ICP-WATERS REPORT 63/2001

# National presentations from the 16th meeting og the ICP Waters Programme Task Force in Riga, Latvia

October 18-20, 2000

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#### Abstract

Reports of national monitoring activities and results from Latvia, Switzerland and UK presented at the 16<sup>th</sup> meeting of the ICP Waters Programme Task Force in Riga, Latvia, October 18-20, 2000

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### CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

### INTERNATIONAL COOPERATIVE PROGRAMME ON ASSESSMENT AND MONITORING OF ACIDIFICATION OF RIVERS AND LAKES

National presentations from the 16<sup>th</sup> meeting of the ICP Waters Programme Task Force in Riga, Latvia, October 18-20, 2000

Prepared by Latvian Hydrometeorological Agency, Latvia in cooperation with the ICP Waters Programme Centre, Norwegian Institute for Water Research Oslo, August 2001

### Preface

The International Cooperative Programme on Assessment and Monitoring of Rivers and Lakes (ICP Waters) was established under the Executive Body of the Convention on Long-Range Transboundary Air Pollution at its third session in Helsinki in July 1985. The Executive Body also accepted Norway's offer to provide facilities for the Programme Centre, which has been established at the Norwegian Institute for Water Research, NIVA. Berit Kvæven, Norwegian State Pollution Control Authority, has led the ICP Waters programme. The Norwegian State Pollution Control Authority (SFT) provides financial support to the work of the Programme Centre.

At the annual Programme Task Force, national ongoing activities in many countries are presented. This report presents some of the national contributions from the 16<sup>th</sup> Task Force meeting of the ICP Waters programme, held in Riga, Latvia, October 18-20, 2000.

Oslo, August 2001

Brit Lisa Skjelkvåle Project manager

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### 1. ICP-Waters sites in Latvia

#### I.Lyulko, P.Berg and D.Leveika

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#### **1.1 History**

Hilly moraine relief, moist climate and geological structure of the territory of Latvia favour the formation of arterial drainage. A total area of continental water of 1550 km<sup>2</sup> amount to 24% of the territory. There are 12.400 rivers of a total length of approx. 38.000 km, 4.000 lakes and 3 water reservoirs. Most of the rivers (94%) are shorter than 10 km.

The first data on the chemical composition of surface water in Latvia appeared late in the 18<sup>th</sup> century, in designs of a water supply and a wastewater disposal system of the city of Riga. The studies resulted in the first publications on water chemistry in the Lielupe river, Lake Kishezers and small lakes.

Pollution impacts on river chemistry were first addressed in 1937. In 1924-43, studies of water hydrobiology and chemistry were carried out concurrently. Based on the studies, a map of water hardness in Latvian rivers during the summer low water was produced.

Systematic observations have been carried out by the Latvian Hydrometeorological Agency since 1946. First, large rivers were studied. Since 1954, the observations have covered medium and small rivers. The number of rivers, under observations progressively increased.

In 1970-76, preparatory works were carried out to design a surface water monitoring network (hydrochemical and hydrobiological) as were explored pollution sources, hydrography and economic importance of water objects to select measuring sections. The results of early investigations were considered in designing of the network. The selection of stations to provide the observations was determined by the physico-geographical conditions, location of pollution sources, importance of water objects in cultural and fisheries activities, and water hydrology and dynamics.

It is worth mentioning that the Hydrometeorological Agency is a single institution in Latvia that maintains state surface water quality and hydrometeorological observation networks.

#### **1.2 Description of the water quality network**

According to assessments of environmental status, the following priority problems have been set up in the National Environmental Policy Plan for the protection of surface waters:

- eutrophication of water courses and degradation of aquatic ecosystems;
- transboundary water pollution.

The goals of the water quality observations are:

- to obtain long data series and establish the pollution tendencies;
- to predict spatial pollution transport;
- to trace short and long-term evolution and predict increases (up to extremely high levels) of pollution;
- to provide information to institutions and researchers involved in water use and protection.

The existing network operates on the principle of basins and meets the following requirements:

- sampling sequence from the head of a water course to estuary;
- uniformity in timing of the hydrochemical observations with the hydrological phases;
- running of uniform and applicable water sampling and analysis methods.

The surface water quality network includes (Figure 1):

- rivers (streams, canals) 28 sites 69
- lakes and reservoirs 8 sites - 14

The density of the water quality observation network is 1.1 river site per 1 000 km<sup>2</sup> and 0.2 lake and reservoir sites per 1 000 km<sup>2</sup>.

The sites are included in EUROWATERNET; according to the observation goals the sites was defined as representative, reference and flux (**Table 1**).

	Station	type								
River basin	Represe	ntative		pogenic pact	Back	ground	Frontier	and flow	Hydrobi	ological
	River	Lake*	River	Lake*	River	Lake*	River	Lake*	River	Lake*
Salaca	2		2			2	1		2	
Gauja	7		5		3		1		6	1
Daugava	8	9	5		1		1	1	8	1
Lielupe	10		6				3		9	
Irbe Strait	1					2				
Venta	6		2				2		4	
Baltic Sea, small rivers	6	1	1		4		3		7	1
Baltic Sea coast			4**						3	

Table 1. Surface water stations.

\* lakes and water reservoirs

\*\* Baltic Sea, near Liepaja and Ventspils

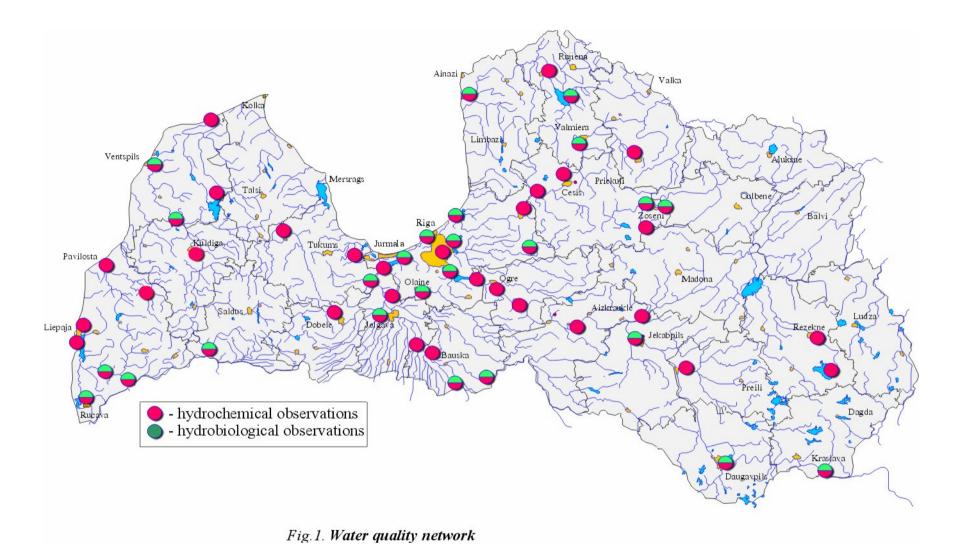


Figure 1. Water quality network in Latvia

#### **1.3 ICP Waters Network**

ICP Waters sites and ICP IM sites are part of the national water quality network and they are reference sites in EUROWATERNET (**Figure 2**). By peculiar river flow regime and the association with the relief and geological structure of the area, climate, vegetation and water flow (main, surface, soil and ground) the territory of Latvia is conventionally divided into 3 regions.

**ZOS-T:** Tulija River is a tributary of the Gauja in its upper reaches (Figure 3). The catchment of the Tulija is part of the Baltic moraine and lake-land periphery of a forested zone (Table 2). The climate of the region is characterised as moderately continental, with some features of maritime formed under the influence of the prevailing west-atlantic circulation. The peculiar landscape of the region is imposed by its location on the Central-Vidzeme Hill the hilly-ridged relief of which has formed due to Quarternary glacial activities. The natural vegetation is typical of the southern zone, a sub-zone of broad-leaved tree forests on sod-podsolic soils. The catchment area of the 15 km long Tulija is 51.3 km<sup>2</sup>, with an outlet of 33.4 km<sup>2</sup> near Zoseni. The catchment extends from south to north, with a length of 8.98 km from the upper reaches to the station at Zoseni and an average width of 3.72 km. Slightly hilly relief is scarred by streamlets and swampy hollows. Perennial river flow is conditioned by abundant springs and the regulating effect of Lake Ilzeni. There are no significant sources that pollute the river and the catchment area. Tulija River has maximum flood-time during spring. About 50% of the annual river runoff comes from snowmelt. During summer flow is very low with periodical increases whenever rainfall is there. Mean duration of spring flood-time is 50 days, but in certain years this can be changeable. Mean duration of ice cover period is 110 days, period with ice phenomena is 135 days.

