The MOLAR Project: atmospheric deposition and lake water chemistry

The MOLAR Water Chemistry Group[1]

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ABSTRACT

In the framework of the Mountain Lake Research (MOLAR) project, the water chemistry of 23 lakes covering Europe from the Svalbard Islands to the South of Spain were studied. The lakes are located above or beyond the timber line in the most important mountain areas in Europe. Atmospheric deposition was sampled at 11 sites, representative of different lake districts. 24 institutions took part in the activity. The comparability of the analytical results performed in 18 laboratories was assured by strict sampling and analysis protocols and by a detailed programme of Analytical Quality Assessment/Control. The paper summarises the main morphometric and hydrological characteristics of the lakes and their watersheds and discusses the results of the atmospheric deposition and lake water chemistry. An overview on the main processes controlling the composition and ionic ratio of deposition and lake chemistry is given.

Key words: remote lakes, water chemistry, deposition chemistry

1. INTRODUCTION

The Mountain Lake Research (MOLAR) project considered the most remote and least disturbed freshwater ecosystems in Europe, mainly located in the Alpine and Arctic regions. Although far from local sources of pollution, these lakes are threatened by the atmospheric deposition of pollutants (acidity and toxic air pollutants) and by climate change. The remote lakes found throughout these regions are especially sensitive to these threats for a number of related reasons:

- many are sensitive to acidification because of the poor buffering capacities of soil and rocks in the watershed;
- nitrate levels are higher because their catchments have little soil and vegetation to take up nitrogen deposition from the atmosphere;
- toxic trace metals and trace organics accumulate in the food chain more easily, and some pollutants (e.g. mercury, volatile organics) accumulate preferentially in cold regions;
- climate warming in Europe is predicted to be greatest in the Arctic and Alpine regions.

Because of their sensitivity, remote mountain lakes are not only vulnerable to environmental change, but are also excellent sensors of change, and their high quality sediment records can be used to infer the speed, direction and biological impact of changing air quality and climate.

With these characteristics as its basis, the MOLAR project recognised four overall objectives, each corresponding to a major strand or work package (WP) in the work programme:

1) to measure and model the dynamic responses of remote mountain lake ecosystems to acid (sulphur plus nitrogen) deposition;
2) to quantify and model pollutant (trace metals, trace organics) fluxes and pathways in remote mountain lakes and their uptake by fish;
3) to measure and model the temporal responses of remote mountain lake ecosystems to climate variability on seasonal, inter-annual and decadal time scales;
4) to continue the development of a high quality environmental database on remote mountain lake ecosystems in Europe and to disseminate the results widely.

The MOLAR project, carried out from February 1996 to February 1999, was funded within the EU Environmental and Climate Programme with assistance from INCO. It builds on other previous EU funded projects: AL:PE 1 (Acidification of Remote Mountain Lakes: Palaeolimnology and Ecology) and AL:PE2 (Remote Mountain Lakes as Indicators of Air Pollution and Climate Change), which represented the first comprehensive study of remote mountain lakes at a European level (Wathne *et al*. 1995, 1997; Battarbee *et al*. 1997).

Several physical, chemical and biological aspects of the MOLAR lakes were considered during the execution of the project; we refer to Patrick *et al*. (1998) for a general presentation. A total of 24 Institutions were involved in the project; table 1 lists those contributing to the studies on atmospheric deposition and lake water chemistry, and the personnel responsible for the chemistry activities.

This paper aims to present the results obtained on the chemical fluxes of acid compounds (sulphur and ni-

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[1] See table 1 for the Authors' list.

Tab. 1. Institutions participating in the MOLAR project, acronyms of the Institutes and studied lakes. Lake acronyms refer to table 2.

Institute involved	Institute (acronym)	Lake (acronym)	Persons in charge
Norwegian Institute for Water Research, Oslo (N)	NIVA	Nea, Stav, Arr, Lim	B. Wathne, L. Lien, L.B. Skancke
University College London, Environ. Change Research Centre (UK)	UCL	Loc	N. Rose
Freshwater Fisheries Laboratory, Pitlochry, Scotland (UK)	FFL	Loc	R. Harriman
C.N.R. Istituto Italiano di Idrobiologia, Pallanza (I)	CNR	PaS, PaI	R. Mosello, A. Boggero, A. Marchetto, A. Lami, G.A. Tartari, M. Rogora
Laboratorio Biologico Provinciale, Laives (I)	LBP	Lat	D. Tait, B. Thaler
Univ. Bordeaux, Lab. Neurobiol. Physiologie Comparées, Arcachon (F)	CNRS	Aub	J.C. Massabuau
University of Innsbruck, Inst. of Zoology and Limnology (A)	UIBK	SoS, Gks	R. Psenner, H. Thies, S. Sommaruga-Wögrath, K.A. Koinig
University of Innsbruck, Inst. of Meteorology and Geophysics (A)	UIMG	Gks	U. Nickus
Universitat de Barcelona, Dept. Ecologia (E)	UB-DE	Red	J. Catalan, L. Camarero, M. Ventura
Universidad de Granada, Instituto del Agua (E)	UGR	Cal	L. Cruz Pizarro, P. Carillo, M. Villar, J.M. Medina
Charles University, Dept. Hydrobiology, Prague (CZ)	FSCU	Star, Niz	E. Stuchlík, J. Fott, O. Strunecký
Hydrobiological Institute Czech Rep, České Budějovice (CZ)	ASCR	Star, Niz	J. Kopáček, V. Straškrabová
Inst. of Zoology, Slovak Academy of Sciences, Bratislava (SK)	IZ-SAS	Star, Niz	F. Šporka
Faculty of Ecol. and Env. Sciences, Tech. University in Zvolen (SK)	FEES	Star, Niz	P. Bitušík
Inst. Freshwater Biology, Polish Academy of Sciences, Kracow (PL)	IFB-PAS	Dlu	J. Galas
Universidad Autonoma Madrid, Dept. Ecologia (E)	UAM	Cim	I. Granados
Inst. Ecological Problems, Kola Science Centre, Apatity (SU)	INEP	Chu	T.I. Moiseenko, Kudryavtieva Lubov
National Institute of Biology, Ljubljana (SLO)	NIB	Led	A. Brancelj, G. Muri, A. Gaberscik
S.P.A.A. Laboratorio Studi Ambientali, Canton Ticino (CH)	LSA	Lag	A. Barbieri
University of Helsinki, Dept. of Geography (FIN)	UHEL	Saa	A. Korhola, S. Sorvari, M. Rautio, J. Virkanen
Swiss Federal Institute for Envir. Sci. and Technol., Dübendorf (CH)	EAWAG	Hag	A.F. Lotter
Limnological Research Centre, EAWAG, Kastanienbaum (CH)	EAWAG	Hag	B. Müller
University of Bern, Lab. Environmental and Radiochemistry (CH)	UBERN	Jor	B. Steiner, U. Krähenbühl
University of Zürich, Inst. Plant Biology (CH)	Uzuerich	Jor	M. Gabathuler, K. Hanselmann

trogen) from the atmosphere and the lake water chemistry. It will consider the general features of the lakes and their watersheds, and the characteristics of the sites where atmospheric deposition was sampled. It will also describe sampling methods and treatment of samples and the inter-laboratory studies performed to assure the comparability of chemical results. Separate papers have considered the chemistry and atmospheric deposition of each site; water chemistry is also considered in a different part of the project dealing with modelling. For this reason we consider it useful to collect all the available information concerning methods and site characteristics in one paper, which can also be used as a reference for the other Work Pakages (WPs) making up the MOLAR project.

2. METHODS

2.1. Sampled lakes

All the studied lakes (Fig. 1, Tab. 2) are above or beyond the timber line and are covered with ice for a period during winter. The lakes are located in a range of longitude from 5° 18' W (Laguna Cimera) to 32° 30' E (Chuna), latitudes range from 37° 03' (La Caldera) to 79° 40' (Arresjøen); the altitudes of the latter two lakes are also at the extremes, being at 3050 and 20 m a.s.l. respectively. Lake surfaces range from 0.7 ha (Starolesnianske pleso) to 70 ha (Saanajärvi); 15 of the 23 lakes have a surface area of less than 10 ha. The range of maximum and mean depths is 4.1-73 m and 1.6-32 m respectively. The amount of precipitation in

the watersheds ranges from 350 mm y^{-1} (Limgambergtjern) to over 2000 mm y^{-1} for lakes in the Alps and Pyrenees (Laghetto Inferiore, Jezero v Ledvici, Étang d'Aubé) (Tab. 3). The hydrology is strongly influenced by the long period of ice cover during the winter, as most of the lakes are ice-free only from June to October, and the period of maximum hydrological activity is during the snowmelt, from April to July. These seasonal variations are of great importance in determining the hydrology, so that the mean annual values of lake water retention time and annual runoff (Tab. 3) should be considered only as indicative.

Most of the watersheds of the MOLAR lakes (Tab. 4) are formed of gneiss (7 lakes) or granite (7 lakes), while three of them are formed mainly of calcareous rocks (Jezero v Ledvici, Saanajärvi, Hagelsee). Soils are thin and constitute only a fraction of the whole watershed, as bare rocks, moraine and debris are an important component of the drainage basin. In most cases the vegetation consists of alpine meadows, with a few exceptions where sparse trees are present (Tab. 4).

