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Geomorphology and hydrochemistry of 12 Alpine lakes in the Gran Paradiso National Park, Italy

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ABSTRACT

Twelve Alpine lakes located in the Gran Paradiso National Park, in the western Italian Alps, were sampled during the ice free period in 2008 and analysed for the main morphological, chemical and physical variables in relation to the characteristics of their watershed, with the aim to create a reference database for present and future ecological studies and to support conservation politics with scientific data. The results highlighted that weathering process and direct precipitation input are the main factors determining the hydrochemistry of the studied lakes; moreover the morphological characteristics highly affects the physical properties of the lakes starting from stratification process. The acidification status, the atmospheric input of N compounds and the supply of nutrients were considered in detail. The studied lakes seem to be well preserved by acidification risk. Comparing data from Gran Paradiso National Park with data from European mountain regions ranging in N deposition rates, allows to consider long range anthropogenic impact: the detection of relative low Total Nitrogen (TN) concentration is not necessarily a synonym of a soft impact of long range pollutants, being the final nitrogen concentration dependent from retention process, closely related to catchment characteristics, besides N deposition rates; moreover the dominance of Inorganic Nitrogen (IN) on Organic Nitrogen (ON) highlights that the lakes are interested by N deposition and probably by long range transport of pollutants produced in the urbanized area surrounding the massif. However the Gran Paradiso National Park area is by far less affected by atmospheric pollutants than other Alpine regions, as the Central Alps. Total Phosphorus (TP) concentration in Gran Paradiso lakes (1-13 $\mu g\ L^{-1}$, mean level = 4 $\mu g\ L^{-1}$) is an index of oligotrophic and ultraoligotrophic conditions and according to Redfield's ratio phosphorus is mainly the phytoplankton growth limiting element, assuming a key role in biological processes and food-web dynamics; the high TN:TP ratio values detected in the studied lakes reflects the low N retention capacity of alpine sparse vegetation by comparison with prairies or forests.

Key words: mountain lakes, Alps, morphology, hydrochemistry

1. INTRODUCTION

The Convention for the Protection of the Alps, signed jointly in 1991 by the EU and the countries surrounding the Alps (Germany, France, Liechtenstein, Italy, Monaco, Austria, Switzerland and Slovenia) contains an explicit commitment to preserve or restore alpine water systems. Since high elevation lakes are sensitive to several local and global anthropogenic impacts (CIPRA 1992; Rosa 1995; Eby 2006), the Gran Paradiso National Park started a monitoring project, aimed at preventing or evaluating the environmental risk connected to water exploitation, alien species introduction and other local threats.

Besides the above mentioned threats, Alpine lakes are particularly sensitive to global anthropogenic impacts: the hydrochemistry of mountain lakes is highly conditioned by the chemical composition of atmospheric deposition and by climate features (Rogora *et al.* 2003) and remote lakes are considered "early response" indicators of climate change, atmospheric deposition and air pollutants (Rogora *et al.* 2008). The effects of climate warming appear to be especially pronounced in high altitude areas (Battarbee *et al.* 2002; Rogora *et al.* 2003; Filippelli *et al.* 2006; Sommaruga 2007) and acid deposition affects the Alpine region (Marchetto *et al.* 1994). Both factors contribute to ecosystem changes (Mills & Schindler 1986; Parmesan 1996; Parker *et al.* 2008). Besides acidification and climate change, trace metals, POPs (Persistent Organic Pollutants) and increased UV radiation can contaminate high altitude environments (Allan 1999; Carrera *et al.* 2002; Heit *et al.* 2004; Kallenborn 2006; Dag 2007).

Finally, according to our opinion, studying alpine lakes is important for at least two reasons:

a) mountain water system are in the middle of strong economical interests which have compromised several aquatic environments of the Alps; the pristine lakes and rivers must be preserved, the compromised ones can be recovered (Rosa 1995; Knapp & Matthews 1998; McNaught *et al.* 1999; Drake & Naiman 2000; Knapp *et al.* 2001; Vredenburg 2004).
b) Alpine lakes are often mainly affected by regional threats, being negligible the local ones, so they can be used as models for the effect of regional and global changes to freshwater ecosystems.

Whatever the research topic, morphological data are essential and functional to other data analysis: lake

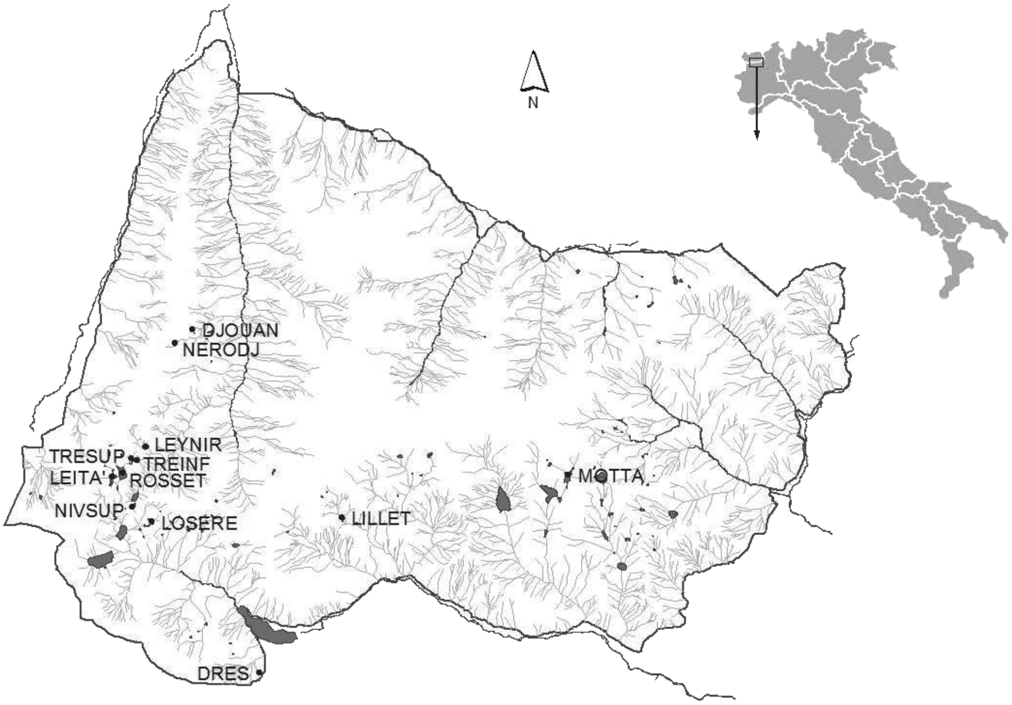

Fig. 1. Study area: Gran Paradiso National Park hydrographic system and studied lakes.

morphology influences physic properties and chemistry of water, like turbulence, circulation, thermal properties and thermal stratification (Ambrosetti & Barbanti 2002; Bronmark & Hansson 2006); it can also affect lake productivity, suggesting that lakes features can be very important for biological processes (Ryder *et al.* 1974; Bronmark & Hansson 2006).