**ZAK-LJ:** Conventionally, the Liela Jugla River (Zaki) (Figure 4), a tributary of Lake Jugla (Daugava basin), may be considered part of Region I. The central part of the region is the Middle-Latvian Lowland. The area of the catchment is 1.620 km<sup>2</sup> (**Table 3**). The site Zaki is located 19 km off the estuary. The surrounding area is plain, mostly (75%) covered by mixed forests, with prevailing coniferous trees. The grounds composing the river valley are sandy and sandy-loam. The mother bedrocks are represented by Upper Devonic deposits, dolomite and dolomitized limestone, emerging at the surface 1.5-2.0 m above the measuring section. The flat-bottom and clean river is 1.47 to 6.82 m deep. The ground is sandy-gravel, near the banks fine-grained sands. Significant polluting sources are unavailable in the region. Liela Jugla River has typical hydrological regime like most of East-European rivers with the maximum flood in spring. The spring snowmelt mostly begins in the end of March. Mean duration of flood-time is 50 days, but it can vary from 90 to 20 days. More than 40% of annual runoff falls to the spring floods period. During summer runoff is minimum, in winter it little bit higher. Increase of flow can be observed during intensive rainfall period of autumn. Mean duration of ice cover is 80 days, period with ice phenomena is 120 days.

**DUK-B:** The Barta River (farm Dukupji) belongs to Region III (**Figure 5**). The region is characterised by lower summer and higher winter air temperatures. The middle and southern parts of the region are taken up by the Kurzeme and Zhemajkiaj Highlands. The Barta has a catchment area of 1.750 km<sup>2</sup> (**Table 4**). The farm Dukupji is situated 18 km from the inflow estuary to Lake Liepaja. The river 98 km in length originates in the territory of Lithuania. The surrounding area is a low-hilly plain, covered with mixed forests (90%) and agricultural lands (10%). In consequence of marine climate with thaws during winter time in the Barta River frequent winter floods are observed, some of that is higher then spring floods. Approximately 35% of annual runoff fall to the winter period and 30% to the spring. During summer runoff is minimum. Increase of flow in autumn is caused by intensive rainfall. Mean duration of period with ice cover is 55 days, period with ice phenomena is 100 days.

BURT-1: Lake Burtnieki (Figure 6) is a glacial lake formed as a result of glacial ploughing. The surrounding area, an open low-hilly plain, is scarred with gently slopping gorges. Coniferous trees dominate widely spaced groves(Table 5). The ground is sands, sandly-loams and clays. The mother bedrocks are of Devonian origin. The lake extends south-west to north-west. The major parameters are: area - 38.4 km<sup>2</sup>, length - 13.3 km, maximum width - 5.7 m, maximum depth - 3.3 m, average depth - 2.4 m, total storage - $91.1 \cdot 10^6$  m<sup>3</sup> in high water level. The lake is flowing, unstratified and eutrophic and is used in fish breeding. The western bank is more swampy, including the site water sampling is made. The bank is overgrown with sedge and shrubs. The grounds in the swampy part are peats, in the more dry part-sandy-loam. The bottom of the lake basin is flat, muddy at depth and sandy near the shore. In winter, the ice thickness may be 50-60 cm, up to 80 cm in severe frosts. The lake debacles in April, sometimes early in May. The Salaca River flows out of the lake in its north-western part and flows across a natural reserve. The Ruja and the Seda Rivers, located 350 m apart, inflow the lake in the north, the Briede - in the south and the Staizupe and Eikinuzhe - in the south-east. The largest tributary, the Ruja, is 85 km long, with a catchment area of 992 km<sup>2</sup>. The lake is among shallow lakes with significant flowage. Winter retention time is normally every 1.5 month, in flooding - once in 2 weeks, in summer - every 3 months and in autumn - during a month. No polluting source is available in the area.

**ZVIR:** Zvirbuli stream (**Figure 7**) is formed due to merging of 2 ditches flowing nearly along the edge of the swamp Tireli. An uneven topography of the swamp is represented mostly by sloping-concave forms of relief, with a flat space with many small lakes of secondary origin and peats and dunes in the north-east (**Table 6**). Microlandscapes are markedly expressed, from ridged lake land in the edges of the swamp to peat mosses, cotton grass and shrub-covered areas in the centre, with scarce pine-covered spaces. The stream Zvirbuli is a drain that collects discharge from two ditches located south-west of the swamp. The canalised bottom is 0.8-1.5 m wide and 0.1-0.8 m deep. The steep banks, precipitous at places, are peat grounds, turfed and of changing shape. It dries up in the low water periods.

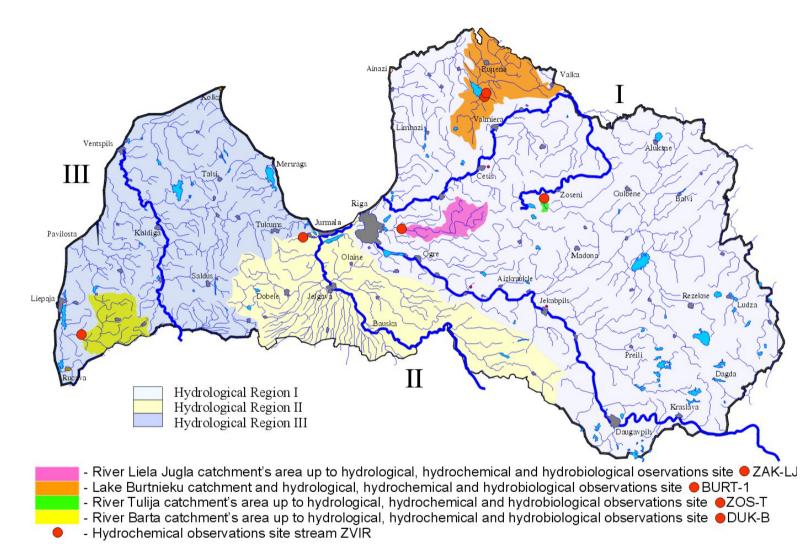
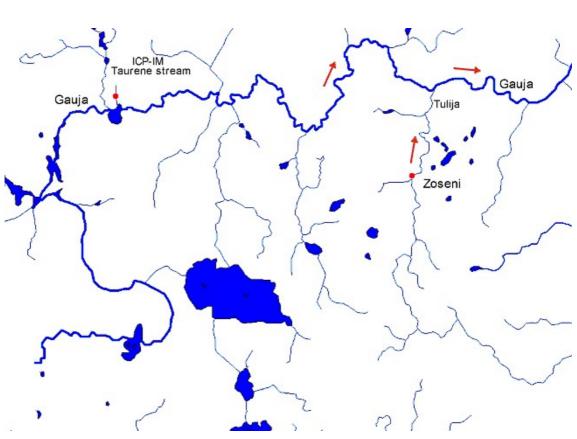


Fig.2. ICP - Water network in Latvia

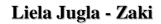
Figure 2. ICP Waters network in Latvia



Tulija - Zoseni

Figure 3. Tulija – Zoseni ZOS-T

Major basin or catchment		Gauja		
Site (ZOS	-T)	Tulija, 0.3 km downstr. of Zoseni		
Observa	Hydrochemistry	1946		
tion start	Hydrobiology	1996		
Flow information		measured		
Catchment area, km <sup>2</sup>		33.4		
Average precipitation, mm.yr <sup>-1</sup>		727		
Main type of bedrock		clay, dolomite, gypsum		
Forest cover (total), %		30		
Wetlands/Bogs, %		0		
Elevation at site, m		178.50 BS		
Average runoff, mm.yr <sup>-1</sup>		321		
Average depth, m		0.28-1.97		