2.2. Sampling of atmospheric deposition (rain, snow)

The flux of ions and nutrients from the atmosphere to the watershed/lake surface was evaluated by sampling and analysis of direct deposition and snowpack. All aspects of sampling, field and laboratory measurements were described in detail in a manual prepared by the various specialists at the beginning of the project (Wathne & Hansen 1997). In particular, atmospheric
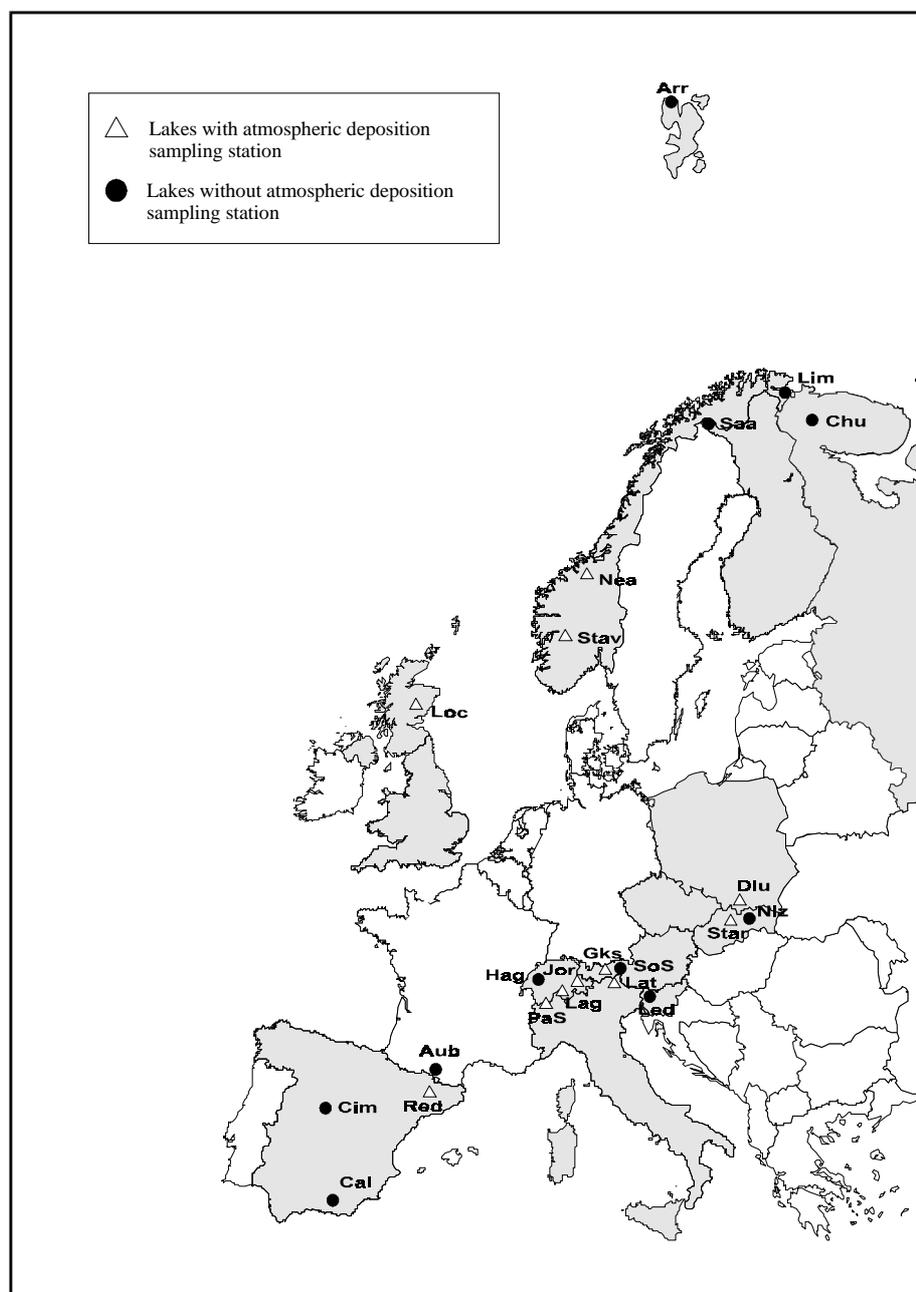
Fig. 1. Location of the MOLAR lakes (acronyms refer to table 2) and atmospheric deposition sampling stations.

deposition, including sampling and analysis of direct deposition and snow pack, was dealt with by Mosello *et al*. (1997a). The primary goal of these measurements is to provide a basis for evaluation of the total deposition of atmospheric pollutants, as this variable plays a fundamental role for most of the modelling, including comparisons with critical loads. The characteristics of the sampling stations, their distance from the lake and eventual local disturbances are reported in table 5. Each site was chosen to be representative of the atmospheric deposition on the lake/watershed surface, and not greatly affected by local sources of pollution that might lead to misinterpretation of the chemical results.

Wet-only sampling was chosen for the sites where electric power is available; alternatively, bulk sampling was used (two sites). Sampling frequency varied according to the accessibility of the sites, as indicated in table 6. Heavy snow events were sampled using a cylindrical bulk collector, made of polyethylene and 1.5 m high, raised about 0.5 m off the ground.

A study on the differences between wet-only and bulk deposition chemistry was carried out in the framework of the MOLAR project at Lake Redó, in the Pyrenees. Precipitation samples were collected using a bulk deposition collector, consisting of a polypropylene funnel with a diameter of 28 cm and a collection tank

Tab. 2. Morphometric characteristics of the MOLAR lakes. See table 1 for the explanation of the acronyms.

Lake	Acron.	Country	Institute	Analytical laboratory	Latitude	Longitude	Lake alt. (m a.s.l.)	Cat. area (km²)	Lake (ha)	Max depth (m)	Mean depth (m)	Volume (m³ 10⁶)
Øvre Neådalsvatn	Nea	N	NIVA	NIVA	62° 46' 30"	09° 00' E	728	16.00	50.0	18.0	3.9	1.95
Stavsvatn	Stav	N	NIVA	NIVA	59° 38'	08° 07' E	1053	2.43	40.0	17.0	6.2	2.50
Lochnagar	Loc	UK	UCL	FFL	56° 57' 29"	03° 13' 05" W	785	1.02	9.8	24.0	8.4	0.82
Paione Superiore	PaS	I	CNR	CNR	46° 10' 26"	08° 11' 27" E	2269	0.55	1.4	11.5	5.1	0.07
Paione Inferiore	PaI	I	CNR	CNR	46° 10' 01" N	08° 11' 23" E	2002	1.14	1.4	13.5	7.4	0.10
Lago di Latte	Lat	I	LBP	LBP	46° 43' 32" N	11° 04' 21" E	2540	0.65	2.3	12.3	5.3	0.13
Étang d'Aubé	Aub	F	CNRS	CNRS	42° 44' 44" N	01° 20' E	2091	0.77	8.6	45.0	-	-
Arresjøen	Arr	N	NIVA	NIVA	79° 40' N	10° 48' E	20	3.00	35.0	32.0	10.9	3.80
Schwarzsee ob Sölden	SoS	A	UIBK	UIBK	47° 51' 56" N	10° 56' 45" E	2799	0.14	3.4	18.0	10.0	0.34
Gossenköllesee	Gks	A	UIBK	IMG / IZL	47° 13' 49" N	11° 00' 51" E	2417	0.01	1.7	9.9	4.7	0.08
Redó	Red	E	UB	DE	42° 38' 34" N	00° 46' 13" E	2240	1.55	24.0	73.0	32.0	7.75
La Caldera	Cal	E	UGR-ES	UGR-ES	37° 03' N	03° 20' W	3050	0.18	2.3	11.3	4.6	0.11
Starolesnianske pl.	Star	SK	FSCU	FSCU/HBI -ASCR	49° 10' N	20° 10' E	2000	0.03	0.7	4.1	1.6	0.01
Nižné Terianske pl.	Niz	SK	IZ-SAS	FSCU/HBI -ASCR	49° 10' N	20° 00' E	1941	1.10	4.8	44.4	18.4	0.89
Długi Staw	Dlu	PL	IFB-PAS	IFB-PAS	49° 13' 36" N	20° 00' 39" E	1783	0.66	1.6	10.6	5.1	0.08
Laguna Cimera	Cim	E	UAM	UAM	40° 15' 50" N	05° 18' 15" W	2140	0.85	4.5	9.4	4.8	0.22
z. Chuna	Chu	SU	INEP	INEP	67° 55' N	32° 30' E	420	2.05	12.5	18.0	10.0	1.25
Jezero v Ledvici	Led	SLO	NIB	NIB	46° 20' 30" N	13° 47' 20 E	1830	-	2.4	15.0	5.7	0.14
Limgambergtjern	Lim	N	NIVA	NIVA	69° 41' N	30° 21' E	172	-	14.0	14.0	4.1	0.57
Saanajärvi	Saa	SF	UHEL	UHEL	69° 05' N	21° 27' E	679	4.60	70.0	24.0	-	-
Hagelsee	Hag	CH	EAWAG	EAWAG	46° 40' N	08° 02' E	2339	0.36	3.0	18.5	8.3	0.19
Jörisee	Jor	CH	Uzuerich	UBERN	46°46'40" N	09°57' 20" E	2490	1.10	57.8	21.8	10.5	0.60
Laghetto Inferiore	Lag	CH	LSA	LSA	46° 28' 37" N	08° 35' 38" E	2074	1.78	4.8	33.0	10.6	0.65

Tab. 3. Hydrology and atmospheric loads of S and N for the MOLAR lakes. * (July-October) approximating that 70% of the deposition occurred as snow (no evaporation correction)

Lake	Country	Precipitation (mm y⁻¹)	Retention time (d)	Annual runoff (l s⁻¹ km⁻²)	Ice free period	Deposition (S) (g S m⁻² y⁻¹)	Deposition (N) (g N m⁻² y⁻¹)
Øvre Neådalsvatn	N	1500	24	60	June-October	0.24	0.35
Stavsvatn	N	1000	380	31	June-Sept./Oct.	0.55	0.50
Lochnagar	UK	1034	315	30	ca. 8 months	0.47	-
Paione Superiore	I	1400	33	44	August-October	0.4-0.6	-
Paione Inferiore	I	1450	23	46	July-October	0.4-0.6	-
Lago di Latte	I	1000	71	31	July-October	0.53	-
Étang d'Aubé	F	2500-3000	-	>1000 mm	June-October	-	-
Arresjøen	N	500	1095	13	July-September	0.17	0.13
Schwarzsee ob Sölden	A	-	not available	not available	July/August-October	-	-
Gossenköllesee	A	1200	tracer exper. still running	-	Jun/Jul - Oct/Nov	-	-
Redó	E	1300-1500	1217-1404	41-48	June-December	1.0	0.44
La Caldera	E	710	390	18	June-October	-	-
Starolesnianske	SK	1145	134	33	June-September	1.00	0.7
Nižné Terianske	SK	1145	293	33	Juli-October	1.00	0.7
Długi Staw	PL	1800	34	42	May-July/Sept-Nov	2.60	1.26
Laguna Cimera	E	1700	62	46	June-Oct/Nov	-	-
z. Chuna	SU	1000	-	18	June-October	0.6 - 1.5	-
Jezero v Ledvici	SLO	2500-2800	-	-	May-Nov	-	-
Limgambergtjern	N	350	330	17.00	June-October	0.7	0.25
Saanajärvi	SF	-	-	-	July-October	-	-
Hagelsee	CH	1700	-	-	August-October	-	-
Jörisee	CH	1100-1400	120	50	June-October	0.28*	0.52*
Laghetto Inferiore	CH	2300	55	60	July-October	0.72	0.9

with a capacity of 5 l. A 200 μm nylon mesh was placed between the funnel and the tank to filter out coarse particles. The sampler was emptied daily, the total collected volume measured and a subsample taken for chemical analysis. In order to assess the amount of dry deposition collected by the sampler, on days when no precipitation water was collected, funnel and bottle were carefully rinsed with a known amount of de-ionised water and a sample of this rinsing water taken for chemical analysis. Sampling was performed from 5 July 1997 until 11 January 1998.

Snowpack was sampled at several sites generally not easily accessible during winter. It was especially important to sample the total snow pack before the first

Tab. 4. Characteristics of the watersheds and notes on fish presence of the MOLAR lakes.

