trend of phytoplankton biomass [ $\text{g m}^{-2}$ ] and chlorophyll *a* [ $\bullet$ ,  $\text{mg m}^{-2}$ ] on the integral sample (0-27.5 m).

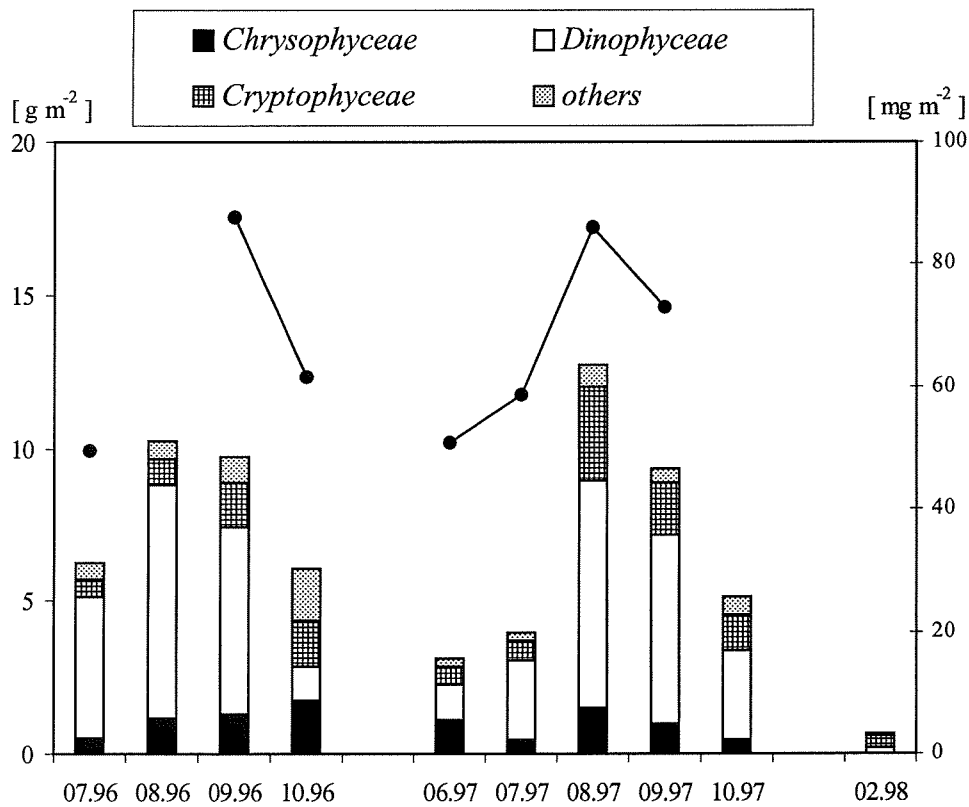


Figure 4 Distribution of phytoplankton biomass [ $10^2 \text{ mg m}^{-3}$ ; fresh weight] and of chlorophyll *a* [ $\text{mg m}^{-3}$ ] on the vertical profile (10 September 1996).