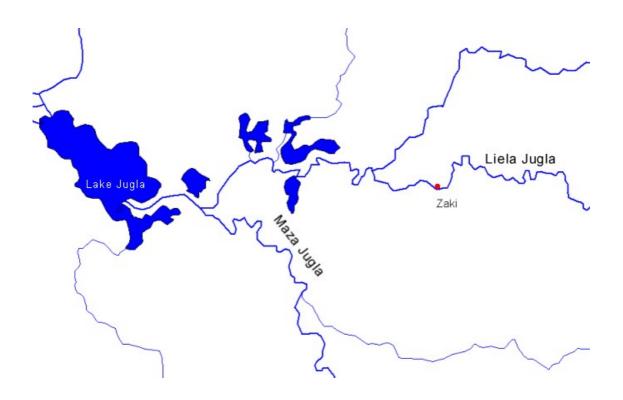
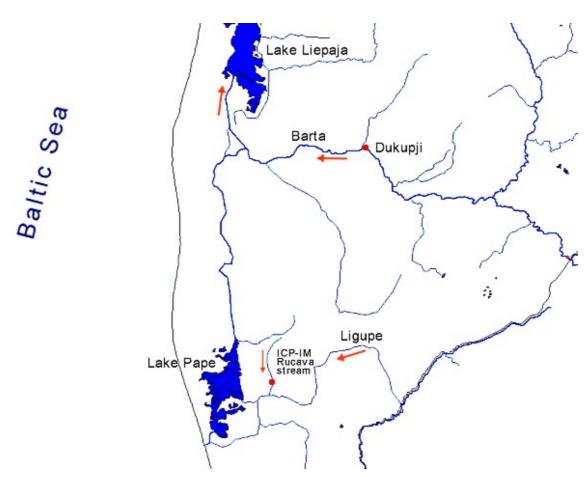


Figure 4. Liela Jugla – Zaki ZAK-LJ

Major basin or	catchment	Daugava		
Site (ZAK-LJ)		Liela Jugla, 0.2 km upstr. of Zaki		
Observation	Hydrochemistry	1954		
start	Hydrobiology	1986, 1995		
Flow informat	ion	measured		
Catchment are	a, km <sup>2</sup>	663		
Average precip	pitation, mm.yr <sup>-1</sup>	724		
Main type of b	edrock	clay, dolomite, gypsum		
Forest cover (t	otal), %	40		
Wetlands/Bogs	s, %	10		
Elevation at sit	te, m	12.50 BS		
Average runof	f, mm.yr <sup>-1</sup>	301		
Average depth	, m	1.11-6.61		

 Table 3. Catchment data of Liela Jugla - Zaki



Barta - Dukupji

Figure 5. Barta – Dukupji DUK-B

Table 4. Catchment data of Barta - Dukupji

Major basin or	catchment	Baltic Sea, small river basin		
Site (DUK-B)		Barta, 0.2 km upstr.of Dukupji		
Observation	Hydrochemistry	1954		
start	Hydrobiology	1989, 1995		
Flow information	ion	measured		
Catchment are	a, km <sup>2</sup>	1700		
Average precip	pitation, mm.yr <sup>-1</sup>	862		
Main type of b	edrock	limestone, dolomite		
Forest cover (t	otal), %	15		
Wetlands/Bogs	s, %	<5		
Elevation at sit	te, m	50 BS		
Average runof	f, mm.yr <sup>-1</sup>	374		
Average depth	, m	1.28-6.32		



#### Lake Burtnieku

Figure 6. Lake Burtnieki BURT-1

Major basin or	catchment	Salaca
Site (BURT-1)		-Burtnieki, hydropost -1.0 km W of hydroposrt
Observation	Hydrochemistry	1956-1959, 1973
start	Hydrobiology	1999
Flow information	ion	water level
Catchment area	a, km <sup>2</sup>	2220
Average precip	oitation, mm.yr <sup>-1</sup>	655
Lake area, km <sup>2</sup>	2	40.2
Main type of b	edrock	Sandrock, clay
Forest cover (t	otal), %	51
Elevation at sit	te, m	39.9
Average depth	, m	2.4

### Zvirbuli Stream

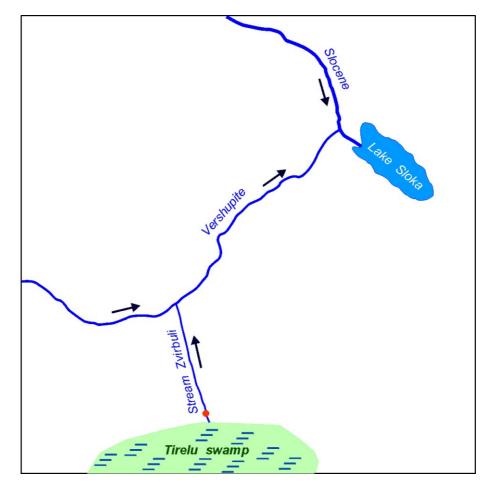


Figure 7. Zvirbuli Stream ZVIR

Table 6. Catchment data of Zvirbuli Stream
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Major basir	n or catchment	Kemeri peat			
Site (ZVIR)	)	Hydroprofile Zvirbuli			
Observati	Hydrochemistry	1967			
on start	Hydrobiology	-			
Flow inform	nation	measured (to 1997)			
Catchment	area, km <sup>2</sup>	1.55			
Average pro	ecipitation, mm.yr <sup>-1</sup>	681			
Main type of	of bedrock	peat			
Forest cove	r (total), %				
Wetlands/B	ogs, %	100			
Elevation a		8.37 BS			
Average run	noff, mm.yr <sup>-1</sup>	177			
Average de	pth, m	0.1 - 0.8			

#### **1.4 Some results reported from long-term observation**

The mean oxygen concentrations at the ICP Waters sites (according to more regular measurements in the Barta) have been at the same level since 1946. The decreasing tendency has been observed in the minimum concentrations in the Stream Zvirbuli during the last decade (**Figure 8**).

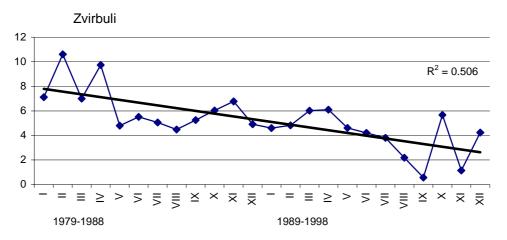


Figure 8. Oxygen minimum concentration in Stream Zvirbuli.

The long-term mean concentrations of **nitrates** at the ICP Waters sites widely variate between 654 and 1235  $\mu$ g/l, with the minimum in the Tulija River and the maximum in the L.Jugla (70  $\mu$ g/l in the Stream Zvirbuli) (**Figure 9**).

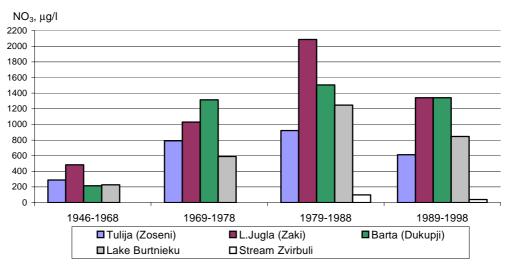


Figure 9. Long-term mean concentrations of nitrates, ICP Waters sites.

The long-term mean **phosphate** concentrations at the ICP Waters sites range between 16.4  $\mu$ g/l (Tulija) and 35.6  $\mu$ g/l (Barta), 16  $\mu$ g/l in the Stream Zvirbuli and 33.3  $\mu$ g/l in Lake Burtnieku. The variations are associated with hydrography of the sites. As in nitrates, sites located in low-lying areas close to the Gulf of Riga and the Baltic Proper are richer in phosphates.

The phosphate concentrations had decreased by the last decades of the measurements, especially in the lake (Figure 10).

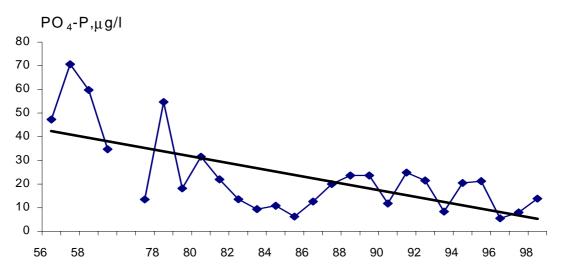


Figure 10. Year-to-year dynamics of phosphates, Lake Burtnieku.