Moreover the size, bedrock, soil, vegetation of the catchment area affect the nutrient input, pH and many other abiotic factors shaping the chemical composition of the lake water (Bronmark & Hansson 2006) and the biotic community consequently. Particularly, the larger the catchment area, the longer it takes for the water to reach the lake, and the more pronounced is the impact of the catchment area on lake water chemistry (Bronmark & Hansson 2006). Alpine lakes drainage areas are often small, determining a low concentration of nutrients since the rainwater has a short distance to gather nutrients before it reaches the lake.

Despite their interest, data concerning alpine lake morphology are scarce and rarely published; this is also true in the Gran Paradiso National Park (North-western Italian Alps), where limnological interest has been discontinuous and mainly localized (Vanni 1931; Tonolli & Tonolli 1951; Tortonese 1954; Bovio 1982-83; Alessio *et al.* 1987; Gaggino & Cappelletti 1984; Giussani *et al.* 1986; Frezet 2003) and the research activity focused almost exclusively on terrestrial environments. Moreover, in the Alpine setting, western lakes are probably the less known, and we intend to partially make up for knowledge deficiencies.

Our purpose is to emphasize the utility of environmental data in water management and conservation policy, starting on a morphological description of 12 Alpine lakes in a protected area and on their characterization from a chemical and physical point of view. We aim to create a reference database on the physical and hydrochemical characteristics of a representative number of high elevation lakes in the Park area, to allow monitoring of how man-driven environmental change (as climate warming or hydroelectric exploitation) would eventually affect their protected fauna and flora and their ecosystem functioning.

2. AREA

Gran Paradiso National Park (PNGP) is located between 45°25' and 45°45'N and between 7° and 7°30'W in the Western Italian Alps (Fig. 1). The protected area shows a large altitudinal extension (between 800 and 4061 m) and a typical alpine climate.

PNGP includes all the 12 studied lakes (Fig. 1) belonging to the catchments of rivers Orco and Savara. These lakes are not affected by hydromorphological alterations, they are larger than 10,000 m^2 and are all located above 2000 m a.s.l., where the ice-free period lasts only three to five month each year, in dependence of altitude and exposure. Main geographical data are reported in table 1. In this paper, toponims will be replaced by abbreviations: Nivolet Superiore – NIVSUP, Trebecchi Inferiore – TREINF, Trebecchi Superiore – TRESUP, Losere – LOSERE, Lillet – LILLET, Motta – MOTTA, Leità – LEITÀ, Nero (in Leynir Valley) –

Tab. 1. Geographic and morphometric data of PNGP lakes and catchment carachteristics; Z_m: maximum depth; A: area; L: perimeter; V: volume; Z_r: relative depth; Z_{med}: average depth; DL: shore development; DV: volume development; B: catchment area; B/A: B/A ratio; LC: Land Cover index (Mosello *et al*. 1991). Geology - AC: cathment entirely composed by Acidic Gneiss; geology - CS: catchment dominated by thick covering of Calcareous Schists.

Code		NIVSUP	TREINF	TRESUP	LOSERE	LILLET	MOTTA	LEITÀ	LEYNIR	NERODJ	DJOUAN	DRES	ROSSET
Latitude N		45°28'41"	45°30'08"	45°30'07"	45°28'33"	45°28'00"	45°29'55"	45°29'28"	45°30'28"	45°33'07"	45°33'28"	45°24'46"	45°29'47"
Longitude E		07°08'55"	07°08'48"	07°08'40"	07°09'25"	07°12'26"	07°24'26"	07°07'56"	07°09'06"	07°10'07"	07°10'43"	07°13'26"	07°08'17"
Altitude	(m)	2538	2723	2729	2568	2765	2656	2701	2747	2671	2515	2087	2703
Z_m	(m)	17.1	8.1	7.5	7.2	13.2	51.0	11.0	22.1	6.0	3.0	7.4	46.9
A	(m^2)	34,482	14,812	14,172	21,401	36,249	101,396	62,171	44,691	17,121	13,341	26,112	168,643
L	(m)	986	493	565	684	846	2223	1992	956	548	458	713	2116
V	(10^3m^3)	162.1	61.8	48.9	70.4	233.1	1257.4	244.6	466.4	41.6	19.8	86.1	3347.1
Z_r	%	8.16	5.90	5.58	4.36	6.14	14.19	3.91	9.26	4.06	2.30	4.06	10.12
Z_{med}	(m)	4.70	4.17	3.45	3.29	6.43	12.40	3.93	10.44	2.43	1.48	3.30	19.85
DL		1.50	1.14	1.34	1.32	1.25	1.97	2.25	1.28	1.18	1.12	1.24	1.45
DV		0.27	0.51	0.46	0.46	0.49	0.24	0.36	0.47	0.41	0.49	0.45	0.42
B	(ha)	29.11	43.76	23.66	43.48	91.86	289.87	315.59	156.47	86.55	30.60	291.85	133.04
B/A		8.44	29.54	16.69	20.32	25.34	28.59	50.76	35.01	50.55	22.94	111.77	7.89
Land Cover													
Shrubs	%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.96	0.00
Prairies	%	12.94	71.46	77.59	0.00	0.00	0.00	8.55	22.34	10.37	21.86	6.29	24.71
Debris	%	55.60	6.56	6.37	8.65	41.37	43.47	53.02	50.38	70.91	20.57	42.44	51.94
Rocks	%	19.63	14.98	11.58	86.55	33.85	48.80	26.70	20.82	16.75	53.19	44.40	10.60
Glaciers	%	0.00	0.00	0.00	0.00	20.84	4.03	9.36	3.63	0.00	0.00	0.00	0.00
Water	%	11.85	7.00	4.46	4.81	3.95	3.70	2.37	2.84	1.98	4.36	0.90	12.72
LC		11	12	12	7	3	4	5	5	11	11	9	11
Geology		AG	CS	CS	AG	AG	AG	CS	CS	CS	AG	CS	CS

LEYNIR, Nero (in the Djouan area) – NERODJ, Dres – DRES, Rosset - ROSSET.