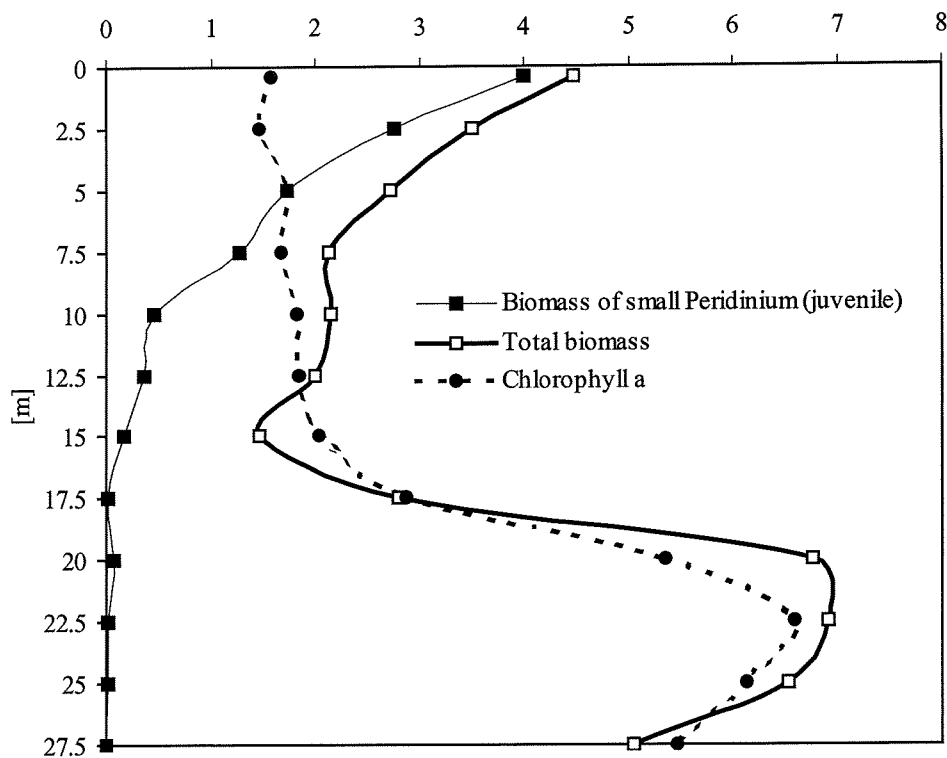


Table 5: Mean surface and hypolimnetic values of temperature, conductivity (*k*), density anomaly ( $\rho-1$ ),  $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ , pH and oxygen saturation.

Variables	Layer	Tomeo	Barone	Crosa	Superiore	Morghirolo	Inferiore	Nero	Alzasca
T [°C]	Surface	13.6	11.0	12.5	11.8	12.0	11.8	10.8	15.4
	Bottom	5.8	4.0	4.2	5.2	4.6	4.2	4.0	4.2
Cond at 20°C [cm s <sup>-1</sup> ]	Surface	8.81	9.43	7.23	8.03	10.64	9.00	14.73	14.50
	Bottom	10.15	10.83	9.14	8.98	11.05	17.30	18.90	20.37
$\rho-1$ [mg l <sup>-1</sup> ]	Surface	-688	-408	-544	-469	-473	-468	-343	-937
	Bottom	-18	10	7	-4	5	12	12	50
$\text{SO}_4^{2-}$ [mg l <sup>-1</sup> ]	Surface	1.83	2.05	1.32	1.54	2.28	1.64	2.95	2.51
	Bottom	2.05	1.36	1.26	1.71	2.19	2.98	3.66	3.05
$\text{Ca}^{2+}$ [mg l <sup>-1</sup> ]	Surface	0.95	1.26	1.05	1.04	1.38	1.18	2.18	2.08
	Bottom	1.17	2.19	1.43	1.26	1.31	2.38	2.78	2.71
$\text{HCO}_3^-$ [mg l <sup>-1</sup> ]	Surface	0.25	0.72	0.91	1.51	2.12	1.71	3.99	4.29
	Bottom	0.75	0.98	1.77	2.07	2.34	4.90	5.33	6.83
pH [-]	Surface	5.7	6.3	6.4	6.6	6.8	6.6	7.2	6.9
	Bottom	5.9	5.8	6.2	6.5	6.3	7.0	6.5	6.4
O <sub>2</sub> %	Surface	100	101	106	99	110	105	110	111
	Bottom	96	84	77	100	78	91	65	48



Figure 5: Reactive aluminium concentration versus pH for lakes Tomeo, Inferiore and Superiore. Solubility equilibrium lines for aluminium hydroxides (1 =  $\text{Al}^{3+}$ ; 2 =  $\text{AlOH}^{2+}$ ; 3 =  $\text{Al(OH)}_2^+$ ; 4 =  $\text{Al(OH)}_4^-$ ; 5 = total Al) are also reported.