In summer low water content, episodically phosphate values may reach spring and winter levels (**Figure 11**).

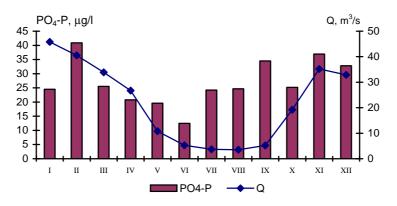


Figure 11. Intraannual mean phosphate concentration dynamics in Barta, 1989-1998.

In 1994-1998, the mean BOD<sub>7</sub> concentrations measured 1.25-1.50 mg/l at all the ICP Waters sites. The concentrations showed an insignificant difference between the seasons, with lower concentrations of 1 mg/l in winter and maximum concentrations of above 2 mg/l in the summer low water and spring flooding (Fig.12). Generally, organic matter concentrations were higher (up to 35-40 mg/l) in the spring flooding and summer-autumn flood periods, e.i. in the periods of organic matter run-off from the catchments; concentration minima of 15-20 mg/l were on record in winter (**Figure 12**).

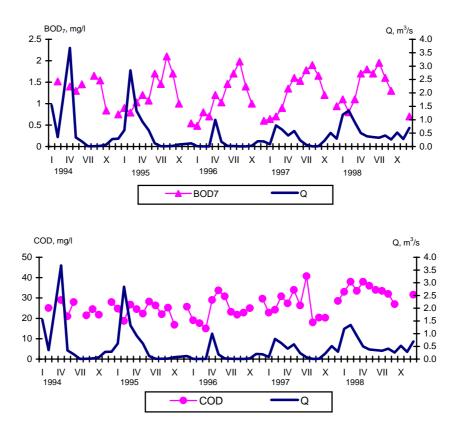


Figure 12. Seasonal dynamics of organic matter, Tulija.

The long-term measurements evidence to an insignificant decrease in the mean sulphate concentration in the stream Zvirbuli (Figure 13).

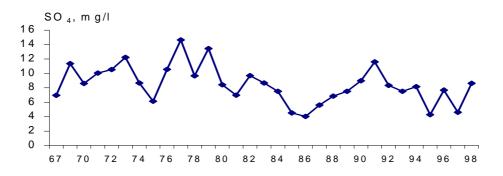


Figure 13. Year-to-year dynamics of sulphate, stream Zvirbuli.

The long-term observations showed somewhat alkalinity increase in the L.Jugla alone (Figure 14).

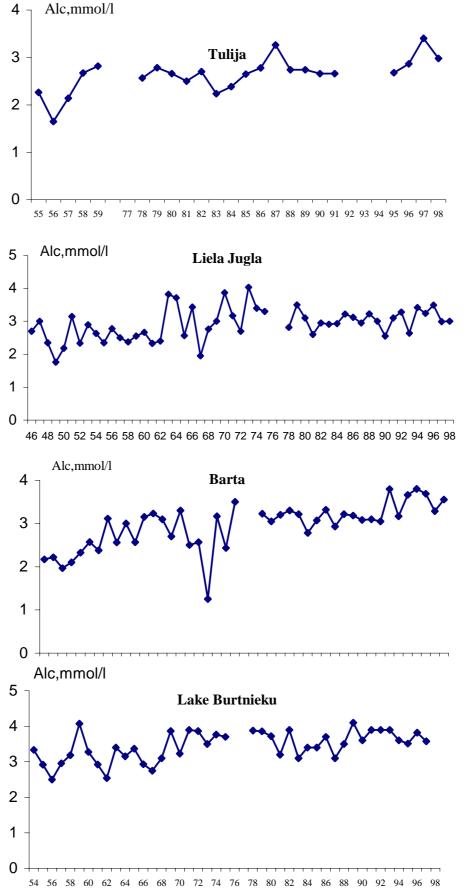


Figure 14. Year-to-year alkalinity dynamics.

As the rivers Jugla, Tulija and Barta are classed as salmonid waters, more tough water quality standards have been applied to those rivers.

The mean zoobenthos saprobity index (according to Pantle and Buck) varied between 1.55 and 2.5 in the Liela Jugla, 1.91 and 2.3 in the Barta and 2.16 and 2.51 in the Tulija (did not meet good ecological quality standard) (**Figure 15**). In 1996-1998, the mean phytoplankton saprobity index ranged between 2.22 and 2.3 in the Liela Jugla, 2.13 and 2.38 in the Barta and 2.29 and 2.68 in the Tulija (**Figure 16**).

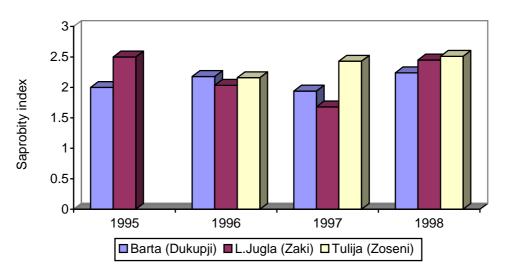


Figure 15. Zoobentos saprobity index, 1995-1998.

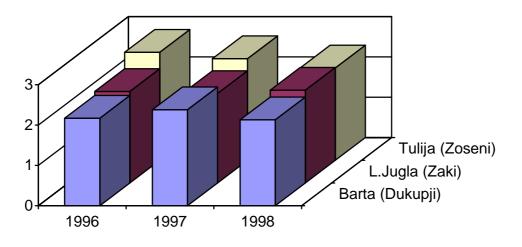


Figure 16. Phytoplankton saprobity index, 1996-1998.

## 2. Field demonstration of ICP sites in Latvia

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#### 2.1 ICP Water Tulija-Zoseni site

The Tulija River belongs to the Gauja River basin. The total length of the Tulija River is 15 km and the total area is 53 km<sup>2</sup>. Main characteristics of catchment in place of hydrometric outlet Zoseni are shown in **Table 7**. The observation programmes carrying out at Zoseni site are represented in **Table 8**.

Area of catchment	$33.4 \text{ km}^2$
Forest	33%
Absolute altitude above sea level	178 m in Baltic System
Yearly mean temperature	4.5°C
Annual total precipitation	727 mm
Period of active plant vegetation	130 days
Mean annual discharge	0.35 m3/s
Maximum discharge	17.7 m3/s
First day with ice phenomena	19-Nov
Duration of ice cover	110 days
Beginning of spring flood	21-Mar
Duration of spring flood	50 days

 Table 7. Main characteristics of Tulija-Zoseni catchment.

Table 8. Observation	rogrammes provided at Tulija-Zoseni ICP Water site	e.

Name of programme	Started
CLIMATE	
Meteorological parameters	1946
GAW/EMEP	
Gases and aerosols chemistry	1996
Precipitation chemistry	1991
HYDROLOGY	
• Water level, water temperature	1940
Water discharge	1940
WATER CHEMISTRY	1946
• PH, color number, O <sub>2</sub> , Na, K, Ca, Mg	
• NH <sub>4</sub> N, NO <sub>2</sub> N, NO <sub>3</sub> N, Ntot, alkalinity,	
hardness	
• CL, conductivity, SO <sub>4</sub> S, SiO <sub>2</sub> , PO <sub>4</sub> P, Ptot,	
Fe	
• Pb, Cu, Zn, Cd	
Hydrobiology	1992
Phytoplankton, zoobethos	

Meteorological observations are provided at a special meteorological plot.

In the place of hydrometrical outlet Zoseni, water level, water temperature and discharge are measured and chemical composition of water is determined. Water level is measured with the "Valday" mechanical water level recorder with daily regime and with staff gage. A current meter is used to measure the discharge. On the basis of the readings of the recorder daily runoff is calculated. For the estimation of water quality water samples are taken once a month. Chemical analyses of major cations and anions, pH, colour, suspended substances, heavy metals are provided. The changes of annual precipitation and annual mean discharge during the period 1960-1999 are represented in **Figure 17**.