All the study sites, but DRES, lie above the tree line and their watershed belong to the Alpine and nival belts. They are placed in two geologically separated areas: the former is entirely dominated by the same acidic gneiss that forms the Gran Paradiso massif; while the latter is dominated by thick covering of calcareous schists variously metamorphosed, derived from marine sediments of the Mesozoic Era, surrounding the Gran Paradiso igneous massif and overlapping its margins (Leporati *et al.* 1999). The geology affects the vegetation development; the most abundant plants in the Alpine zone are *Festuca halleri*, *Festuca varia* and *Carex curvula* living in the acidic grassland, whereas basic grassland are less widespread (Scotta *et al.* 1999). The nival zone is characterised by bare rock, moss, liverworts and lichens. The altitudinal vegetation belts are not always clearly separated, and transition zones with mixed vegetation are common throughout the range.

3. METHODS

3.1. Geomorphology

Lake surface area (A) and perimeter (L), catchment area (B) and land cover are obtained from digital maps using ArcView 3.2. Land cover data were transformed in Land Cover classes (LC) (Mosello *et al.* 1991), estimated on the relative importance of the following features: glacier, bare rocks, alpine prairie, coniferous forest, deciduous forest.

Bathimetric maps and maximum depth were obtained measuring depth every 10-20 meters along linear transects using a metric rope from an inflatable boat. Bathimetric maps were then converted in vectorial file using JPEG Analyst.

Geology of the catchment area were obtained from Mattirolo *et al.* (1912). Other morphological data were calculated following (Wetzel & Likens 1991; Boscaini & Cantonati 2002): catchment:lake ratio (BA-1), volume (V), maximum depth (Z_m), average depth (Z_{med}), relative depth ($Z_r = (50_{zm}{}^{0,5})A^{-0,5}$), perimeter development ($DL = L\,[2(A)^{0,5}]^{-1}$) and volume development ($DV = Z_{med}\,Z_m{}^{-1}$, Hutchinson 1957).

3.2. Water sampling and analytical methods

Lake water samplings were performed twice during Summer 2008: once during thermal overturn (June-July) and once during maximum stratification (August-September 2008). We collected 500 mL integrated samples with a Patalas-Schindler bottle on the whole water column in the point of maximum depth. *In situ* temperature and oxygen profiles were obtained through a multiparameter probe, while transparency was estimated using a Secchi disc. Lake samples were analysed for the main chemical variables: pH, conductivity, alkalinity (acidimetric titration, Gran's method), ammonium, total nitrogen, total phosphorus and reactive silica (spectrophotometry), major anions (SO_4^{2-}, NO_3^-, Cl^-, F^-) and cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) (ion chromatography). Organic Nitrogen (ON) concentrations were calculated from the difference between Total Nitrogen (TN) and Inorganic Nitrogen ($IN = N\text{-}NO_3^- + N\text{-}NH_4^+$) concentrations. Details on the analytical methods used can be found in Tartari & Mosello (1997).

3.3. Statistical analysis

We assume it is incorrect to use temperature and oxygen profiles data to deduce any ranking among lakes; in fact they were not sampled at the same time, but almost one month elapses since the first to the last measurement, thus seasonal thermal gradients are not negligible. Besides, temperature and oxygen show important depth gradients and strong daily patterns in the surface layers. Despite this fact, collected data are useful to describe thermal properties, thermal regimes and oxygenation status. A binomial factor (stratified/non stratified) was used to assess, using the Mann-Whitney test, the importance of lake depth in stratification development.

We look for the effect of the large water input during snowmelt in the 16 remaining chemical and physical variables comparing early Summer and late Summer samples with a paired-sample non-parametric Wilcoxon test. Then we calculated the average values of the chemical and physical variables (measured twice in 2008 summer) to set a data frame for Principal Components Analysis and to calculate a Spearman correlation matrix.

Spearman's ρ (corrected with Holm-Bonferroni method for multiple tests) allowed us to quantify relationship between 28 variables (16 chemical and physical variables and 12 morphological variables); we preferred using non-parametric tests because of the relatively small number of case-studies.

A multivariate numerical analysis was performed on the average values of each chemical variable, apart pH, were log transformed using natural logarithms. Principal Components Analysis (PCA) with varimax rotation method and Kaiser normalization was used to identify the principal environmental gradients. We excluded from the analysis lake temperature and oxygen data, because of their strong seasonal variability and Secchi depth, as in most lakes it was larger than maximum depth; besides we excluded those variables that are a linear combination of others (Alkalinity, Conductivity, TN) to avoid communality among factors. To avoid the excess of variables compared to the number of cases we excluded Mg^{2+} too, since, coupled with SO_4^{2-}, it have the highest Spearman Rho in a cross-correlation analysis between the remaining variables. PCA scores were then related to the morphological variables to highlight the factors influencing water chemistry.

4. RESULTS

4.1. Morphology, origin and catchments characteristics

The glacial landscape in the study area shows a wide geomorphological diversity, hosting still active morphogenetic processes (Leporati *et al.* 1999); the same diversity is detectable in lake origin: the glacial activity is involved in the origin of all the studied lakes, sometimes interacting with other morphogenetic agents.

MOTTA, NIVSUP, LEYNIR, LILLET, LOSERE and NERODJ are all placed in glacial cirques, filling depression where a cirque glacier was present. In the valleys hosting NIVSUP, LOSERE and MOTTA, it is often possible to observe series of glacial lakes connected by a single stream or a braided stream system (chain lakes). They were formed by terminal moraines or rock dams due to glacier advance and retreat. Nevertheless, other agents contribute to shape the studied cirque lakes: NIVSUP water level was raised by a rock slide dam (Vanni 1931); tectonic faults would be involved in the origin of MOTTA lake, explaining high sloping shores; moraine sediments surround lake NERODJ, being important in determining its morphology.

An elongated, rounded, asymmetrical, bedrock knob can be produced by glacier erosion generating sheepback rocks, frequently hosting shallow depressions filled by water: TREINF and TRESUP origin is attributable to this morphogenic process. Glacial generic erosion is responsible for the origin of the other lakes, DRES, LEITÀ and DJOUAN. Finally, ROSSET is dammed by an imposing moraine.

Lakes morphology is summarized in table 1, bathimetric maps are reported in figures 2, 3 and 4 and ipsographic curves are reported in figure 5: MOTTA and ROSSET are by far the largest and deepest lakes, while lake DJOUAN is the smallest and shallowest.