Lake	Cat. geology	Cat. soil	Cat. vegetation	Fish presence
Øvre Neådalsvatn	Gneiss	Alpine soil	Alpine heath, pasture, bare rock	Brown trout, reproduction
Stavsvatn	Granite	Alpine soils and peat	Rocks, pasture, alpine heath, some birch trees	Brown trout, no reproduction
Lochnagar	Granite	Peat and alpine soil	Dwarf shrub (alpine) heath, bare rock	Brown trout, reproduction in outflow
Paione Superiore	Gneiss	Alpine soil	Rocks and debris, some hay meadows	No fish
Paione Inferiore	Gneiss	Alpine soil	Rocks and debris, some hay meadows	Rainbow trout
Lago di Latte	Gneiss	Alpine soil	Bare rocks, alpine pasture, permanent ice	Arctic char (reproduction)
Étang d'Aubé	Granite	-	Rocks, debris, some pasture	Brown trout, no reproduction, lake char, rep. very dace, no rep.
Arresjøen	Migmatite	Permanent frozen	Rocks, debris	Arctic char, (landlocked with rep.)
Schwarzsee ob Sölden	Gneiss, granite, diorit	Bare rocks, thin alpine soil	Rocks, alpine mats	Arctic char (reduced reproduction)
Gossenköllesee	Gneiss, granite, amphibolites	Alpine and podsolic rankers	Alpine meadows and bare rock	Brown trout
Redó	Granodiorite, rocks bearing calcite	Bare rocks, ranker soil	Festuca eskia fields, few mosses	Brown trout
La Caldera	Micaschists, brechoid, marbles, amphibolites	Distryc cambisols, distryc regosols	Rocks, debris	No fish
Starolesnianske pl.	Granite	Primitive soil	Alpine meadows and bare rocks (3:1)	No fish
Nižné Terianske pl.	Granite	Primitive soil	Alpine meadows and bare rocks (1:1)	No fish
Długi Staw	Granitoids covered by moraine	Primitive soil-podsolic soil	Dwarf pine, alpine meadows, rocks	No fish (brook trout stocked in 1960)
Laguna Cimera	Granite	Stone, hydromorphic and psychroxerophilous soils	Rocks and debris with small alpine meadows	Brook trout (*Salvelinus fontinalis*)
z. Chuna	Bazalts	Tundra	Tundra	Brown trout
Jezero v Ledvici	Jurassic limestone	Alpine soil	Alpine meadows, dwarf pine, European larch	No fish
Limgambergtjern	-	-	-	-
Saanajärvi	Paleozoic Caledonian schist and gneiss, dolomitic limestone and sedimentary rocks	-	Subalpine vegetation, bare rock, boulder fields	Arctic char (introduced), lake trout (*Salmo trutta lacustris*)
Hagelsee	Jurassic limestone	Alpine soil	Alpine meadows and bare rock	No fish
Jörisee	Granite	Podsol 10%	Alpine grass tundra	Brown trout and *Salvelinus namaicush*
Laghetto Inferiore	Gneiss alkalipheldsphat, anphibolite, presence of carbonate	Podsol 7%	Rocks and debris, some hay meadows and sparse shrubs	Brown trout by artificial immission

snowmelt in order to evaluate the amount of deposited substance load between the first snow fall (October to December) and the end of the accumulation period (February to April). The main criterion for the selection of the site was the representativity of the catchment area as regards to snow accumulation. In addition, the site should not be influenced by avalanches or frequent snowdrift, causing either additional snow accumulation or ablation. To take the snow samples, a pit 1 × 2 m wide was dug and the samples taken along a vertical profile. Density, stratigraphy and temperature of the snow cover was determined in some of the sites (e.g., Gossenköllesee). The results of these measurements are presented elsewhere (Nickus *et al.* 1998). All material expected to come into contact with the sampled snow was carefully cleaned in the lab before use (diluted HCl, soaked and rinsed with de-ionised water). During sam-

pling fibrous cloths were avoided, and mouth masks and clean rubber gloves were used. Samples were keep frozen until analysed (e.g., Nickus *et al.* 1997).

2.3. Sampling of surface water

Water chemistry data used in this paper refer to the results obtained in WP 1, relative to surface water. Details on the sampling methods are given by Mosello *et al.* (1997b). In most of the lakes, in the framework of WP 2 and 3, other depths were also sampled; how far the surface concentrations are representative of the whole water column will be discussed in the text. Sampling frequencies varied according to the accessibility of the lake, from 1-2 to 12 or more samplings per year. Details for each lake are given in table 9. In this paper, mean concentrations obtained in the period June 1996-July 1998 will be mainly used; however, seasonal and

Tab. 5. Characteristics of the atmospheric deposition sampling sites.

Atm. deposition sampling site	Country	In charge person	In charge Institute	Lake acronym	Latitude	Longitude	Altitude (m a.s.l.)	Distance from lake	Accessibility months	Period of measurement	Number of samples	Local disturbs
Kårvatn	N	Berg T.	NILU	Nea	62° 47' N	08° 53' E	210	6	11	16/01/96 - 30/04/98	433	-
Møsvatn	N	Berg T.	NILU	Stav	59° 38' N	08° 07' E	940	30	12	01/07/96 - 01/05/98	102	-
Lochnagar	UK	Rose N.	UCL	Loc	56° 57' N	03° 13' W	785	0	11-12	29/08/96 - 07/10/98	66	Occasional tourists
Starolesniamske pl.	SK	Stuchlik E.	FSCU	Star	49° 18' N	20° 23' E	2000	0	12	15/08/96 - 22/06/98	52	Chalet with heating
Skalnaté pl.	SK	Stuchlik E.	FSCU	Star, Niz	49° 18' N	20° 23' E	1778	5-12	12	08/11/96 - 16/7/98	74	Astronomical observatory (electric power)
Hala Gasienicowa	PL	Galas J.	IFP-PAS	Dlu	49° 15' N	20° 00' E	1520	2	5-6	01/05/96 - 01/08/98	112	Tourists
Gossenköllesee	A	Nickus U.	UIMG	SoS, Gks	46° 14' N	10° 01' E	2417	15	12	01/10/96 - 30/09/98	76	Tourists
Texel	I	Tait D.	LBP	Lat	46° 44' N	11° 05' E	2390	0.7	12	02/10/95 - 09/12/97	15	-
Renon/Ritten	I	Tait D.	LBP	Lat	46° 35' N	11° 26' E	1780	30	12	08/01/96 - 29/12/97	W 80 B 78	-
Jörisee	CH	Steiner B.	UBERN	Jor	46° 47' N	09° 57' E	2500	0	4/5	12/07/96 - 17/10/97	67	Tourists
Robiei	CH	Barbieri A.	LSA	Lag	46° 27' N	08° 31' E	1890	7	12	26/06/96 - 27/07/98	52	Cable way (electric power)
Graniga	I	Mosello R.	CNR	PaS, PaI	46° 07' N	08° 11' E	1080	5	12	01/01/96 - 26/10/98	103	Paved road
Redó	E	Camarero L.	UB-DE	Red	42° 39' N	00° 46' E	2240	0	12	07/06/97 - 05/07/98	13	-
CRAM	E	Camarero L.	UB-DE	Red	42° 39' N	00° 46' E	1600	1	12	08/04/97 - 05/07/98	186	Paved road, chalet with heating

Tab. 6. Characteristics of the area surrounding the MOLAR atmospheric deposition sampling sites.

Atm. deposition sampling site	Geo-lithology	Vegetal cover	Sampler	Frequency	Snowpack measurement	Precipitation amount measurement
Kårvatn	Gneiss, quartzite	Pine, pasture	Bulk	Daily	Yes	meteo station/weight of samples
Møsvatn	Metarhyolitt and metamorf tuff	Alpine heath	Bulk	Weekly	No	weight of samples
Lochnagar	Granite	Alpine heath, bare rock	Bulk	Weekly (S) Bi-weekly (W)	Yes	rain gauge AWS*
Starolesnianske pl.	Granite	Alpine meadows	Bulk	Weekly	Yes	weight of samples
Skalnaté pl.	Granite	Alpine meadows, bare rock	Wet-only	Weekly	No	weight of samples
Hala Gasienicowa	Granitoids and moraine	Alpine meadows, dwarf pine	Bulk	Weekly	No	weight of samples
Gossenköllesee	Granite-Gneiss	Alpine grass heath	Bulk/Wet-only	Weekly	Yes	meteo station/weight of samples
Texel	Acidic rocks	Rocks	Bulk	Every 2/3 mon.	No	weight of samples
Renon/Ritten	Quartz-Porphir	Forest (Picea abies)	Bulk/Wet-only	Weekly	No	weight of samples
Jörisee	Granite	Hay meadows, sparse coniferous plants	Bulk/Wet-only	Weekly	Yes	meteo station/weight of samples
Robiei	Cristalline rocks	Hay meadows and sparse shrubs	Wet-only	Weekly	Yes	meteo station/weight of samples
Graniga	Gneiss	Pasture	Wet-only	Weekly	No	meteo station/weight of samples
Redó	Granite	Grassland	Bulk	Monthly	No	AWS/volume of samples
CRAM	Granite	Grassland	Wet&dry; bulk since Jan 98	Daily, single event since Jan 98	No	volume of samples

long term variations in the chemistry of some selected lakes will also be considered.

2.4. Chemical analysis and Analytical Quality Control (AQC)

Procedures and suggested methods for the chemical analyses were described by Mosello & Wathne (1997).

Ion chromatography was indicated as the most reliable method for major ion analysis, while molecular spectrophotometry was suggested for the analysis of ammonium (indophenol blue, Fresenius *et al.* 1988), reactive and total phosphorus (molybden blue, A.P.H.A., A.W.W.A., W.P.C.F., 1992), reactive silica (molibdosilicate reduced to heteropoly blue, A.P.H.A., A.W.W.A., W.P.C.F., 1992), aluminum (pyrocatechol

Tab. 7. Volume weighted averages of concentrations in atmospheric deposition collected at MOLAR sites (conductivity μS cm^{-1} at 25 °C; concentrations μeq l^{-1}).