Average concentrations of main chemical components in water of Tulija River are represented in **Table 9**.

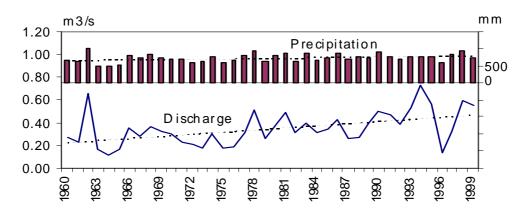


Figure 17. Annual total precipitation and annual mean discharge. Tulija - Zoseni, 1960-1999.

**Table 9.** Average concentrations of main chemical components in water (mg/l) Tulija - Zoseni 1989-1998.

pН	$O_2$	Ca	Mg	Na	K	Cl	SO <sub>4</sub> S	NH <sub>4</sub> N	NO <sub>3</sub> N	Ptot	Si
8.01	10.4	54.6	13.1	3.15	1.9	6.4	9.7	0.15	0.61	0.05	2.07

#### 2.2 ICP IM Taurene site

The Taurene brook belongs to the Gauja River's basin. The Integrated Monitoring site is located in undisturbed forested area. Observations under Integrated Monitoring Programme started in 1994. Total area of catchment is  $0.27 \text{ km}^2$ . Mean annual discharge of Taurene brook 0.9 l/s. The observation programmes in charge of LHMA carrying out at Taurene site are represented in **Table 10**. Average concentrations of main chemical components in water of Taurene brook are represented in **Table 11**.

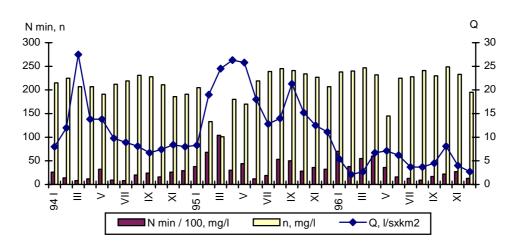
The dynamics of runoff, mineralization of water and content of mineral nitrogen in water of Taurene brook are shown in **Figure 18**.

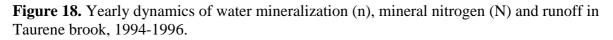
HYDROLOGY	<ul><li>Water level, water temperature</li><li>Water discharge</li></ul>
RUNOFF CHEMISTRY	<ul> <li>PH, color number, O<sub>2</sub>, Na, K, Ca, Mg</li> <li>NH<sub>4</sub>N, NO<sub>2</sub>N, NO<sub>3</sub>N, Ntot, alkalinity, hardness, conductivity, Cl, SO<sub>4</sub>S, SiO<sub>2</sub>, PO4P, Ptot, Fe</li> <li>Pb, Cu, Zn, Cd</li> </ul>
HYDROBIOLOGY	• Specimen density, biomass, Shannon-Wiener index
GROUNWATER CHEMISTRY	<ul> <li>Groundwater level</li> <li>pH, color number, conductivity, SO<sub>4</sub>S</li> <li>NH<sub>4</sub>N, NO<sub>2</sub>N, NO<sub>3</sub>N, Ca, Na, K, Mg, Cl, alkalinity, hardness, Ptot, Fe, SiO<sub>2</sub>, Cd, Cu, Pb, Zn</li> </ul>
SOIL WATER CHEMISTRY	<ul> <li>Soil water flow</li> <li>pH, color number, conductivity, SO<sub>4</sub>S</li> <li>NH<sub>4</sub>N, NO<sub>2</sub>N, NO<sub>3</sub>N, Ca, Na, K, Mg, Cl, alkalinity, hardness, Ptot, Fe, SiO<sub>2</sub>, Cd, Cu, Pb, Zn</li> </ul>
PRECIPITATION CHEMISTRY, THROUGFALL AND STEMFLOW CHEMISTRY	<ul> <li>Precipitation amount, pH, conductivity, SO<sub>4</sub>S, NO<sub>3</sub>N, NH<sub>4</sub>N, PO<sub>4</sub>P,</li> <li>Cl, Na, K, Ca, Mg, Cd, Cu, Pb</li> </ul>

 Table 10. Observation programmes provided at Taurene ICP IM site.

**Table 11.** Average concentrations of main chemical components in water (mg/l)Taurene 1994-1999.

pН	02	Ca	Mg	Na	Κ	Cl	SO <sub>4</sub> S	NH <sub>4</sub> N	NO <sub>3</sub> N	Ptot	Si	Fe
7.36	6.83	38.8	9.30	2.20	0.50	3.00	7.07	0.20	0.13	0.034	3.00	0.19





### 3. Surface Water acidification in Southern Switzerland: current and past monitoring programme

#### Alberto Barbieri & Stefano Pozzi

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#### **3.1 Introduction**

Since 1980, a survey programme to assess damage of the atmospheric deposition in alpine lakes located on the southern slopes of the Swiss Alps (Canton Ticino) has been carried out by our Laboratory. Canton Ticino, one of the 23 Cantons of the Swiss Confederation, borders with northern Italy (**Figure 19**) where high amounts of pollutants are emitted. The survey started very soon after a report by one fishermen's club concerning fish mortality observed in one alpine lake during summer fry introduction. Since than, between 20 and 55 alpine lakes have been surveyed and analysed every 3-5 years.

Generally the precipitation on the southern slopes of the Alps are due to wet air masses coming from the south, which pick up the pollutants on their way across northern Italy (Barbieri and Pozzi, 2001). Furthermore, the majority of the alpine lakes are characterised by crystalline bedrock (**Figure 20**) and are very sensitive to pollutant depositions (Boggero *et al.*, 1998, Barbieri *et al.*, 2001).

Since January 2000 a new programme funded by the Federal Office for Environment, Forest and Landscape (FOEFL) has been started. Three mountain streams (Vedeggio, Maggia and Verzasca) and 20 high alpine lakes, located in crystalline areas are now regularly investigated. Into these surface waters nutrients, main ions, heavy metals and aluminium are monthly measured. Biological investigations concerning macrobenthos fauna and fish are also included. Finally, POPs, heavy metals and aluminium in the fish are also measured.

#### **3.2 Analytical methods**

During the current survey the chemical parameters measured and their limits of quantification (LOQ) are reported in **Table 12** and **Table 13**.

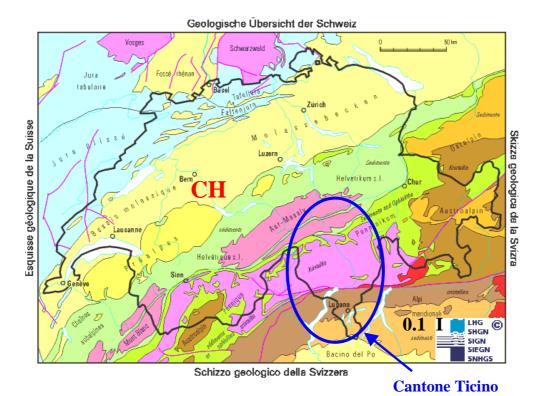


Figure 19. Geological draft of Switzerland.

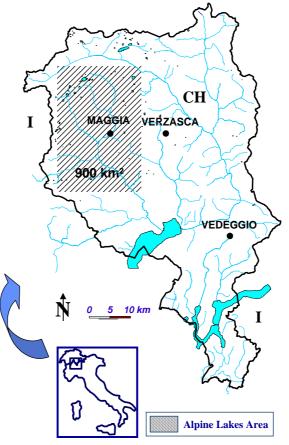


Figure 20. Studied area and sampling sites location.