Water supply is assured by tributaries coming from the drainage area, but they are often absent or intermittent, suggesting that underground water flow will be important in lakes water balance; at the studied lakes altitude, inflowing and outflowing streams are mainly observable at the beginning of summer, when the lake is abundantly supplied by melting snow and ice; in the case of TREINF, its emissary is always hidden, sinking in a karstic hole. Water supply is involved in lake-level seasonal changes that alter lakes morphology. However, during the ice free period, water level fluctuations are modest: a few centimeters in NIVSUP and ROSSET, and about one meter in TREINF and NERODJ.

Lakes shores are covered by alpine grassland or rocks, and in the highest areas by glacier. Trees (*Picea abies* and *Larix decidua*) and shrubs are only found in DRES watershed. In general, catchments land cover is dominated by rocks (glacial debris, srees or solid rocks), but in some cases the prairies are dominant and the glaciers cover a significant area. Using Land Cover classes (Mosello *et al.* 1991), most of the lakes fall in the first classes, because of their altitude (Tab. 1).

A few lakes are interested by cattle and sheep breeding: area around DJOUAN is annually exploited as pasture; DRES, ROSSET, LEITÀ and NIVSUP surrounding areas are less exploited.

4.2. Oxygen, temperature and transparency

In figure 6 the temperature and oxygen profiles of the 12 studied lakes, all lake were measured twice during the study season with the exception of TRESUP, measured just once in September.

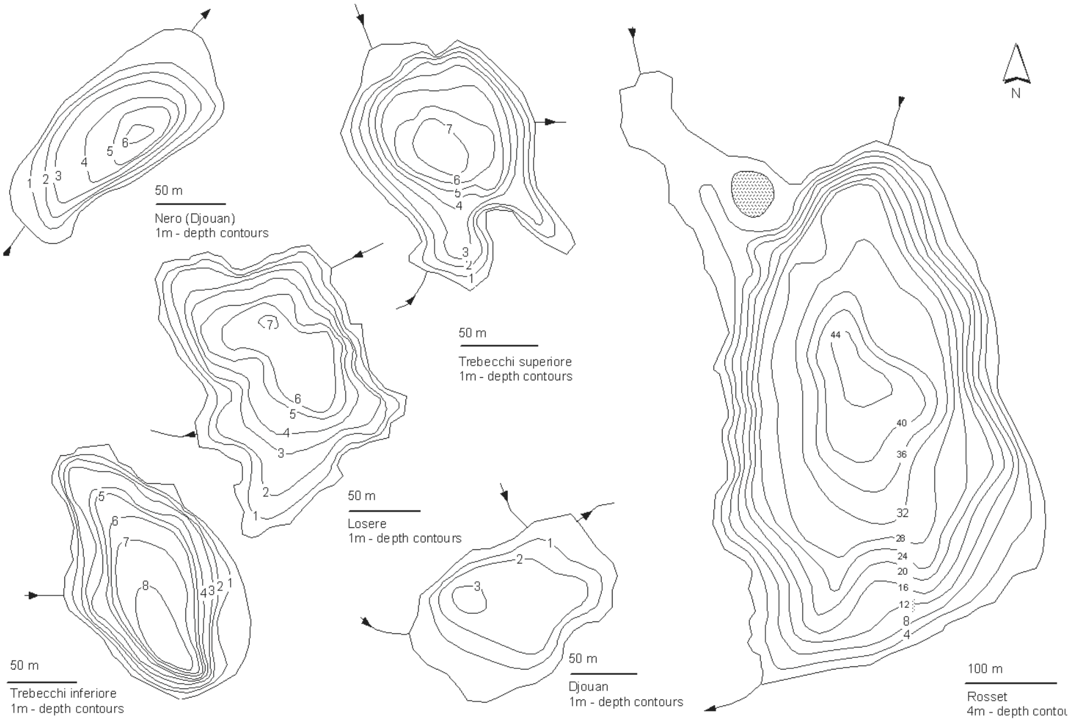

Fig. 2. Bathymetry of NERODJ (Nero, in the Djouan area), TRESUP and TREINF (Upper and lower Trebecchi lakes), LOSERE, DJOUAN and ROSSET.

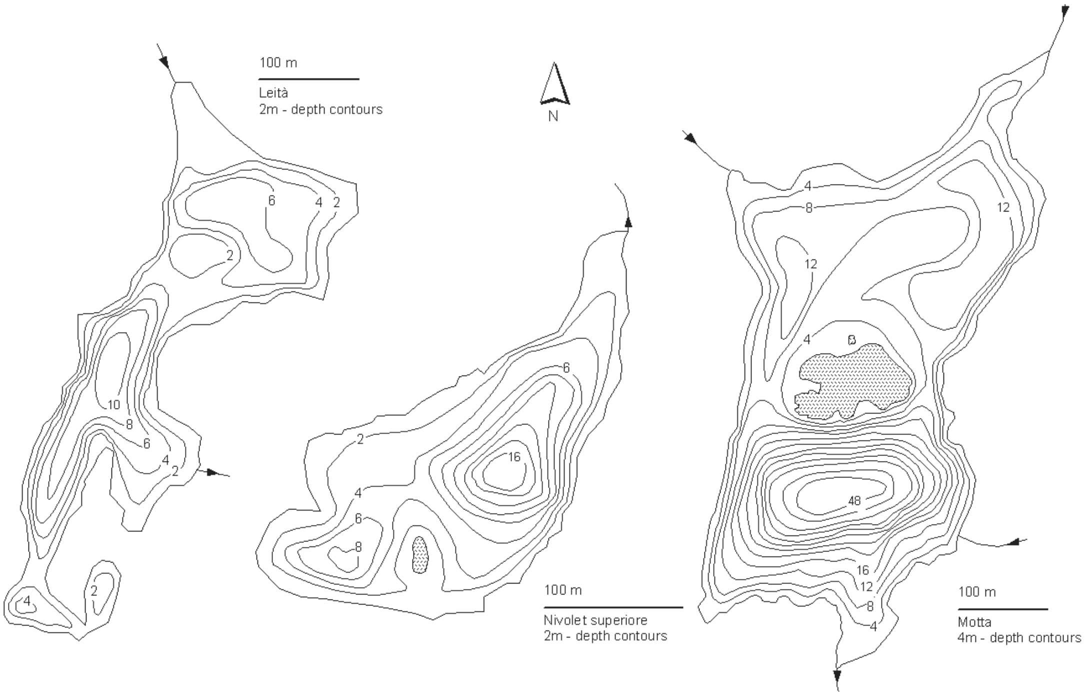

Fig. 3. Bathymetry of LEITÀ, NIVSUP (Nivolet Superiore) and MOTTA.