Sampling sites	Starting date	Ending date	Volume (mm)	pH	H$^+$	NH$_4^+$	Ca^{++}	Mg^{++}	Na$^+$	K$^+$	Alk	SO$_4^=$	NO$_3^-$	Cl$^-$	Cat.	An.	Meas. cond.	Calc. cond.
Kårvatn (W)	01/07/96	30/06/97	1655	5.18	7	7	7	19	77	3	-	15	4	98	116	115	16	17
Kårvatn (W)	01/07/97	30/06/98	1698	5.25	6	8	4	15	64	2	-	13	4	76	96	92	14	13
Møsvatn (W)	01/07/96	30/06/97	690	4.74	18	14	4	3	9	1	0	18	16	11	49	45	11	11
Møsvatn (W)	01/07/97	30/06/98	746	4.72	19	12	3	1	5	1	0	19	16	6	40	42	7	6
Lochnagar (W)	29/08/96	30/06/97	1426	4.79	16	20	14	13	39	3	-	28	18	39	106	84	16	17
Lochnagar (W)	01/07/97	30/06/98	1627	4.64	23	19	10	12	35	2	-	31	17	35	100	83	22	19
Starolesnianske pl. (B)	15/08/96	30/06/97	851	4.42	38	24	11	2	4	1	0	53	19	6	81	79	22	22
Starolesnianske pl. (B)	01/07/97	30/06/98	1302	4.55	28	24	12	3	7	3	0	50	17	7	78	75	19	19
Skalnaté pl. (W)	08/11/96	30/06/97	485	4.39	41	29	14	3	3	1	0	54	24	5	92	84	21	24
Skalnaté pl. (W)	01/07/97	30/06/98	1169	4.49	33	18	9	3	3	1	0	41	15	3	65	60	17	18
Hala Gasienicowa (B)	01/07/96	01/06/97	1684	-	-	24	16	5	4	-	0	79	28	-	124	165	22	32
Hala Gasienicowa (B)	01/07/97	01/06/98	1829	-0	-	13	8	3	6	-	0	28	23	-	122	69	21	25
Gossenköllesee (W)	01/10/96	30/06/97	877	5.05	9	11	6	3	3	0	1	11	13	3	32	28	7	6
Gossenköllesee (W)	01/07/97	30/06/98	979	4.97	11	15	7	2	2	1	2	13	13	3	38	31	8	7
Texel (B)	17/07/96	14/07/97	898	5.30	5	45	10	5	4	2	8	33	25	6	72	73	13	12
Texel (B)	15/07/97	22/06/98	729	5.11	8	40	16	9	3	6	21	35	32	8	81	95	15	14
Ritten (B)	01/07/96	30/06/97	1189	5.20	6	27	12	5	7	12	13	24	23	8	69	67	11	11
Ritten (B)	01/07/97	30/06/98	853	5.27	5	36	16	8	6	13	17	28	26	9	85	81	13	13
Ritten (W)	01/07/96	30/06/97	1265	5.07	8	23	11	4	4	2	5	23	19	7	53	54	10	10
Ritten (W)	01/07/97	30/06/98	820	5.17	7	26	13	7	4	3	6	25	20	7	60	58	10	10
Jörisee (B)	12/07/96	03/10/96	405	5.02	10	9	13	2	6	4	6	19	21	8	44	54	10	8
Jörisee (S core)	17/02/97		326	5.67	2	2	2	0	1	0	1	2	4	1	7	8	3	2
Jörisee (B)	23/07/97	17/10/97	295	5.01	10	7	20	4	9	7	-	22	19	11	57	51	15	13
Jörisee (S core)	10/03/98		324	4.98	10	3	3	1	1	0	0	3	7	2	18	12	5	5
Robiei (W)	01/07/96	30/06/97	2401	5.02	9	14	9	3	2	1	0	24	12	3	38	39	7	8
Robiei (W)	01/07/97	30/06/98	2221	5.05	9	16	15	3	4	1	5	20	15	3	46	43	8	9
Graniga (W)	01/07/96	01/06/97	1885	4.67	21	34	10	2	5	2	1	32	28	5	75	66	17	16
Graniga (W)	01/07/97	01/06/98	846	4.70	20	22	9	3	4	3	1	24	24	4	61	53	14	14
Redó (W, B)	30/06/97	30/06/98	1381	4.97	11	17	20	3	13	3	0	22	11	11	66	49	10	10

violet, ISO 10566: 1994) and aluminum fractions (Rogeberg & Henriksen 1985).

As part of the AQC within each laboratory, checking the ion balance and comparing measured and calculated conductivity were suggested as a routine operation for all the analyses performed. The same checks were repeated on the whole set of data by the two co-ordinating laboratories (surface water: NIVA, atmospheric deposition: CNR). They were performed using an MS-Excel sheet, distributed to all laboratories, and also used for mailing the data from each laboratory to the co-ordinating centres.

Inter-laboratory exercises were carried out for the whole period of the project to assure the comparability of the results produced by each institution. Two different intercomparison networks were used: the first referred to the circuit of the ICP on Assessment and Monitoring of Acidification of Rivers and Lakes (ICP Waters), co-ordinated by NIVA, the second to the circuit of the Analytical Quality Control and Assessment Studies in the Mediterranean Basin (AQUACON), carried out by the CNR in collaboration with the Environment Institute of the Joint Research Centre at Ispra. Results were published in reports (e.g., Hovind 1997; Mosello *et al*. 1998a, b) and discussed in an annual technical workshop. Besides their function in checking the comparability of the results, these exercises provide the possibility for exploring specific analytical problems,

such as the measurement of pH and low values of alkalinity, both variables important to the aims of the project (Mosello & Wathne 1997; Marchetto *et al*. 1997).

3. RESULTS

3.1. Atmospheric deposition

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 difficulties in reaching the sites. The period considered for each station is indicated in table 7, which also reports the precipitation volumes and the mean volume weighted concentration of the main ions, separately for the two study years. The values refer both to rain and snow deposition, with the aim of evaluating the total ion deposition. Even in the stations which worked regularly for the whole period, the volumes of precipitation show considerable differences in the two study years; for example, Graniga (Central Alps), has annual volumes of 1885 and 846 mm .

The analytical quality of the data was generally good, as emerges from the ion balances and from the comparison between measured and calculated conductivity (Tab. 7). The pH values range from 4.1-4.5 in the Tatra Mountains (Starolesnianske pleso, Skalnaté pleso, Hala Gasienicowa sampling sites), to 4.7-5.0 in the other sites. Sulphate and nitrate prevail among the ani-

ons in most of the stations, with the exception of Kår-vatn and Lochnagar, which have a marked contribution of chloride of marine origin. The sulphate to nitrate ratio is close to 2 in the stations in the Tatra Mountains and Spain, while it approaches 1 in the sites in the Alps and in Møsvatn (Central part of Southern Norway). The higher ratio for the Tatra Mountains is probably due to higher sulphur emissions deriving from fuel combustion. Even the frequency of dust deposition events, more frequent in Southern Europe, could affect the mean annual sulphate concentration, as these events are characterised by high sulphate content (Carratala *et al.* 1996).

Alkalinity was measured in significant amounts in some stations in the Eastern Alps (Ritten, Texel). Its deposition is mainly related to the transport of Saharan dust (Guerzoni & 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 60 μeq l^{-1} in Gossenköllesee (Eastern Alps) and 200 μeq 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 (Fig. 2) improves if they are corrected for seasalt, assuming that all chloride is of marine origin and that the ratio with the other ions (Na$^+$, Mg^{++}, Ca^{++}, SO$_4^=$) is the same as in seawater. Results (Fig. 2b) show that the lowest ion concentrations were then found in Kårvatn (25 μeq l^{-1}), while in the other stations the correction does not substantially affect the concentrations of sulphate and the sulphate to nitrate ratio.

Relationships among ions in deposition were tested for each sampling site using cluster analysis. Results showed marked similarities in the grouping of ions, so that four examples were chosen, on the basis of (a) strong influence of marine salts (Lochnagar), (b) high acidity (Skalnaté pleso) (c) low acidity in the Alps (Ritten) and (d) in the Pyrenees (Redó) (Fig. 3). All the stations show a strong correlation between sodium and chloride, due to the fact that most of these ions are from sea-spray, and a grouping of SO$_4^=$, NH$_4^+$, NO$_3^-$, i.e. the ions mainly deriving from anthropogenic activity. The hydrogen ion concentration is directly linked to the group of "acid" compounds at Lochnagar, Skalnaté pleso and Redó, while in the less acidic deposition of Ritten, H$^+$ is correlated to the group of ions of marine origin.

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 presented in table 8 as mean values for the two years of study, and in figure 4, where the depositions are also shown without the marine contribution.
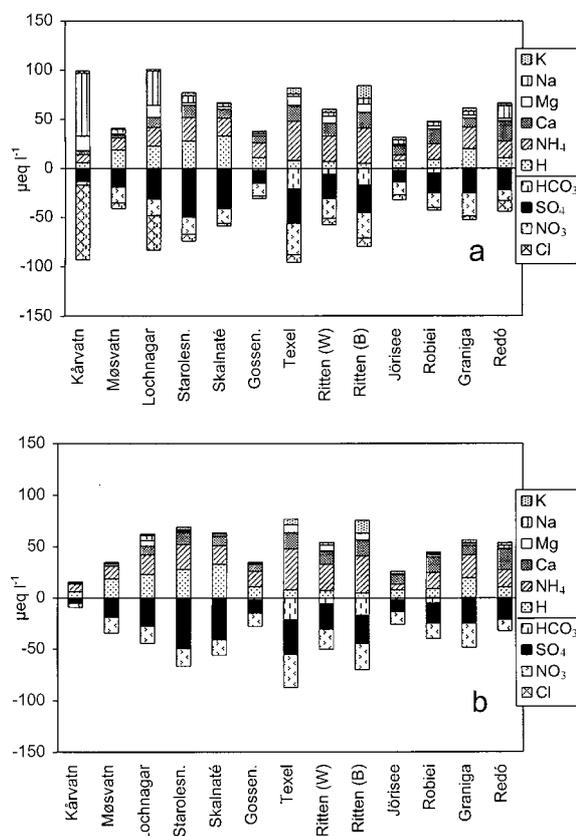

Fig. 2. Ion balance for the mean annual concentration of atmospheric deposition before (a) and after (b) sea-salt correction.

The stations in the Alps show wide variability in the deposition of acidity, from relatively high values (20-30 meq m^{-2} 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 9-10 meq m^{-2} y^{-1} for the stations of Gossenköllesee 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 northermost stations of Kårvatn and Møsvatn, where both hydrogen and ammonium loads are low (Tab. 8).
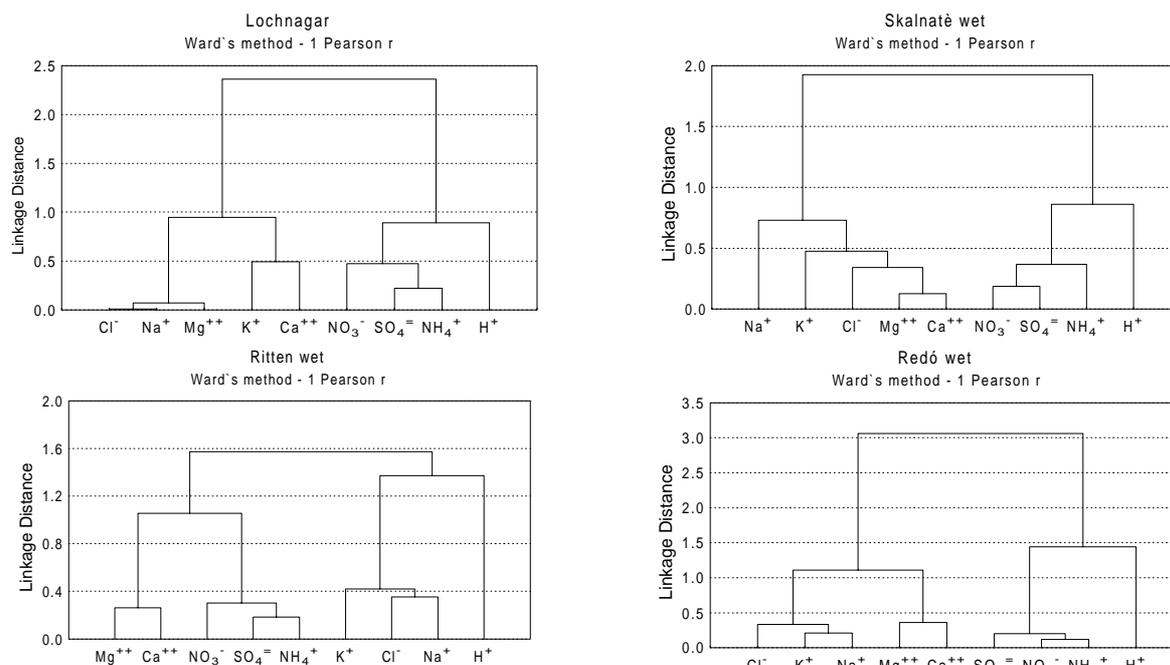
Fig. 3. Cluster analysis of the ion concentrations in atmospheric deposition of four sampling stations.