#### **Table 12.** Analytical parameters measured in surface water.

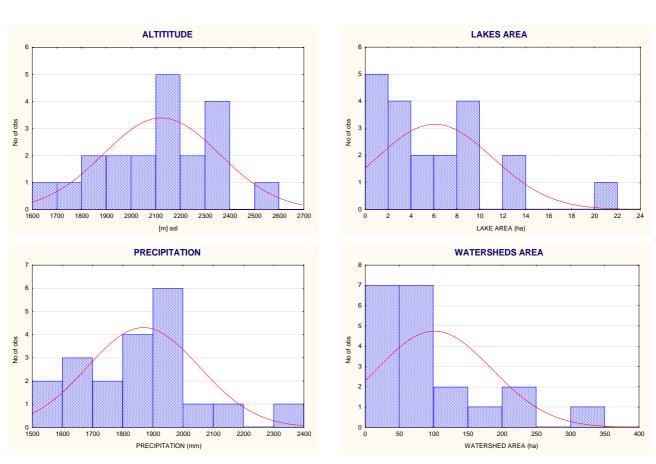
Physical-chemical p	arameters	Nutrients and majo	or ions	Heavy N	Vetals
Temperature pH	°C	Calculated Acidity Measured Acidity	meq l <sup>-1</sup> meq l <sup>-1</sup>	Al Al tot	µg l <sup>-1</sup> µg l <sup>-1</sup>
Conductivity 20°C Conductivity 25°C dissolved O <sub>2</sub> O <sub>2</sub> saturation	μS cm <sup>-1</sup> μS cm <sup>-1</sup> mg l <sup>-1</sup> %	Alkalinity DOC TOC POC	meq l <sup>-1</sup> mg l <sup>-1</sup> mg l <sup>-1</sup> mg l <sup>-1</sup>	Fe Fe tot Mn Mn tot	µg   <sup>-1</sup> µg   <sup>-1</sup> µg   <sup>-1</sup> µg   <sup>-1</sup>
<b>Bio-chemical param</b> BOD <sub>5</sub>	eters mg l <sup>-1</sup>	Reactive Phosphorus Total Phosphorus NO <sub>2</sub> -N	µg l <sup>-1</sup> µg l <sup>-1</sup> µg l <sup>-1</sup>	Pb Pb tot Cd	μg Ι <sup>-1</sup> μg Ι <sup>-1</sup> μg Ι <sup>-1</sup>
		NO₃-N NH₄-N Total Nitrogen	mg l <sup>-1</sup> mg l <sup>-1</sup> mg l <sup>-1</sup>	Cd tot Cu Cu tot	μg l <sup>-1</sup> μg l <sup>-1</sup> μg l <sup>-1</sup>
		Reactive Silica Ca Mg	mg l <sup>-1</sup> mg l <sup>-1</sup> mg l <sup>-1</sup>	Ni Ni tot Cr	µg l <sup>-1</sup> µg l <sup>-1</sup> µg l <sup>-1</sup>
		Na K SO₄ Cl	mg l <sup>-1</sup> mg l <sup>-1</sup> mg l <sup>-1</sup> mg l <sup>-1</sup>	Cr tot Zn Zn tot	µg l <sup>-1</sup> µg l <sup>-1</sup> µg l <sup>-1</sup>

Parameters	Methods	Unit	Min	Max	Accuracy estimation
pН	Potentiometric method				0.02
Conductivity	Kolrausch bridge (20°C)	µS cm <sup>-1</sup>	0.5	150	0.5
					L. O. Q.
Alkalinity (Bicarbonate)	Potentiometric titration, two end points	µeq l <sup>-1</sup>	0	200	1
	4.5 and 4.2 (Gran & Rodier method)				
Sulphate	lonic chromatography	µeq l <sup>-1</sup>	5	83	1
Nitrite	Automated method (reddish purple azo dye)	µg N I <sup>-1</sup>	2	20	0.55
Nitrate	Ionic chromatography	µeq l <sup>-1</sup>	4	107	1
Chloride	Ionic chromatography	µeq l <sup>-1</sup>	1.5	22.5	0.5
o-Phosphate	Automated method (molybdate blue, ascorbic acid reduction)	µg P I <sup>-1</sup>	6	60	4.3
Calcium	Ionic chromatography	µeq l <sup>-1</sup>	5	200	1.5
Magnesium	Ionic chromatography	µeq l <sup>-1</sup>	1.5	66	0.5
Ammonium	Automated method (Indophenol blue)	µeq l <sup>-1</sup>	1	10	1.5
Sodium	Ionic chromatography	µeq l <sup>-1</sup>	2	87	0.5
Potassium	Ionic chromatography	µeq l <sup>-1</sup>	2	51	0.5
Total Nitrogen	Persulphate digestion (hydrolysis with $K_2S_2O_8$ + $H_3BO_3$ + NaOH, PSB	mg N ľ <sup>1</sup>	0.03	1.50	0.01
	Spectrophotometry (UV 210 nm)				
Total/Dissolved Organic Carbon	UV/peroxodisulphate digestion	mg l <sup>-1</sup>	0.2	3	0.2
Particulate Organic Carbon	Catalytic combustion	mg	0.1	0.5	0.02
Total Phosphorus	Persulphate digestion (PSH), automated method	µg P l <sup>-1</sup>	6	60	4.3
	(molybdate blue, ascorbic acid reduction)				
Aluminium	Automated method (Eriochrome Cyanine R method)	µg l⁻¹	20	200	7
Reactive Silica	Automated method (molybdenum blue, ascorbic acid reduction)	mg Si ľ <sup>1</sup>	0.3	4.0	0.035
Oxygen	Winkler method	mg l <sup>-1</sup>	0.5	15.0	0.5
Chlorophyll a	Ethanol 90% extraction, spectrophotometry (665 nm), cell path 4cm	mE	0	1500	100
Lead	Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS)	µg l⁻¹	2.5	10	3.0
Cadmium	GFAAS	µg l⁻¹	0.5	2	0.2
Copper	GFAAS	µg l⁻¹	10	100	1.5
Nickel	GFAAS	µg l⁻¹	10	100	3.0
Chromium	GFAAS	µg l⁻¹	2.5	10	1.1
Zinc	GFAAS	µg ľ¹	2.5	10	0.5

#### Table 13. Analytical methods, working ranges and limits of quantification (L.O.Q.).

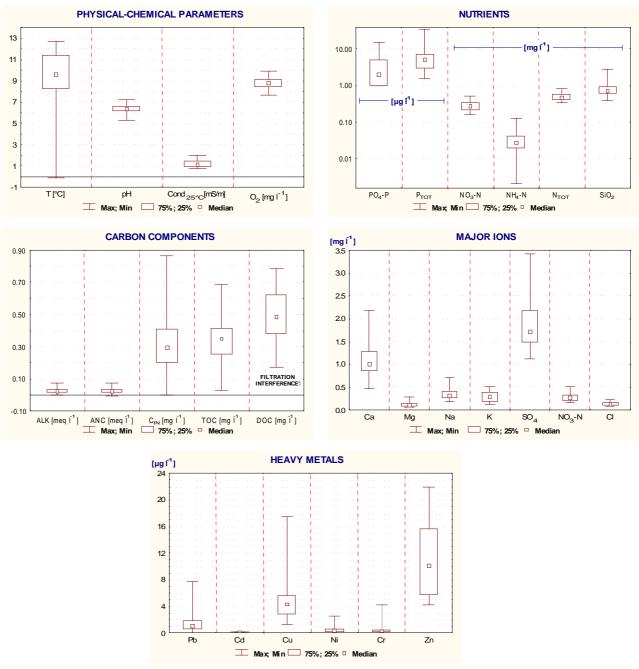
#### **3.3 Alpine lakes**

The alpine lakes are located between 1600 and 2600 m asl, and are characterised by a surface area ranging from 0.7 to 20 ha (**Figure 21**). The maximum depth reaches 70 m, and the watershed area varies between 24 and 320 ha. During the first nine months of 2000 the pH values, observed in the surface water of the alpine lakes, ranged between 5.2 and 7.1, and the conductivity was very low, between 0.9 and 2 mS m<sup>-1</sup> (**Figure 22**). The nutrients concentrations were very low and the reactive phosphorous present median values less than 8  $\mu$ g P l<sup>-1</sup>. Nitrate and total nitrogen showed median values very similar respectively of around 0.4 and 0.7 mg N l<sup>-1</sup>. The reactive silica reached values of 0.9 mg Si l<sup>-1</sup>. The components of the carbon indicated alkalinity neutralising capacity between 0.8 and 80  $\mu$ eq l<sup>-1</sup> while the inorganic carbon and the TOC showed very similar values ranging between 0 and 0.9 meq l<sup>-1</sup> with the same median values of about 0.3 meq l<sup>-1</sup>. At this low level the DOC was generally affected by filtration interference and their values weren't reliable. The major ions were bicarbonate (alkalinity), sulphate and calcium followed by nitrate, sodium and potassium. The



measurable heavy metals were zinc, copper and lead and their values were very low (10, 5,1  $\mu$ g l<sup>-1</sup>, respectively).