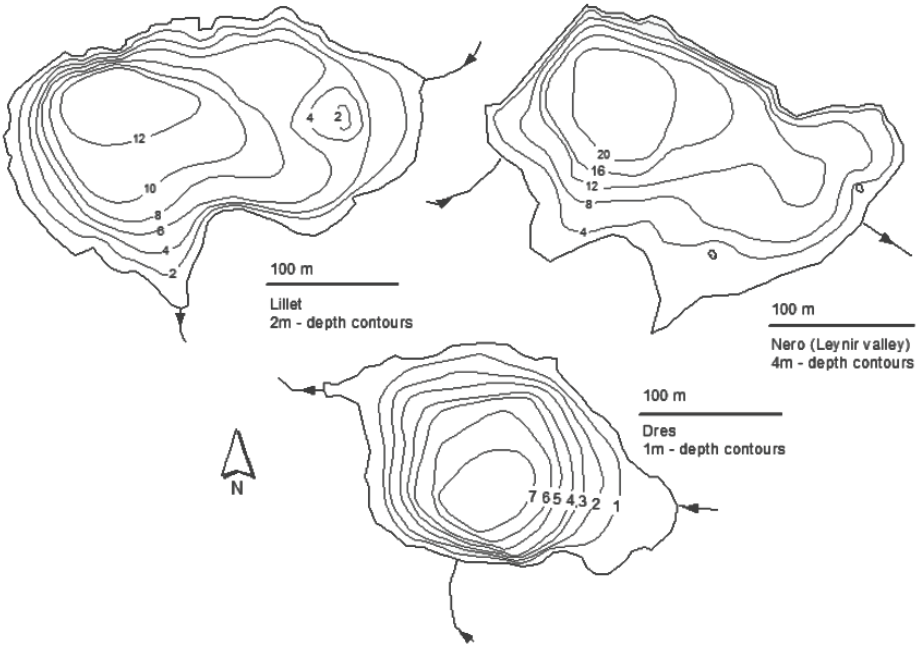

Fig. 4. Bathymetry of LILLET, LEYNIR (Nero, in the Leynir Valley) and DRES.

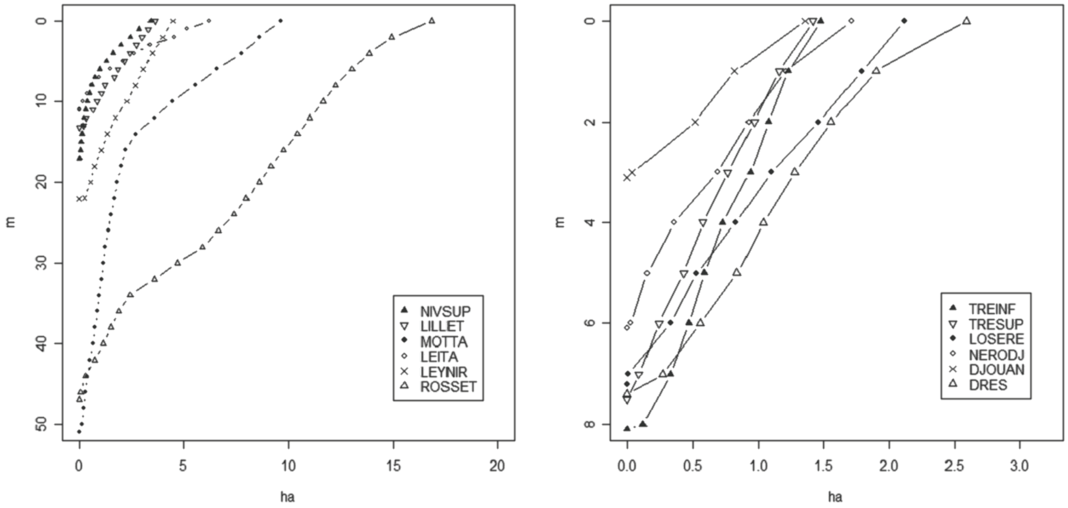

Fig. 5. Ipsographic curvae of the PNGP lakes; the two graphics have different scale but identical proportion.