As regards the marine contributions of sodium and chloride, it is consistent with the concentration values that the highest depositions are found in the stations of Kårvatn and Lochnagar, both close to the sea.

The base cation deposition of non-marine origin is mainly represented by calcium. The highest deposition values were found in the stations of Robiei and Redó. In Robiei, it was determined by several episodes of Saharan dust deposition, whereas in Redó it represented background values, since no acute dust deposition events were recorded. In years in which such episodes occur, the calcium deposition may triplicate (Camarero & Catalan 1993).

3.2. Lakes

The mean concentrations for surface water in the MOLAR lakes are shown in table 9, where the number of samplings performed in each site is also indicated. The ion concentrations have quite a wide range of variation (88-3360 meq l^{-1}), from very diluted to highly buffered waters. The corresponding range of variation of conductivity is 6-148 μS 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 μeq l^{-1}), ranges between 118-343 μeq l^{-1} for lakes Jöri-see, Saanajärvi and La Caldera, and is lower than 50 and 20 μeq l^{-1} in 15 and 7 lakes, respectively.
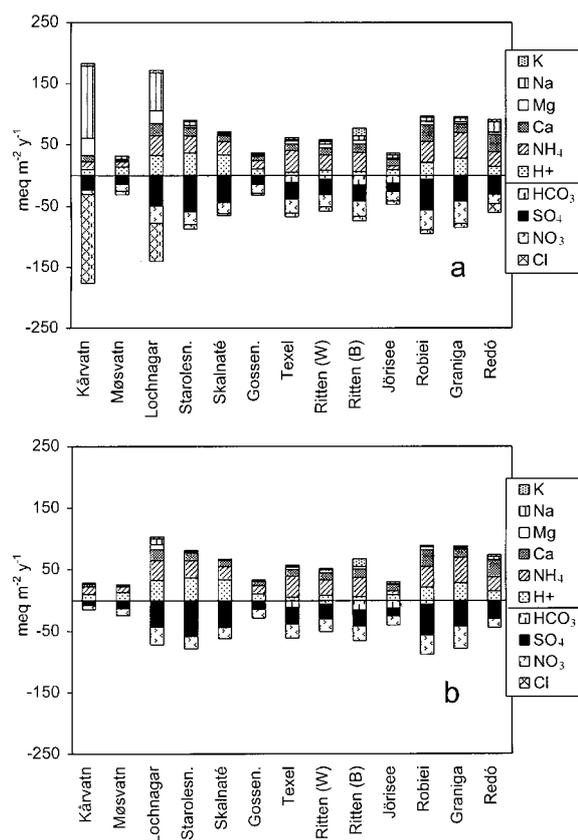
Fig. 4. Deposition of ions from atmospheric deposition before (a) and after (b) sea-salt correction.

Tab. 8. Deposition of ions (meq m^{-2} y^{-1}) from atmospheric deposition.

Sampling sites	Starting date	Ending date	H$^+$	NH$_4^+$	Ca^{++}	Mg^{++}	Na$^+$	K$^+$	Alk	SO$_4^=$	NO$_3^-$	Cl$^-$	Cations	Anions
Kårvatn (W)	01/07/96	30/06/98	10	13	9	29	118	5	0	23	7	146	178	173
Møsvatn (W)	01/07/96	30/06/98	13	9	2	1	5	1	0	14	12	6	25	19
Lochnagar (W)	29/08/96	30/06/98	33	32	20	21	62	4	0	49	29	62	172	140
Starolesnianske pl.(B)	15/08/96	30/06/98	37	27	14	3	7	2	0	59	21	8	90	89
Skalnaté pl.(W)	08/11/96	30/06/98	34	21	10	2	3	1	0	44	18	4	71	66
Hala Gasienicowa (B)	01/07/96	01/06/98	120	32	21	7	9	-	0	92	45	-	166	173
Gossenköllesee (W)	01/10/96	30/06/98	10	14	7	2	3	0	2	12	14	3	36	28
Texel (B)	17/07/96	22/06/98	5	35	10	5	3	3	11	27	23	6	62	67
Ritten (B)	01/07/96	30/06/98	6	31	14	7	7	13	15	27	25	8	77	74
Ritten (W)	01/07/96	30/06/98	8	25	12	6	5	3	6	24	21	7	58	58
Jörisee (B)	12/07/96	10/03/98	9	6	11	2	5	3	0	14	15	6	37	37
Robiei (W)	01/07/96	30/06/98	21	34	27	6	7	2	6	50	32	6	97	95
Graniga (W)	01/07/96	01/06/98	29	41	14	3	6	3	1	41	37	7	96	85
Redó (W, B)	30/06/97	30/06/98	15	23	28	4	18	4	0	30	15	15	91	68

Tab. 9. Mean chemical characteristics of MOLAR lakes (conductivity µS cm^{-1} at 25 °C; concentrations µeq l^{-1}).

Lake name	n° data	pH	H$^+$	NH$_4^+$	Ca^{++}	Mg^{++}	Na$^+$	K$^+$	Alk	SO$_4^=$	NO$_3^-$	Cl$^-$	Cations	Anions	Σ Ions	Meas. cond.	Calc. cond.
Øvre Neådalsvatn	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
Aubè	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	-3	43	13	5	59	58	116	11.8	11.5
Nižné 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 Cimera	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
Limgambergtjern	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

Sulphate ranges from 11 to 252 µeq 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 µeq l^{-1}) in the northernmost lakes in Norway (Øvre Neådalsvatn, Stavsvatn, Limgambergtjern and Arresjøen), Finland (Saanajärvi), Russia (z. Chuna) and Spain (Laguna Cimera), while the highest values (36-42 µeq l^{-1}) are found in the lakes in the Tatra Mountains (N. Terianske pl. and Dlugi Staw). The lakes in the Alps show values between 15-26 µeq l^{-1}, with the lowest value for Hagelsee (12 µeq l^{-1}). Nitrate concentration is also relatively low (below 12 µeq l^{-1}) in the lakes in Spain (Redó, Cimera and La Caldera).

A comparison between the different lakes is possible on the basis of the results of the cluster analysis (Fig. 5), performed on the concentrations of the main ions, log-normalised and using Ward's method and the Euclidean distances as clustering criteria. Four main groups emerge; the main chemical characteristics of each group are given in figure 6. The first group comprises two lakes (Hagelsee and Jezero v Ledvici), characterised by high alkalinty values, calcium and magnesium concentrations. The mean total ion concentration is 3140 µeq l^{-1}, with a conductivity of 170 µS cm^{-1}. The chemistry of the lakes of the second group (4 lakes: Limgambergtjern, Arresjøen, Saanajärvi, Lochnagar) is characterised by a lower ion concentration (500 µeq l^{-1}, conductivity of 32 µS cm^{-1}) and by the importance in the ionic balance of sodium, chloride, calcium and sulphate, which altogether represent up to 70% of the total ionic concentrations. Groups 3 and 4 (11 and 6 lakes, respectively) show minor differences, the most important being the lower ionic concentrations in group 4 (148 µeq

l[-1] *vs* 296 µeq l[-1] of group 3), the higher nitrate and sulphate concentrations in group 3 (21 and 52 µeq l[-1] respectively *vs* 6 and 24 µeq l[-1] of group 4) and the higher concentrations in sodium and chloride in group 4 (21 and 17 µeq l[-1] respectively *vs* 14 and 5 µeq l[-1] of group 3).
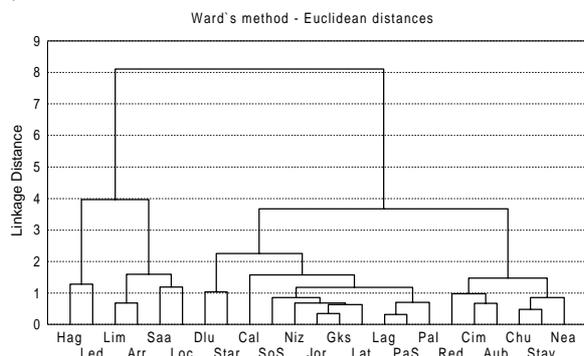

Fig. 5. Cluster analysis of the chemistry of MOLAR lakes.
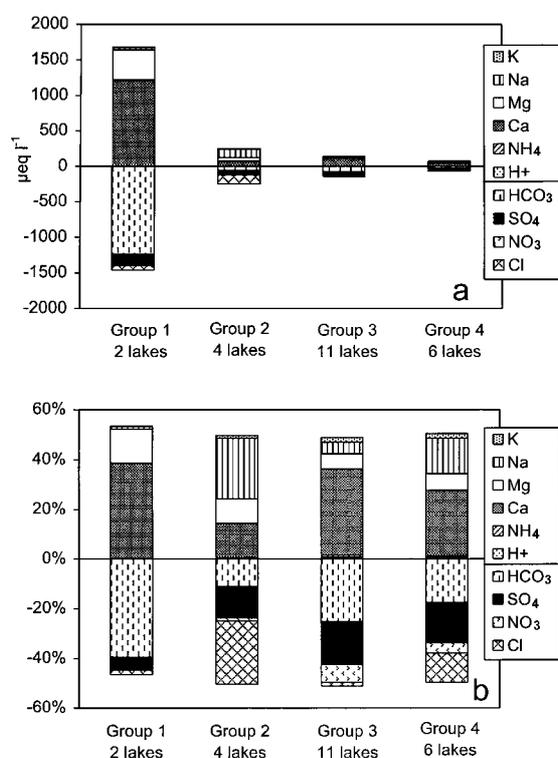
Fig. 6. Mean chemical characteristics of the four clusters of the MOLAR lakes.

4. DISCUSSION

4.1. *Bulk* vs *wet-only chemistry of atmospheric deposition*

The type of sampling employed in determining the chemistry of atmospheric deposition is of major importance. Wet deposition should be measured using wet-only samplers, i.e. funnels which are open to the atmosphere only during precipitation events. Continuously open funnels (bulk samplers) were used in some stations where no power source was available. Several studies considering the ratio between bulk and wet-only chemistry have shown considerable variability (Draajers & Erisman 1993; Van Leeuwen *et al*. 1996). A comparison of 40 annual or pluriannual studies carried out in different European sites shows a mean wet/bulk ratio between 0.67 ± 0.16 and 0.73 ± 0.16 for K, Ca and Mg, of between 0.81 ± 0.17 and 0.89 ± 0.17 for Na^+, Cl^-, NO_3^-, $SO_4^=$, NH_4^+, while the ratio was 1.03 for hydrogen ion (Draajers *et al*. 1998).