Figure 21. Geographical and morphological features of alpine lakes.



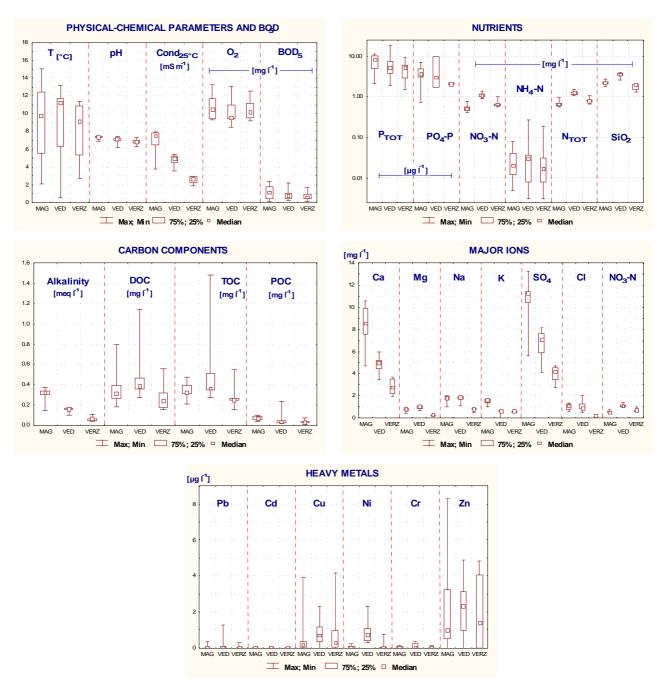
**Figure 22.** Alpine lakes: physical-chemical parameters, nutrients, carbon components, major ions and heavy metals, for the first 9 months of 2000.

#### **3.4 Streams**

The investigated streams are located between 600 and 900 m asl and generally lie in the higher part of the watershed (**Table 14**).

The pH ranged from 6 to 7.5 and the conductivity between 2.5 and 7.5 mS m<sup>-1</sup> (**Figure 23**). The dissolved oxygen normally reached saturation and the biochemical oxygen demand was less than 1 mg  $O_2 l^{-1}$ . The alkalinity varied between 40 and 350 µeq l<sup>-1</sup>, DOC and TOC ranged

from 0.2 to 1.4 mg  $I^{-1}$  and the POC was less than 0.1 mg  $I^{-1}$ . The phosphorus concentrations were between 1 and 10 µg  $I^{-1}$  while nitrate and total nitrogen concentrations were very similar and varied at around at 1 mg  $I^{-1}$ . In the streams the major ions were respectively alkalinity, sulphate and calcium too. As in the alpine lakes, the heavy metals above the LOQ were zinc and copper.



**Figure 23.** Streams: physical-chemical parameters, nutrients, carbon components, major ions and heavy metals, for the first 9 months of 2000.

			Х	Y		Distanc	e from
Valley	Stream	Sampling	coordinate	coordinate	Altitude	source	mouth
		Site	km	km	m asl	km	km
Maggia	Maggia	Brontallo	692.125	134.375	590	24	26
Verzasca	Verzasca	Sonogno	704.200	134.825	910	8	22
Vedeggio	Vedeggio	Isone	719.900	109.800	720	6	14

Table 14.	Geographical	and morphological	features of streams.
I abic 14	Geographical	and morphological	reaction of streams.

		Watershed area		Watershe	d altitude	tributary of the
Stream	Sampling	up s. site	up mouth	maximum	minimum	
	Site	km <sup>2</sup>	km <sup>2</sup>	m asl	m asl	
Maggia	Brontallo	193.6	926.1	3128	194	Lake Maggiore
Verzasca	Sonogno	23	236.8	2864	194	Lake Maggiore
Vedeggio	Isone	19.7	96.1	2228	271	Lake Lugano

#### 3.5 Fish

Finally, some micro-elements and micro-pollutants in the fish of alpine lakes and streams were also analysed and their main biometrics characteristics are presented in **Table 15**.

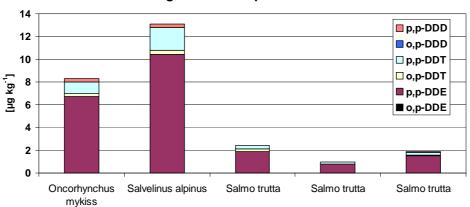
Table 15. Fish species and biometric data.

	Lakes		Streams		
sampling date	19-23/6/00		08/05/00	13/04/00	13/04/00
	Laghetto Inferiore		Vedeggio	Maggia	Verzasca
Italian	Trota Iridea	Salmerino	Trota Fario	Trota Fario	Trota Fario
Latin	Oncorhynchus mykiss	Salvelinus alpinus	Salmo trutta	Salmo trutta	Salmo trutta
age (years)	2+; 3+	2+ (dwarfism??)	2+	2+	2+
No. of fish	4	10	10	13	13
Total length [cm]	18-21	15-18	19-23	21-24	19-22,5
Mean weight [g]	81.7	37.4	86.6	110.8	82.4
Total weight [g]	326.8	374.1	866	1440.4	1071.2
fat %age in the muscle	2.3	1.9	2.0	1.3	1.4
Condition (state) index	1.03	0.83	0.96	0.98	0.91

In Laghetto Inferiore only two species, *Oncorhyncus mykiss* and *Salvelinus alpinus*, both more than 2 years old, were caught. Both fish had a length of around 18 cm and 2% of fat in the muscles. *Oncorhyncus mykiss* and *Salvelinus alpinus* showed a low mean weight of 82 g and 37 g respectively because they had been probably affected by dwarfism.

In the streams only *Salmo trutta* was caught, with a length of 20 to 30 cm and a weight of 82 to 110 g.

In alpine lake DDT's and PCB's content in fish ranged between 8 and 12  $\mu$ g l<sup>-1</sup> and between 10 and 16  $\mu$ g l<sup>-1</sup> respectively while in the streams varied from 1 to 2.5  $\mu$ g l<sup>-1</sup> and from 5 to 8  $\mu$ g l<sup>-1</sup> respectively (**Figure 24**).



#### Organochlorine pesticides

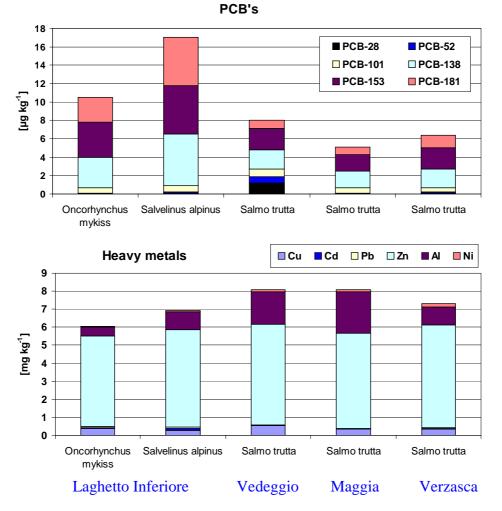


Figure 24. Organochlorine pesticides, PCB's, heavy metals and aluminium in fish muscles.

DDT's and PCB's in fish of Laghetto Inferiore (**Figure 24**) showed values higher than those measured in stream fish. This may be explained by "cool condensation phenomenon" concerning volatile organic pollutants, mainly emitted during the early nineties in Lake Maggiore watershed by a chemical factory, only recently closed by the Italian Government. Zinc and aluminium, followed a lower level by copper principally represent metals in fish. Heavy metal concentrations were quite similar and may have originated mainly from geochemical weathering.

Macrobenthos sampled in the streams and alpine lakes are still under analyses.

An annual analytical report will be prepared for the FOEFL and will be distributed to all the members of ICPW's task force. A scientific report will also be prepared every three years with the aim of discussing and presenting inter-annual variations of the investigated parameters.