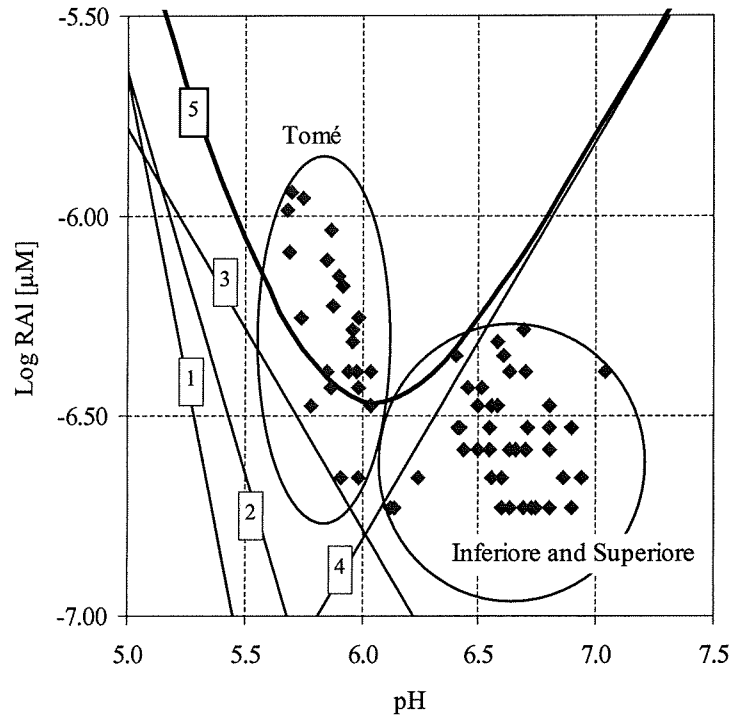


Figure 6: Mean seasonal nitrate concentrations versus pH.

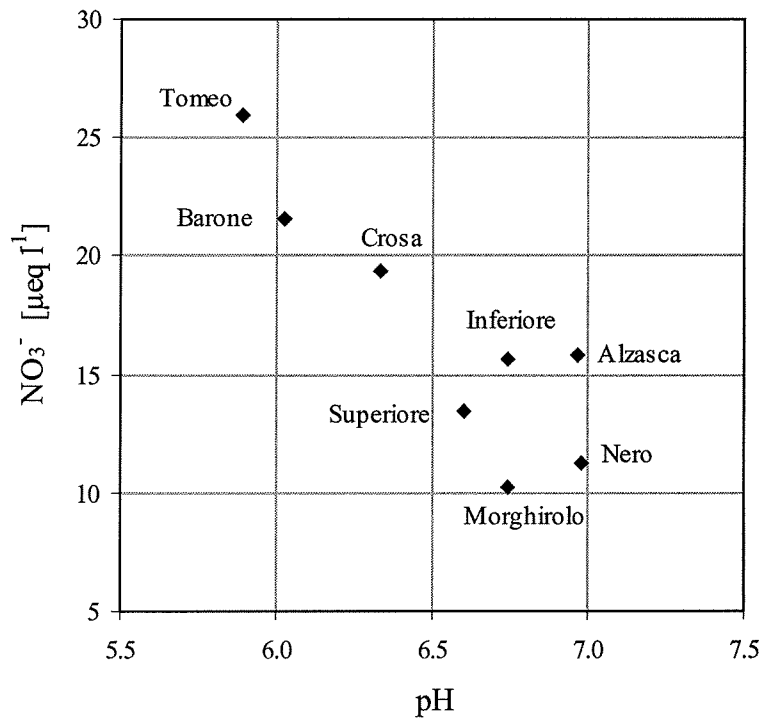


Table 6: Seasonal mean biomass of main phytoplankton and zooplankton groups [mg m<sup>-2</sup>].