In one of the MOLAR stations in the Alps (Ritten), both bulk and wet-only samples were collected during the whole study period. A comparison of the results, for both concentration and deposition, shows wet/bulk ratios in the same range as that indicated above, with the exception of potassium, where the contribution due to dust is much higher and the ratio falls as low as 0.2.

A further study was made in the Pyrenees, at Redó, by Camarero & Catalan (1996). The volume of precipitation collected in the period July 1997-January 1998 was 966 mm, with the precipitation occurring on 137 days as opposed to 83 dry days. Dry deposition, expressed as a percentage of bulk (wet+dry) deposition, varied among the elements: from 5-6% in the case of NO_3^- and $SO_4^=$, to 11-14% for NH_4^+, Ca^{++} and Mg^{++}, 17-19% for Cl^- and Na^+, and up to 35% for K^+. Assuming that the difference between bulk and total deposition is not relevant to the purpose of this discussion, the ratios of wet/total deposition are still in the range indicated above (Tab. 10).

These results suggest certain characteristics of the transport and deposition of the different ions:

- the sum of NO_3^- and $SO_4^=$ (in equivalents) practically equals NH_4^+ in wet deposition, indicating that $NO_3(NH_4)$ and $SO_4(NH_4)_2$ aerosols are the main source of these ions. Ammonium aerosols seem to be very efficiently scavenged by precipitation as condensation nucleii: only about 5% of both NO_3^- and $SO_4^=$ is deposited as dry deposition. Dry deposition of NH_4^+ is approximately double (c. 12%), which suggests that other mechanisms of dry deposition, gaseous NH_3 for instance, may be of the same order as that of ammonium aerosols;
- Cl^- and Na^+ have an ionic ratio very close to 1, in both wet and dry deposition. This indicates that aerosols originating as sea spray are the main mechanism of transport, and are deposited mainly as condensation nucleii in wet deposition (c. 80%), but also by settling as dry deposition in a significant fraction (c. 20%);
- as for the other cations, K^+ presents the highest dry deposition rate (35%), although the absolute amounts are the lowest compared to the other ions. The relative dry deposition of Ca^{++} and Mg^{++} is much lower (13%), indicating that the long range

Tab. 10. Comparison of wet and dry deposition (meq m^{-2}) collected at Lake Redó site during the study period.

	Precipitation (mm)	Occurrence (days)	NH$_4^+$	SO$_4^=$	NO$_3^-$	Cl$^-$	Ca^{++}	Mg^{++}	Na$^+$	K$^+$
Wet-only	966	137	17	7.7	10.2	8.5	21.2	2.7	9	1.6
Dry	-	83	2.3	0.4	0.6	2.0	2.7	0.4	1.8	0.9
Total	-	-	19.3	8.1	10.8	10.5	23.9	3.1	10.8	2.5
Ratio wet/total	-	-	0.88	0.95	0.94	0.81	0.89	0.87	0.83	0.64

Tab. 11. Comparison of water equivalent and ionic loads in precipitation (wet only) and in the snow cover (Pit 1 and Pit 2) at Gossenköllesee, winter 1997/98.

Date	Water equivalent (cm)			NO$_3^-$ (meq m^{-2})			NH$_4^+$ (meq m^{-2})			SO$_4^=$ (meq m^{-2})		
	Wet only	Pit 1	Pit 2	Wet only	Pit 1	Pit 2	Wet only	Pit 1	Pit 2	Wet only	Pit 1	Pit 2
30/12/97	10	18	39	0.78	1.23	2.46	0.34	0.23	0.52	0.45	0.52	1.08
27/01/98	16	26	35	1.21	1.99	2.28	0.58	0.21	0.59	0.75	0.88	0.93
24/02/98	17	35	41	1.48	3.08	2.67	0.79	1.11	0.80	0.92	1.73	1.42
11/03/98	22	42	38	1.90	3.63	2.99	1.11	1.11	1.49	1.31	1.76	1.54
08/04/98	28	45	42	3.44	5.94	3.65	2.54	3.15	1.54	2.50	3.17	1.88

transport of these cations, accompanying wet southerly air masses (Camarero & Catalan 1993; 1996), has more impact on bulk deposition than dust of local origin.

4.2. Snow vs *rain precipitation*

Various practical reasons make it more difficult to sample snow deposition than rainwater (e.g., Sevruk 1993); however, the deposition of snow and the substance load accumulated within the snow cover are very important at the MOLAR sites. There is a good deal of uncertainty as to the estimation of precipitation amounts, especially at high wind speed, and much effort has been made to optimise a sampling procedure (Lovblad 1996).

Two different sampling techniques used to evaluate the chemical load of deposited snow were compared in Austria, in the watershed of Gossenköllesee.

The accumulation period, i.e. the time span until the onset of snow melt, lasted from mid November 1997 to the beginning of April 1998. Snow cores were sampled at two sites in the catchment of Gossenköllesee. The water equivalent and the nitrate, ammonium and sulphate loads of the snow pack were compared with the respective cumulative amounts of weekly sampled precipitation (wet only).

Precipitation amounts collected with the wet-only sampler reached only 40 to 60% of the corresponding water equivalent values of the snow cover. This deficit was, however, offset by higher weighted mean sulphate and ammonium concentrations in the precipitation, resulting in ionic loads that compared fairly well with the respective loads in the snow pack (Tab. 11). The wet-only nitrate loads, in contrast, remained well below the snow pack values due to similar mean nitrate concentrations both in precipitation and in the snow cover (Fig. 7).

Apart from the methods used, a further point concerns the relative importance, in terms of quantity and quality, of snow and rain in the MOLAR site. A specific study was performed at Robiei, in the southern Swiss Alps, at 1890 m a.s.l. (Barbieri & Mosello 1999). Sampling was performed on a weekly basis from July 1996 to July 1997; the total amount of precipitation was 1999 mm, with the snow contribution about 49%.
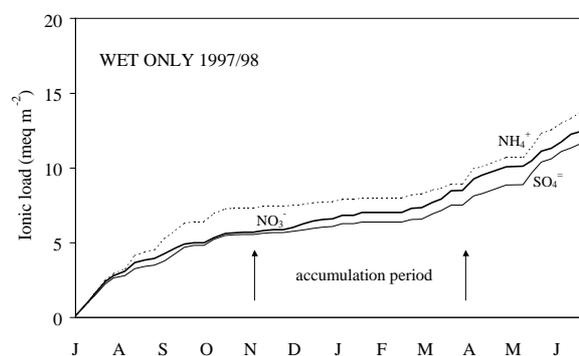
Fig. 7. Cumulative lines of nitrate, ammonium and sulphate loads in atmospheric deposition (wet only) at Gossenköllesee, July 1997 to June 1998. Arrows mark the snow accumulation period.

The comparison of the chemical composition of rain and snow (Fig. 8) shows a solute content lower in snow than in rain (41 and 126 µeq l^{-1}); the difference is more marked for the ions of marine origin, which are below the quantification limit during the winter period. These differences are due to several factors.

The first is the varying stratification of the atmosphere in the course of a year. During the winter period the transport of ions from the lowlands and valleys, where the main sources of pollution (and the sea) are lo-

cated, is very low due to the generally high stability of the atmosphere limiting the vertical mixing of air. During the summer period, in contrast, the contribution of ions transported from the lowlands is high due to enhanced vertical mixing of the atmosphere, determining concentrations of sulphate and ammonium 5 times higher than in winter, and two times higher for nitrate. A second factor responsible for the different composition of rain and snow is the greater light intensity in summer than in winter, increasing the oxidation of sulphur dioxide to sulphur trioxide (Calvert *et al.* 1985). A further point is the different scavenging by rain and snow of the sulphate present in the atmosphere (Mosello *et al.* 1988). In the specific case of Robiei the amount of deposition of the different ions reflects the differences in chemical composition, as the amounts of snow and rain precipitation are practically the same (Fig. 8).
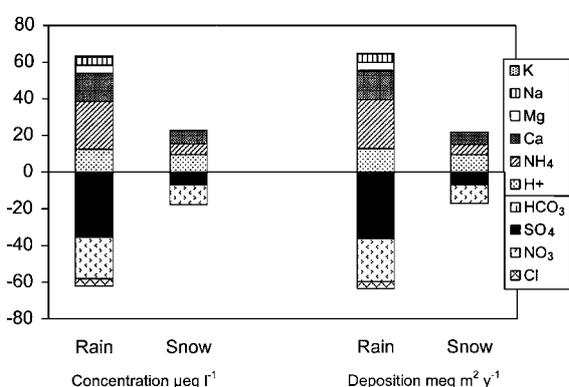
Fig. 8. Chemistry and amount of deposition of rain and snow in the site of Robiei/Laghetto Inferiore (CH).

Similar seasonal variations in the chemistry of deposition were measured in other Alpine sampling stations (Graniga, Jörisee, Ritten): winter and early spring concentrations of sulphate, ammonium and nitrate are far lower than during summer (Puxbaum *et al.* 1991).

4.3. Variation of lake water chemistry with depth and season

The work package of the MOLAR project considered here included performing measurements on surface water. To understand how representative of the mean situation they are, it is important to compare these concentrations with those of deeper water. Surface water monitoring is less expensive and technically easier than sampling over the whole column, in particular in those areas without road access for transporting a boat or other equipment. As an index of the ion content of the water we chose conductivity, which is fairly well related to ion composition, at the end of the summer period, when water stratification, if any, is more likely to be found. The conductivity profiles measured in a group of MOLAR lakes are presented in figure 9.
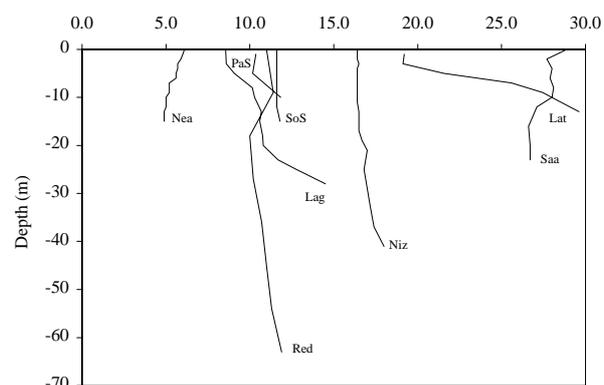
**Fig. 9**. Variation of conductivity (μS cm^{-1} at 25 °C) with depth in selected MOLAR lakes.

They show how surface values could be considered representative of the mean concentrations. In some cases (e.g., Laghetto Inferiore, Lago di Latte) conductivity values increase with depth, while in other lakes, like Øvre Neådalsvatn and Saanajärvi, it is the opposite. However, it must be pointed out that, particularly in the deepest lakes (depth >20-30 m), even a slight increase in solute concentration can affect the possibility of water mixing. These processes and their biological implications are considered in another WP of the MOLAR project (Patrick *et al.* 1998).