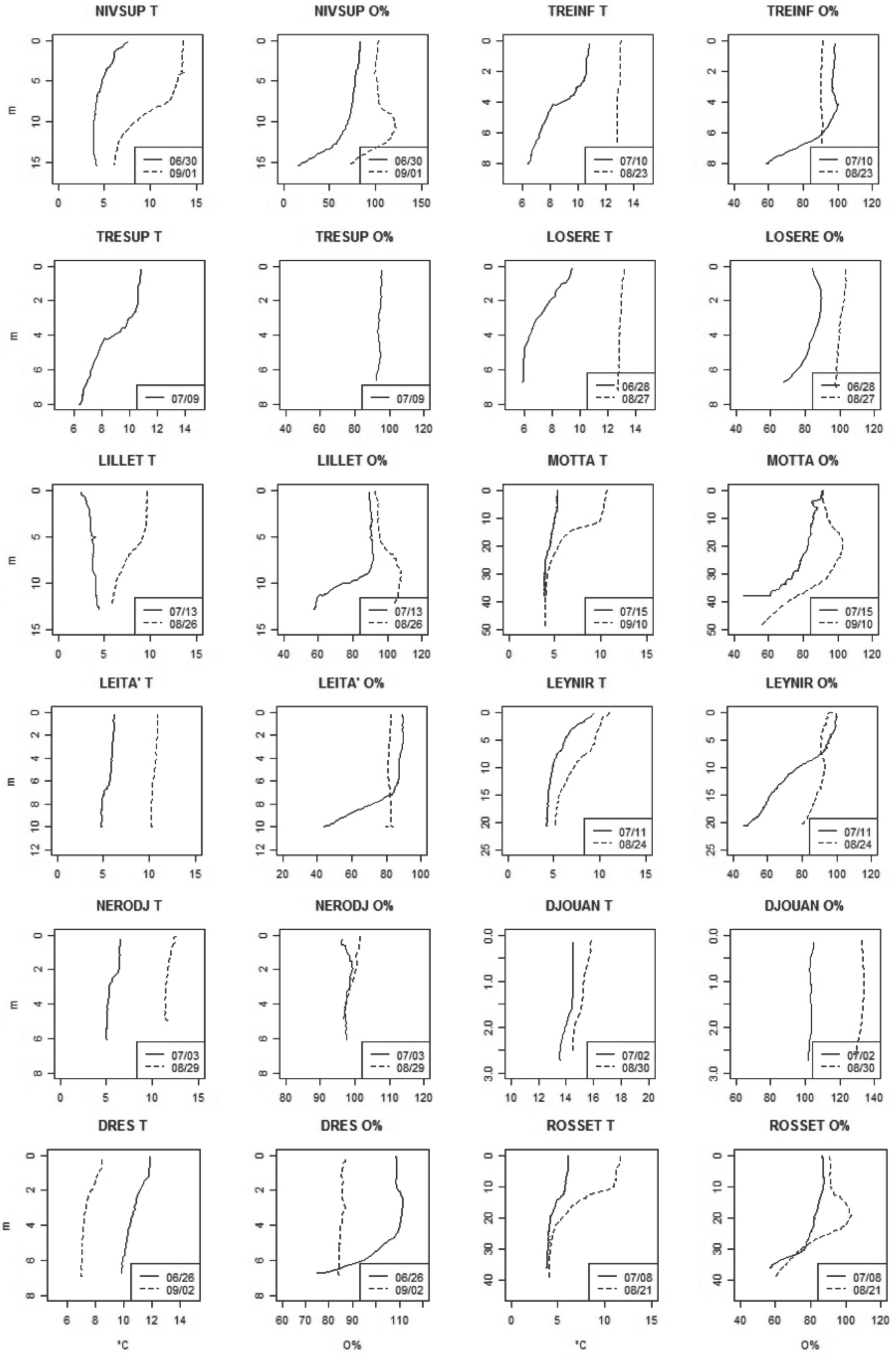

Fig. 6. Temperature and oxygen depth profiles in the PNGP lakes.

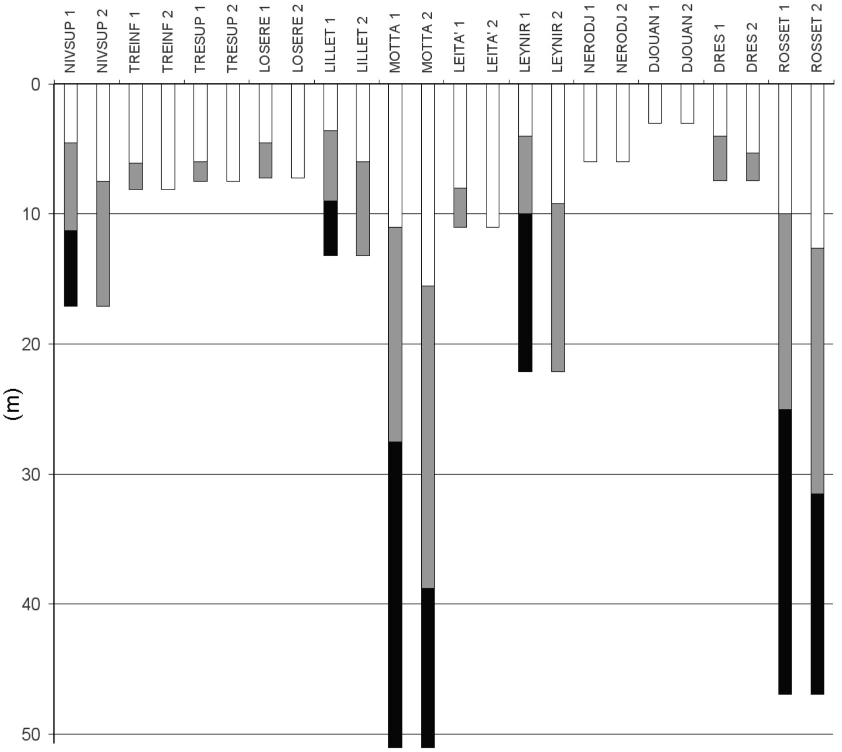

Fig. 7. Early and late summer Secchi depth transparency (white bar) in Gran Paradiso lakes; depth with percentage of penetration of the surface incident light >1% (grey bar) and depth with percentage of penetration of the surface incident light <1% (black bar).

Temperature values increase in all lakes between the first and the last survey; water column profiles of temperature indicate that only deeper surveyed lakes clearly undergo stratification: ROSSET, MOTTA, LILLET, LEYNIR and NIVOLET show pronounced termoclines, clearly visible in the second seasonal measurements and the deeper two, MOTTA and ROSSET, keep their ipolimnion at a constant temperature (about 4 °C) all year long; in addition to the deepest lakes, TRESUP and LOSERE present also stratification, but in early summer and it seems to be a transient stage previous complete warming. On the other hand, especially in August/September surveys, shallow lakes (as TREINF, TRESUP, LOSERE, LEITÀ, DJOUAN, DRES and NERODJ) show slightly depth-decreasing temperature gradients, suggesting that thermal stratification would be mainly unable to offer resistance to wind mixing effect (Fig. 6).

During the July measurement, lake LILLET shows an inverse thermal stratification because of floating ice (Fig. 6).

Very low values of oxygen saturation (17%) were only observed in NIVSUP, just a few days after surface ice melting, probably because of Winter oxygen consumption under the ice cover. Other subsaturation events, through not so extreme, are commonly found during the first survey. While in august September all the lakes were well oxygenated, as expected, during the ice-free period. A maximum saturation value of 132% was measured in DJOUAN in August.

Decreasing oxygen saturation along depth profiles occurs only in the deeper, thermally stratified lakes. In most lakes, oxygen saturation increases during the ice-free season.

Secchi depth transparency (Z_S) increases during the study period (Wilcoxon test for related samples, $p < 0.01$,): it ranged from 3.6 to 11 m in July and from 5.3 to 15.5 in August, excluding data collected in lakes where Z_S is larger than maximum depth. The clearer lake is lake MOTTA ($Z_S = 15.5$, Fig. 7). In absence of photometric measures, we assume the depth of penetration of 1% of the surface incident light (often assimilated to photic zone) to be 2.7 time Z_S (Margalef 1983): ROSSET and MOTTA show <1% light penetration layers all year long, while NIVSUP, LILLET and LEYNIR, at the beginning of summer only.