<b>PHYTOPLANKTON</b>	<b>Tomeo</b>	<b>Barone</b>	<b>Crosa</b>	<b>Superiore</b>	<b>Morghirolo</b>	<b>Inferiore</b>	<b>Nero</b>	<b>Alzasca</b>
<i>Cyanophyceae</i>		20 ± 14	59 ± 65	3 ± 4	120 ± 42		561 ± 31	38 ± 8
<i>Chrysophyceae</i>	64 ± 27	3086 ± 1713	759 ± 131	1574 ± 526	425 ± 251	1004 ± 562	4344 ± 4776	1529 ± 206
<i>Diatomeae</i>	7 ± 6	26 ± 45	26 ± 0	7 ± 5	3200 ± 3917	8 ± 5	3346 ± 3011	4225 ± 2176
<i>Dinophyceae</i>	610 ± 888	525 ± 268	1206 ± 218	2057 ± 1599	3046 ± 2947	2062 ± 939	868 ± 535	369 ± 68
<i>Chlorophyceae</i>	24 ± 39	4631 ± 7862	900 ± 419	75 ± 44	18 ± 26	94 ± 9	178 ± 294	11 ± 19
<i>Conjugatophyceae</i>	40 ± 8	2321 ± 3881	78 ± 30	567 ± 500	1141 ± 1167	193 ± 100	155 ± 156	2133 ± 906
<i>Cryptophyceae</i>	7 ± 10	1758 ± 473	526 ± 308	2517 ± 1674	1394 ± 1036	1940 ± 1064	3269 ± 3644	715 ± 833
Flag. microalgae	13 ± 11	392 ± 415	67 ± 38	155 ± 42	187 ± 161	248 ± 117	305 ± 247	99 ± 13
Nanoplancton		5 ± 5	8 ± 7	8 ± 3	2 ± 2	15 ± 0	1 ± 2	34 ± 37
<b>Edible biomass</b>	658 ± 880	2568 ± 4083	927 ± 207	2501 ± 2065	5587 ± 5619	2263 ± 840	1798 ± 3624	4478 ± 3017
<b>Total biomass</b>	766 ± 963	12764 ± 8747	3629 ± 272	6963 ± 3004	9534 ± 4177	5558 ± 2568	13029 ± 6759	9153 ± 2353

<b>ZOOPLANKTON</b>	<b>Tomeo</b>	<b>Barone</b>	<b>Crosa</b>	<b>Superiore</b>	<b>Morghirolo</b>	<b>Inferiore</b>	<b>Nero</b>	<b>Alzasca</b>
Naupli	14 ± 14	3 ± 1	31 ± 42		37 ± 31	9 ± 9	65 ± 112	28 ± 21
Ciclopoida 1-2	10 ± 15	5 ± 2	158 ± 97	3 ± 3	253 ± 331	13 ± 21	567 ± 780	11 ± 5
Ciclopoida 3-5	12 ± 15	55 ± 84	2784 ± 1421	299 ± 385	3647 ± 1189	20 ± 14	4703 ± 1422	395 ± 88
Copepoda adults	8 ± 9	5 ± 8	1642 ± 338	135 ± 93	1650 ± 421		778 ± 706	1173 ± 450
Cladocera	5 ± 7	11 ± 20	6828 ± 8096	117 ± 67		5 ± 8		6881 ± 5232
<b>Herbivores</b>	29 ± 36	19 ± 17	7017 ± 7975	120 ± 65	290 ± 306	28 ± 27	632 ± 892	6920 ± 5221
<b>Total biomass</b>	48 ± 60	79 ± 109	11443 ± 7870	555 ± 367	5587 ± 1316	48 ± 35	6113 ± 1096	8488 ± 4940

Table 7: Monthly evolution of phytoplankton PIE (probability of interspecific encounters) values in the eight investigated lakes.

	PIE phytoplankton			
	August	September	October	Average
Crosa	0.86	0.87	0.90	0.88
Inferiore	0.78	0.83	0.81	0.81
Superiore	0.69	0.81	0.82	0.78
Barone	0.68	0.55	0.82	0.69
Tomeo	0.63	0.64	0.69	0.65
Nero	0.78	0.63	0.48	0.63
Morghirolo	0.78	0.63	0.42	0.61
Alzasca	0.57	0.52	0.47	0.52