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. Figures 10 and 11 show these variations in the Norwegian Lake Øvre Neådalsvatn, the Alpine lakes Paione Superiore and Gossenköllesee, 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).

4.4. Long-term variations in lake chemistry

Although not included in the MOLAR project, the trend of chemical concentrations can be analysed by pooling the data of four lakes for which long-term series of data are available, thanks to continuity with the EU programs AL:PE1 and AL:PE2, as well as with national studies. In the case of Stavsvatn and Paione Superiore (Fig. 12), pH and alkalinity increased during 1986-1997, while the $SO_4^=$ concentration decreased. The trends were similar in Redó, except that pH slightly decreased in contrast with the increasing alkalinity. The Austrian lake Schwarzsee ob Sölden has had the same increase in pH and alkalinity since 1992, but, unlike the other lakes, it also shows a marked increase in sulphate concentration.
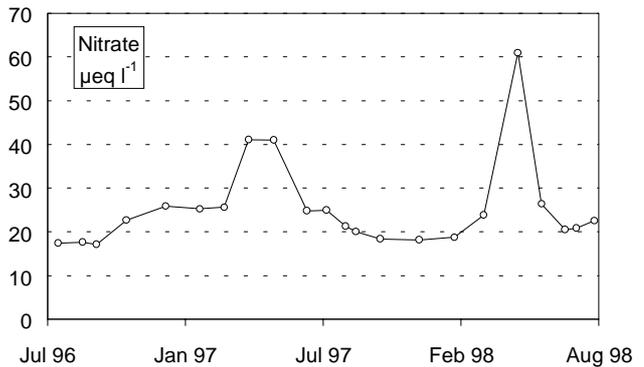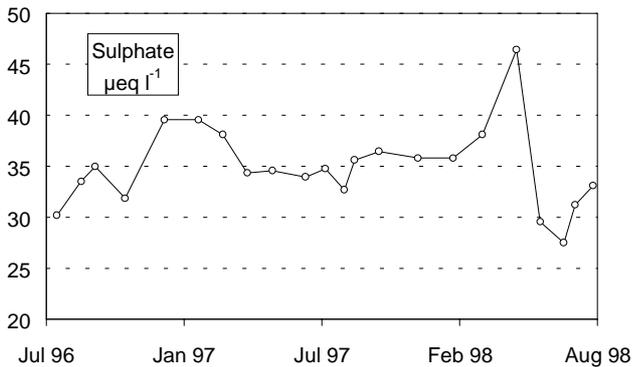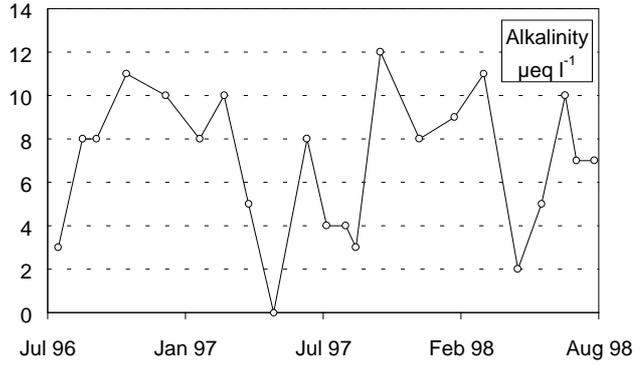
Øvre Neådalsvatn
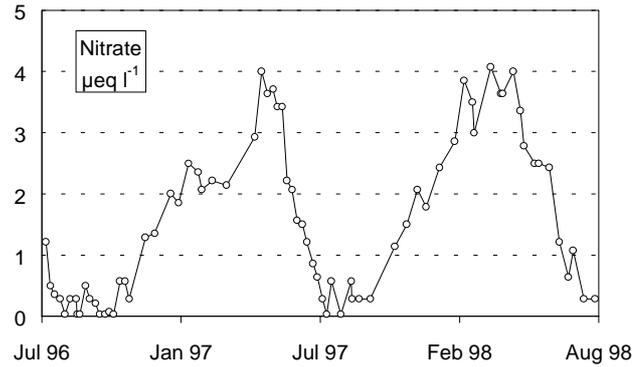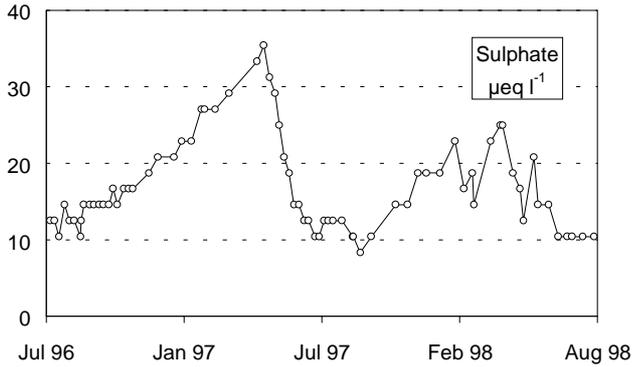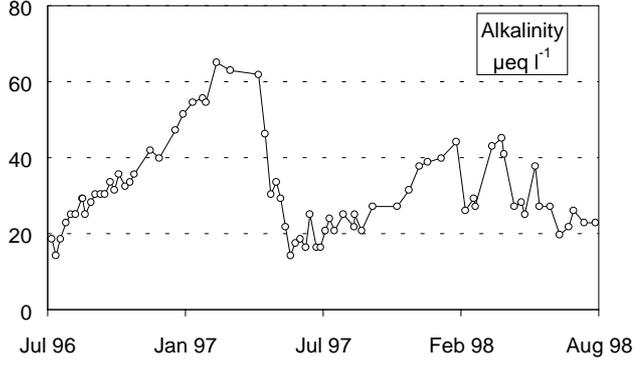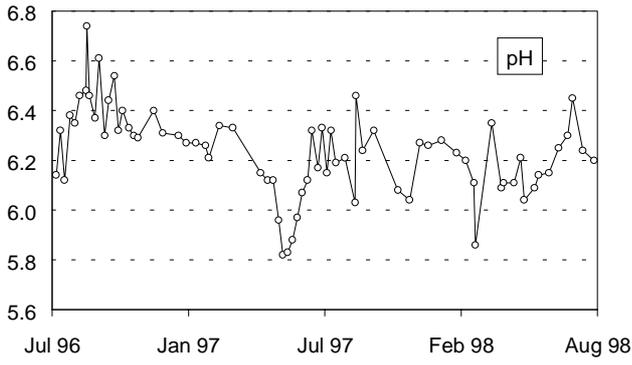
Lago Paione Superiore

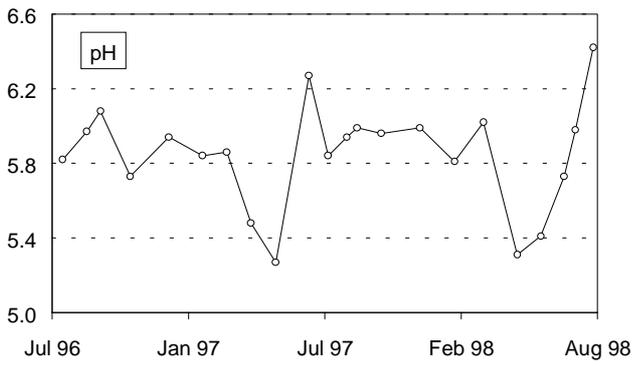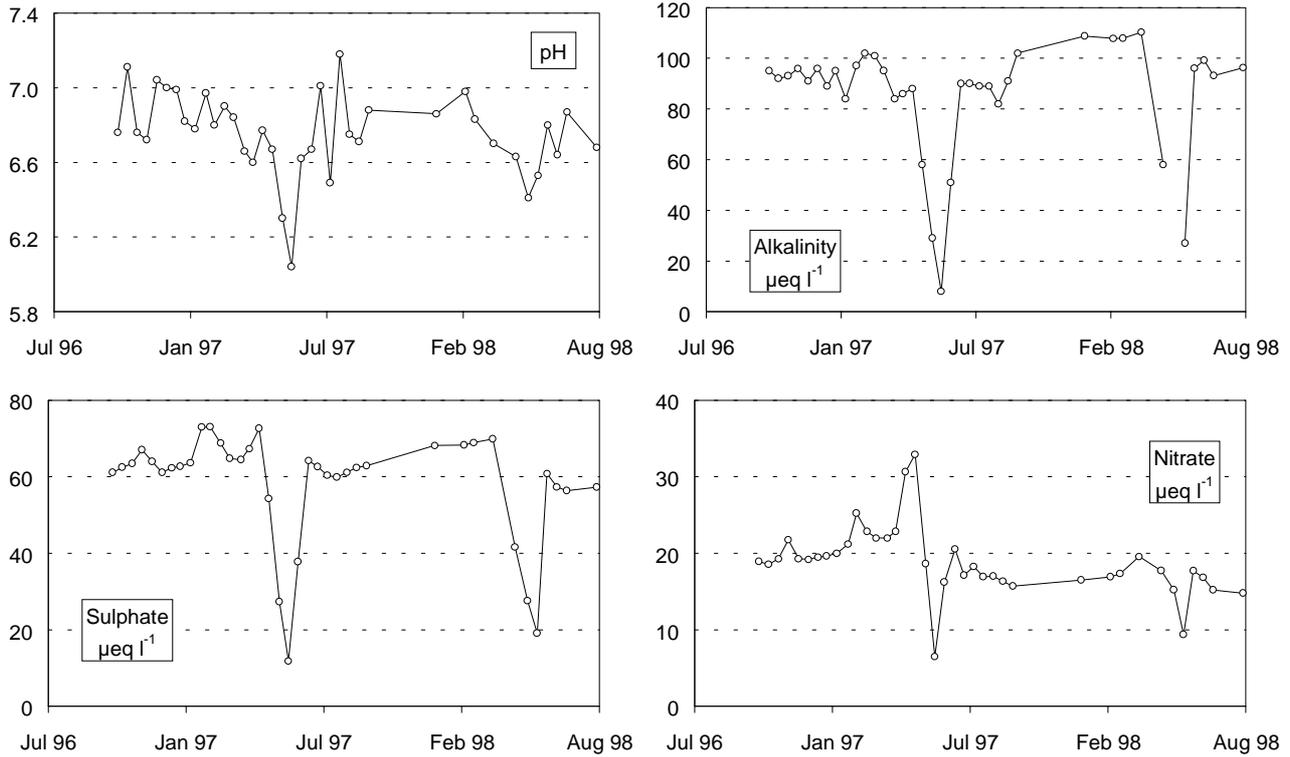**Fig. 10**. Seasonal variations of pH, alkalinity, sulphate and nitrate in lakes Øvre Neådalsvatn and Paione Superiore.
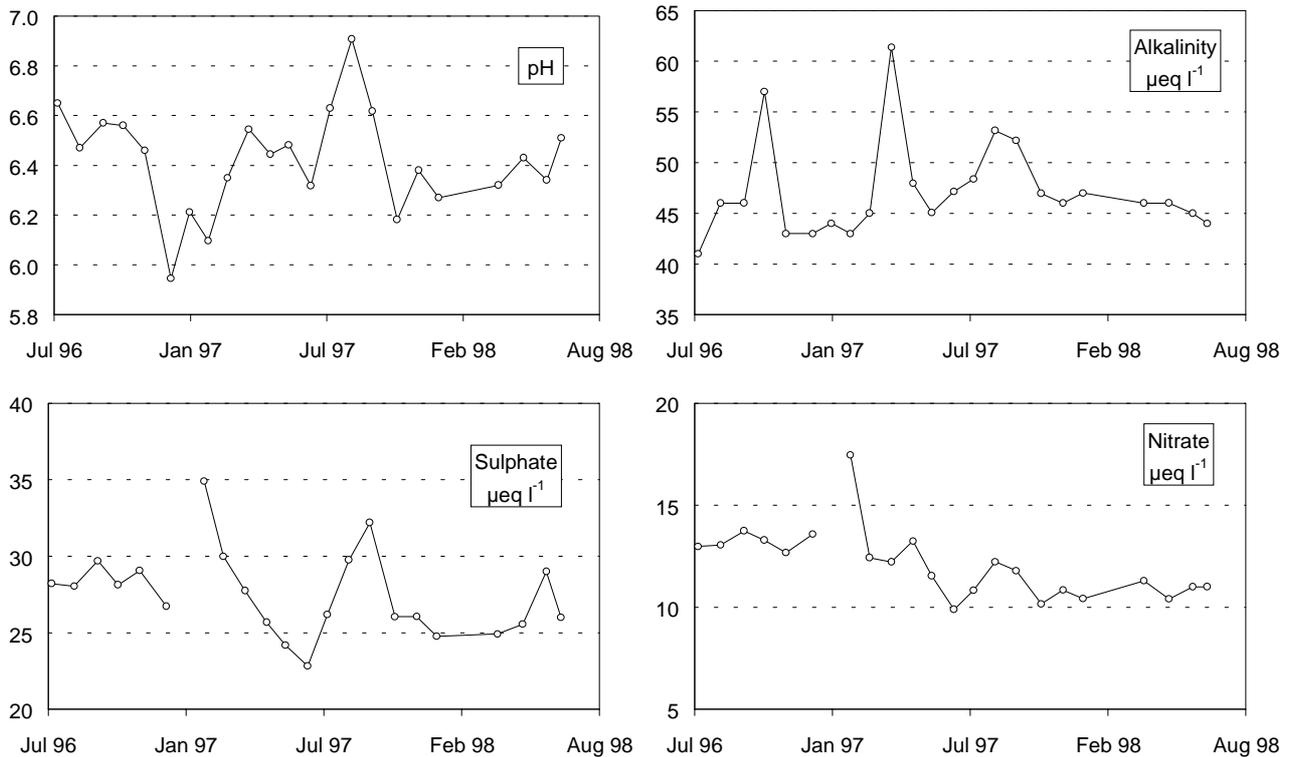
Gossenköllesee