4.3. Chemistry

Lakes hydrochemistry is summarized in table 2. In the studied lakes, pH ranges from 6.95 to 8.62 and alkalinity from 0.10 to 1.11 meq L^{-1}. Conductivity ranges from 17 to 110 µS cm^{-1}, because of the low ionic content. Major ions in the samples are Ca^{2+}, SO_4^{2-} and Mg^{2+}. Potassium, sodium, fluoride and chloride pools are generally lower compared to other ions.

During the survey period, pH significantly increases ($p < 0.01$, Wilcoxon test for related samples), as well as Mg^{2+} and K^+ ($p < 0.05$).

Tab. 2. Main chemical data of PNGP lakes: seasonal and mean values.

	Date	pH	$C_{20°C}$ µS cm^{-1}	T.Alc. meq L^{-1}	Cl^- mg L^{-1}	SO_4^{2-} mg L^{-1}	NO_3^- µg L^{-1}	NH_4 µg L^{-1}	Ca^{2+} mg L^{-1}	Mg^{2+} mg L^{-1}	Na^+ mg L^{-1}	K^+ mg L^{-1}	TP µg L^{-1}	TN mg L^{-1}	Si mg L^{-1}	F- mg L^{-1}	TOC mg L^{-1}	Anions µeq L^{-1}	Cations µeq L^{-1}
NIVSUP	30/06/08	7.14	21.7	0.168	0.13	1.48	94	5	3.32	0.51	0.38	0.16	2	0.14	0.54	0.13	0.4	211	229
	01/09/08	7.35	23.2	0.209	0.22	0.79	10	3	4.17	0.28	0.27	0.17	5	0.09	0.11	0.04	2.3	233	247
	Mean	*7.25*	*22.4*	*0.189*	*0.18*	*1.14*	*52.00*	*4.00*	*3.75*	*0.40*	*0.33*	*0.17*	*3.50*	*0.12*	*0.33*	*0.09*	*1.35*		
TREINF	10/07/08	8.05	76.8	0.812	0.19	2.48	64	6	15.60	0.90	0.32	0.37	3	0.11	1.23	0.01	0.5	874	876
	23/08/08	8.06	87.0	0.980	0.13	3.04	30	10	18.00	0.95	0.31	0.37	3	0.09	0.83	0.01	0.6	1050	1000
	Mean	*8.06*	*81.9*	*0.896*	*0.16*	*2.76*	*47.00*	*8.00*	*16.80*	*0.93*	*0.32*	*0.37*	*3.00*	*0.10*	*1.03*	*0.01*	*0.53*		
TRESUP	09/07/08	7.99	89.8	0.975	0.15	2.72	74	19	18.40	0.99	0.27	0.37	1	0.11	1.13	0.01	0.2	1042	1022
	23/08/08	8.01	91.2	0.998	0.13	3.19	36	23	18.70	1.03	0.29	0.41	7	0.09	0.64	0.01	0.5	1071	1043
	Mean	*8.00*	*90.5*	*0.987*	*0.14*	*2.96*	*55.00*	*21.00*	*18.55*	*1.01*	*0.28*	*0.39*	*4.00*	*0.10*	*0.89*	*0.01*	*0.35*		
LOSERE	29/06/08	7.09	22.1	0.203	0.21	0.90	66	27	4.03	0.26	0.26	0.17	2	0.13	0.42	0.03	3.7	239	240
	27/08/08	7.32	22.3	0.188	0.09	1.69	12	14	3.46	0.58	0.41	0.16	10	0.08	0.36	0.13	0.7	227	243
	Mean	*7.21*	*22.2*	*0.196*	*0.15*	*1.30*	*39.00*	*20.50*	*3.75*	*0.42*	*0.34*	*0.17*	*6.00*	*0.11*	*0.39*	*0.08*	*2.20*		
LILLET	13/07/08	7.51	44.1	0.385	0.12	1.97	327	4	6.80	1.29	0.40	0.39	5	0.32	0.63	0.18	0.5	464	473
	26/08/08	7.64	44.1	0.411	0.10	1.56	256	3	6.98	1.40	0.38	0.44	1	0.25	0.50	0.21	0.2	475	491
	Mean	*7.58*	*44.1*	*0.398*	*0.11*	*1.77*	*291.50*	*3.50*	*6.89*	*1.35*	*0.39*	*0.42*	*3.00*	*0.29*	*0.57*	*0.20*	*0.31*		
MOTTA	15/07/08	6.95	16.9	0.099	0.11	1.63	330	3	2.54	0.11	0.38	0.25	4	0.36	0.46	0.04	0.2	162	159
	10/09/08	6.97	17.4	0.103	0.08	1.68	327	4	2.63	0.11	0.38	0.26	3	0.33	0.47	0.05	0.3	165	164
	Mean	*6.96*	*17.1*	*0.101*	*0.10*	*1.66*	*328.50*	*3.50*	*2.59*	*0.11*	*0.38*	*0.26*	*3.50*	*0.35*	*0.46*	*0.05*	*0.26*		
LEITA'	05/07/08	8.08	109.6	1.006	0.17	10.20	227	4	20.00	2.68	0.23	0.22	2	0.24	1.06	0.01	0.1	1240	1234
	20/08/08	8.25	96.5	0.865	0.17	9.97	186	7	16.60	2.70	0.23	0.21	1	0.20	0.62	0.01	0.3	1091	1066
	Mean	*8.17*	*103.1*	*0.936*	*0.17*	*10.09*	*206.50*	*5.50*	*18.30*	*2.69*	*0.23*	*0.22*	*1.50*	*0.22*	*0.84*	*0.01*	*0.19*		
LEYNIR	11/07/08	7.93	107.9	1.061	0.14	6.61	210	7	20.70	2.04	0.23	0.62	2	0.22	1.00	0.01	0.2	1218	1227
	25/08/08	7.98	108.3	1.072	0.15	6.94	177	1	20.40	2.22	0.24	0.62	3	0.17	0.68	0.01	0.2	1234	1227
	Mean	*7.96*	*108.1*	*1.067*	*0.15*	*6.78*	*193.50*	*4.00*	*20.55*	*2.13*	*0.24*	*0.62*	*2.50*	*0.20*	*0.84*	*0.01*	*0.19*		
NERODJ	03/07/08	8.05	72.0	0.630	0.13	6.33	205	2	13.40	1.27	0.19	0.48	2	0.20	0.54	0.01	0.3	780	794
	29/08/08	8.05	107.1	0.881	0.17	14.20	129	0	19.70	2.07	0.30	0.69	8	0.15	0.46	0.00	1.6	1195	1184
	Mean	*8.05*	*89.6*	*0.756*	*0.15*	*10.27*	*167.00*	*1.00*	*16.55*	*1.67*	*0.25*	*0.59*	*5.00*	*0.18*	*0.50*	*0.01*	*0.95*		
DJOUAN	02/07/08	8.01	124.6	1.114	0.14	12.70	70	10	21.90	3.44	0.46	0.68	5	0.14	0.51	0.00	1.0	1387	1414
	30/08/08	8.62	110.4	0.895	0.11	15.40	24	14	17.50	3.81	0.52	0.76	4	0.16	0.63	0.00	1.6	1230	1230
	Mean	*8.32*	*117.5*	*1.005*	*0.13*	*14.05*	*47.00*	*12.00*	*19.70*	*3.63*	*0.49*	*0.72*	*4.50*	*0.15*	*0.57*	*0.00*	*1.30*		
DRES	26/06/08	7.12	20.6	0.133	0.12	1.88	295	6	2.62	0.57	0.42	0.41	3	0.31	0.67	0.08	0.4	203	207
	02/09/08	7.46	35.2	0.275	0.12	2.99	208	21	4.83	1.10	0.70	0.61	13	0.28	1.08	0.13	0.7	361	379
	Mean	*7.29*	*27.9*	*0.204*	*0.12*	*2.44*	*251.50*	*13.50*	*3.73*	*0.84*	*0.56*	*0.51*	*8.00*	*0.30*	*0.87*	*0.11*	*0.52*		
ROSSET	07/07/08	8.01	83.7	0.838	0.11	3.58	43	0	16.50	1.18	0.22	0.26	4	0.08	0.79	0.01	3.5	919	937
	21/08/08	8.12	77.9	0.824	0.12	3.47	22	10	15.30	1.19	0.23	0.27	4	0.07	0.74	0.01	0.5	902	879
	Mean	*8.07*	*80.8*	*0.831*	*0.12*	*3.53*	*32.50*	*5.00*	*15.90*	*1.19*	*0.23*	*0.27*	*4.00*	*0.08*	*0.77*	*0.01*	*1.97*		