#### **3.6 References**

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### 4. Recent observations on trends in acidified waters in the UK

#### Don Monteith,

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#### 4.1 Descrition of the network UKAWMN

The United Kingdom Acid Waters Monitoring Network (UKAWMN) was established in 1988 with the aim of monitoring the ecological response of acidified aquatic ecosystems to national and international reductions in acidic emissions. The Network comprises 11 lakes and 11 streams situated in most of the acid-sensitive upland regions of the UK (see **Figure 25**). Stream chemistry is measured monthly while lake chemistry is determined quarterly. Populations of epilithic diatoms, aquatic macrophytes, macroinvertebrates and fish (salmonids only) are assessed annually. Chemistry and macroinvertebrate data for six lakes (1. Loch Coire nan Arr, 4. Lochnagar, 7. Round Loch of Glenhead, 10. Scoat Tarn, 15. Llyn Llagi and 21. Blue Lough) are included in the ICP database.



Figure 25. Location of sites on the UKAWMN.

A major assessment of the first ten years of data (1988-1998) was published as a report to the Network's sponsors (the Department of the Environment Transport and the Regions, and the Environment and Heritage Division, Northern Ireland) last year. This is available in downloadable format from the UKAWMN web site <u>www.geog.ucl.ac.uk/ukawmn/</u>). The report focuses primarily on trend tests on the chemical and biological data gathered by the Network, but also incorporates an analysis of recent trends in deposition chemistry, based on data from the UK Acid Deposition Network.

#### 4.2 Chemical trends

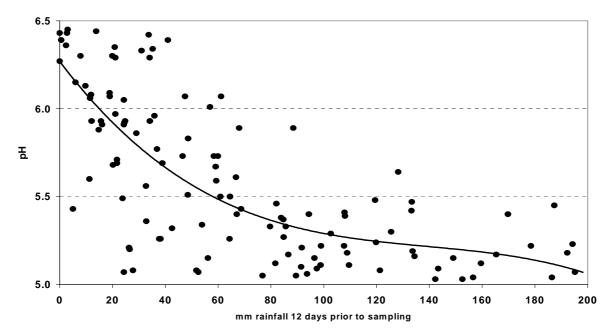
Deposition analysis demonstrated that there had been a large national decline in non-marine  $SO_4$  (xSO<sub>4</sub>) deposition over the decade of interest, but there were large geographical differences in the rate of decline. Large reductions in xSO<sub>4</sub> (of approximately 3 µeq l<sup>-1</sup> year<sup>-1</sup>) occurred in parts of the south-east and in the English Midlands, areas which are relatively close to large industrial sources. At intermediate distances from major source areas the reductions were smaller (circa 1 µeq l<sup>-1</sup> year<sup>-1</sup>), while trends in the most remote areas of the north and west of the UK, where several UKAWMN sites occur, were only significant when data were combined in meta-analyses. No reductions were found in NO<sub>3</sub> deposition.

Only three UKAWMN sites showed significant downward trends in  $xSO_4$ . Two of these (The River Etherow (site 12) and Old Lodge (site 13)) showed large declines and these are located in areas of the country which have experienced the strongest deposition reductions. A smaller reduction was observed in Lochnagar (site 4), which is also situated in a region where deposition reductions have been found. No sites showed reductions in NO<sub>3</sub> concentration. Of these three sites, trends of increasing pH and/or alkalinity were only found at Old Lodge. We attributed the absence of evidence for reduced acidity at the River Etherow partly to hydrochemically driven noise (pH here varies from 6.5 at low flows to less than 4.0 at high flows) and partly to a base-cation decline. Lochnagar experienced a rise in NO<sub>3</sub> which was greater than the reduction in  $xSO_4$  and this site had therefore continued to acidify.

Generally, therefore there was very little evidence for chemical recovery across the Network over the 1988-1998 period. However, several sites with west coast locations exhibited increases in pH and/or alkalinity without showing reductions in acid anions. We attributed this to two climatic influences, both of which can be linked to the North Atlantic Oscillation (NAO). The NAO Index (NAOI) is a measure of the average difference in atmospheric pressure between two major pressure cells over the Atlantic, commonly known as the Azores High and the Icelandic Low (Hurrel, 1995). Over the decade there was a general decline in the NAOI, which resulted in a reduction in winter rainfall and storm induced seasalt deposition events in the west of the UK. A decline in winter rainfall is likely to have increased the proportion of relatively buffered ground-water entering UKAWMN sites (see Figure 26), while a decline in seasalt events will have reduced the number of seasalt induced acid episodes (Evans *et al.*, 2001). We have argued that it is essential that trends in meteorological conditions are taken into account when attempts are made to assess the impact of emissions reductions on freshwater chemistry. This is important even with relatively long datasets, since the NAO can show variability at the decadal scale and beyond.

#### 4.3 Biological trends

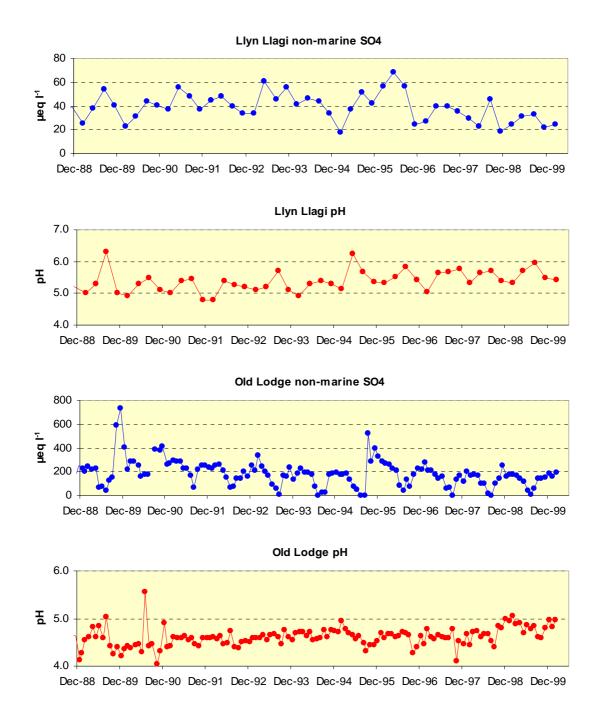
Analysis of the first 10 years of biological data indicated that species changes had occurred in epilithic diatoms and macroinvertebrate populations which were indicative of a recovery response. However, these were again mostly observed at sites on the west coast which showed no indication of declining acid anion concentrations. Once more, therefore, it seemed that these trends were more indicative of short-term climatic fluctuations than long term chemical recovery.



**Figure 26.** The relationship between the pH of water samples collected from Dargall Lane (site 9) and the amount of rainfall over the period 1988-2000. A third order polynomial function (plotted curve) can explain 51% of the variation in pH. The data highlight the importance of taking climatic variation into account when testing for recovery trends.

A more recent analysis of chemistry data up to March 2000 now provides a more encouraging picture of a regional decline in  $xSO_4$  and increase in pH since around 1995.

Due to large inter-annual variability it has taken a further five years to verify these trends. These are generally compatible with deposition chemistry over the same period. Examples of the most recent time series are provided in **Figure 27**.



**Figure 27.** Time series of non-marine sulphate and pH at two UKAWMN sites over the period 1988-2000. The temporal pattern at Llyn Llagi, which shows a large reduction in  $xSO_4$  and rise in pH after 1995, is typical of the majority of sites on the Network.

Having developed a large "base-line" database, over a considerable period when acid deposition remained fairly constant, we are now in a very powerful position to assess how aquatic biology (the real targets of emission reduction policy) will respond to improving chemical conditions. In the mean time UKAWMN data are shedding light on upland water processes, and particularly links between climate and chemistry (e.g. Monteith *et al.*, 2000; Evans, *et al.*, 2001) and biology, that were not foreseen and may never have been revealed in short-term experiments. UKAWMN data are now routinely used to test environmental models, such as MAGIC (Cosby et al., 1985), which provide predictions for policy makers, and we are receiving increased national and international attention from ecologists, hydrologists and water chemists, who recognise the importance of long-term datasets. We are also very fortunate to have benefited from the wide experience and expert advice of colleagues in the ICP community and other external organisations at home and abroad.

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