Redó

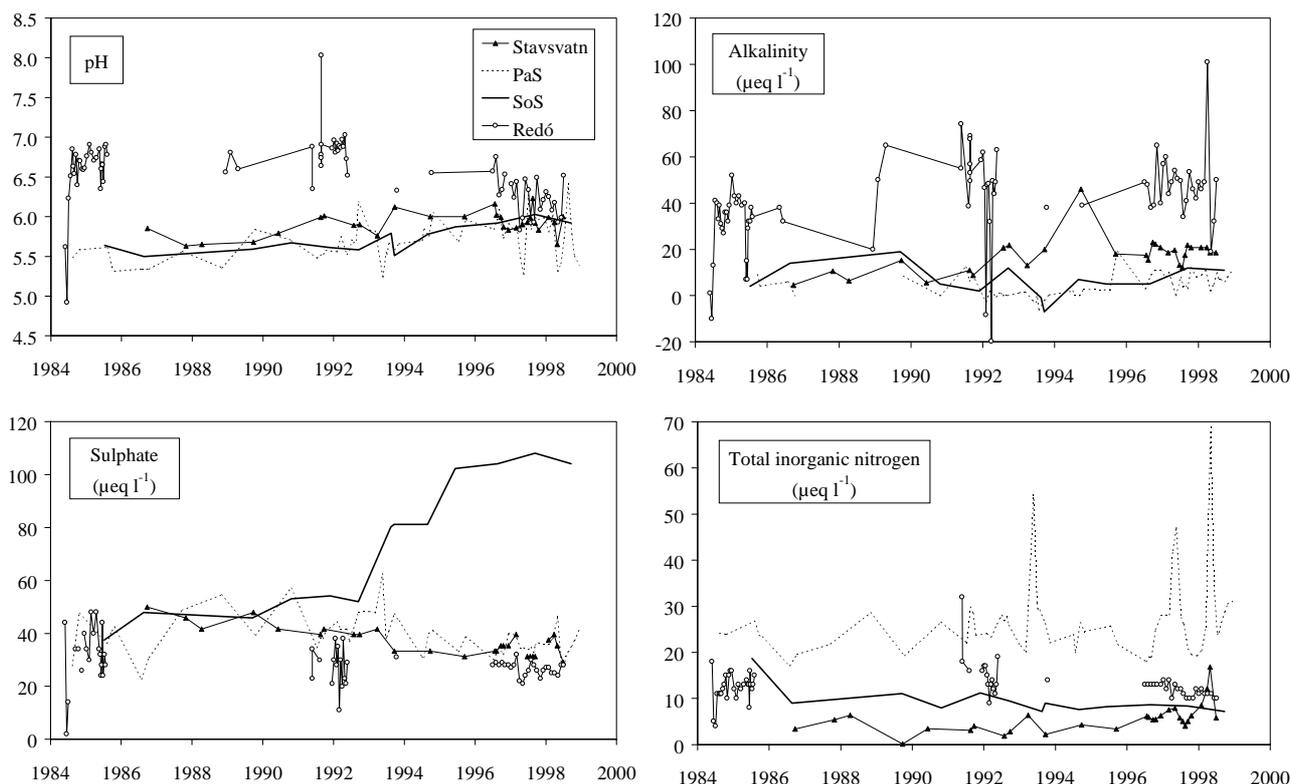**Fig. 11**. Seasonal variations of pH, alkalinity, sulphate and nitrate in lakes Gossenköllesee and Redó.

Fig. 12. Trend of pH, alkalinity, sulphate and total inorganic nitrogen in lakes Stavsvatn, Paione Superiore (PaS), Schwarzsee ob Sölden (SoS) and Redó.

Concentrations of inorganic nitrogen show strong fluctuations in Paione Superiore, it was stable or had slightly decreased in Schwarzsee ob Sölden and Redó, and showed a slight increase during the last few years only in the case of Stavsvatn. Decline of nitrogen was recorded in the high altitude lakes in the Tatra Mountains during the last decade due to significant reduction of N emission in Central Europe (Kopáček *et al.* 1998).

For the Norwegian and Italian lakes, the trends of pH, alkalinity and sulphate are related to a decrease in acidity and the $SO_4^=$ content of atmospheric deposition, whereas nitrogen is constant or in slight increase (Mosello *et al.* 1999; Henriksen *et al.* 1990). In the case of the Austrian lake the increase in sulphate seems to be related to higher temperatures during summer, producing a higher weathering rate (Sommaruga-Wograth *et al.* 1997; Koinig *et al.* 1998). The Spanish lake showed, on the one hand, an apparent increase in the weathering rate (with an increase of calcium strongly related to alkalinity) and, on the other hand, a decrease in atmospheric sulphate deposition.

Other long-term data are available for some of the MOLAR lakes (e.g., Lochnagar, Długi Staw); an overall analysis of these trends and what produced them is the topic of a further EU project.

5. CONCLUSIONS

In Europe, remote mountain areas have considerable importance both as regards the percentage of the surface area they occupy and in terms of their value as a natural and recreative resource. In such a densely populated continent, and one in which, more than in others, natural ecosystems have been altered as a consequence of human impact, these areas are today particularly important. They also have great hydrological importance, as the rivers which feed the lakes, also the lakes of the plains, rise here, providing a reserve of high quality water for a number of civil and industrial uses.

These areas are for the most part far from sources of pollution, though phenomena of atmospheric transport of pollutants mean that they are not inevitably immune from the deposition of these substances. Studying the quality of the water in remote areas can therefore yield important information on levels of background pollution, to the extent that these lakes can be used as early warning systems for the state of health of the environment.

The results of this part of the MOLAR project highlight some of these aspects. The chemistry of atmospheric deposition collected in sites which are represen-

tative of remote areas in the whole of Europe, from the extreme north of Scandinavia to the southern Alps and the Pyrenees, shows that the solutes present may be marine (Na^+, Cl^-, fraction of Mg^{++} and $SO_4^=$), terrigenous (Ca^{++}, K^+, fraction of Mg^{++}, HCO_3^- when present), and deriving from fuel-burning emissions and intensive stock-breeding ($SO_4^=$, NH_4^+, NO_3^-). 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.

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. Gradient on nitrate in the Tatra Mountains lakes is the result of the amount of vegetation in the watershed and the acidification status of each lake (Kopáček *et al.* 1995). 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 comparison of the atmospheric load of acidity (real and potential) and of nitrogen with the respective critical values will be included in the MOLAR project.

The long-term evolution of water chemistry, although considered only for four lakes, clearly shows that the situation is far from the steady state. On one hand, the increase in alkalinity and pH values is a positive indication of the success achieved in reducing the load of acidity from atmospheric deposition, the result of the concerted efforts of most of the European countries. On the other hand, the considerable variations in nitrate and the different levels found in the lakes are evidence that the problems persist, and that it is essential that studies on and monitoring of such sensitive systems should continue. A further issue which has not been entirely clarified is that of the mechanisms responsible for the increase of alkalinity in the lakes. Is the decrease of acid deposition from the atmosphere a sufficient cause, or do climatic variations, as suggested by some results (Sommaruga-Wögrath *et al.* 1997) also play a part?

These questions, and the close relationships existing between water chemistry and biology, emphasise how the presentation of the chemical data in this paper is merely a stage in a more general process of elaboration and evaluation of the data collected in the framework of the MOLAR project. This special volume of the Journal of Limnology devoted to trophic relations shows how complex and in continual evolution is the picture emerging from our data.

Last but not least, the three years of collaboration within the MOLAR project, added to the previous collaboration in the AL:PE 1 and AL:PE 2 projects, has resulted in the establishment of excellent scientific and personal relationships among experts in different disciplines and in different countries, both inside and outside the European Union. We believe that this is at least as important as the scientific results which have been produced, since the formation of relationships of mutual respect between people form a basis for important future scientific collaboration, which will be an essential prerequisite for tackling the environmental problems of the next few years.

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