The Spearman correlation matrix between environmental variables, show a large number of mutual correlations among chemical variables: as expected, alkalinity is related to pH ($\rho = 0.796$; $p < 0.01$), pH to conductivity ($\rho = 0.825$; $p < 0.001$) and conductivity to alkalinity ($\rho = 0.958$; $p < 0.001$), and these variables are significantly related to sulphate, Ca and Mg concentration, while fluoride is negatively correlated with SO_4 ($\rho = -0.856$; $p = < 0.001$).

Nutrient concentrations , including ammonium (NH_4^+), nitrate (NO_3^-), total nitrogen (TN) and total phosphorus (TP), are very low, allowing us to classify these lakes as oligotrophic and ultraoligotrophic: the average TP concentrations is in effect as low as 4 µg L^{-1}. TN average level is 0.18 mg L^{-1}, ranging between 0.08 and 0.35; and NO_3^- accounts for 69% of the total N content. TN:TP ratios for all the collected samples range from 8 to 250 in weight, corresponding to a molar ratio of 18 to 560, with the lower values detected in August in LOSERE and TRESUP. According to the Redfield's ratio, these high molar ratios suggest phosphorus limitation of the algal growth.

The TN:TP ratio is negatively correlated to Land Cover classes (LC) ($\rho = 0.669$; $p < 0.05$). During the study period, NO_3^- concentration significantly decreases ($p < 0.01$), determining a corresponding decrease of TN from 0.20 to 0.16 ($p < 0.01$).

4.4. Multivariate numerical analysis

The first four axes of the PCA account for 84.4% of the total variance (Tab. 3). PCA axes 1 accounts for the 36.5% of the environmental variance in the data set, and loads on variables linked to weathering process, as pH and main ion concentrations (SO_4^{2-}, Ca^{2+}, K^+, F^-). PCA axis 2, accounting for 20.1% of the total variation, is related to Na^+, Cl^- and TP; PCA axis 3 represent a gradient in NO_3^- and TOC; PCA axis 4 represent a gradient in Si and NH_4^+ concentration (Tab. 3).

Tab. 3. Varimax rotated factor matrix and accounted variance.

Component	1	2	3	4
pH	0.925	-0.237	-0.014	0.123
Cl-	0.138	-0.677	0.197	0.093
SO_4^{2-}	0.909	0.018	-0.068	-0.212
NO_3^-	-0.157	0.296	-0.795	-0.423
NH_4^+	-0.099	0.181	0.247	0.887
Ca^{2+}	0.917	-0.304	-0.092	0.125
Na^+	-0.259	0.843	0.011	0.213
K^+	0.707	0.596	-0.177	-0.087
TP	-0.177	0.701	0.526	0.157
Si	0.474	-0.092	-0.503	0.618
F^-	-0.721	0.341	-0.172	-0.093
TOC	-0.070	0.011	0.967	-0.037
Accounted variance	36.5%	20.1%	17.0%	10.7%
Cumulative variance	36.5%	56.6%	73.6%	84.4%

PCA factor scores on the first axes resulted significantly different from lakes lying on acidic and basic rocks (Mann-Whitney test, $p < 0.01$), suggesting that catchment lithology has a leading role in determining hydrochemistry of lakes. Using the Spearman's test, PCA axis 3 resulted significantly inversely related to Land Cover classes ($\rho = -0.594$; $p < 0.05$).

5. DISCUSSION

5.1. Factors influencing temperature, oxygenation and transparency

Lake water temperature and its spatial and temporal variability are influenced by three categories of factors: geographical, morphometric and climatic. As reported above, our temperature profiles data are unsuitable to deduce which lake are colder and which cooler; even if altitude (through its effect on air temperature) and exposition are surely important factors. Thermal stratification and mixing in alpine lakes can be strongly influenced by the particular local conditions given by the size and the shape of the lake and of the catchment, the exposition, the fetch (the longest distance of the lake that the wind can act on uninterrupted by land) and other internal and external factors. As a consequence, direct measurements are needed to distinguish between dimictic and polimictic lakes.

Thermocline development is well described by the comparison between the early and the late summer measurements: during June-July survey, some thermal gradients are detectable and, just once, an inverse thermal stratification persists from wintertime in LILLET; however the lakes are generally still affected by low winter temperature, often elapsing just a few days since the ice melting. However it is in the last August-September survey that thermoclines are well developed and it is possible to distinguish between stratified and mixed lakes. Almost all profiles show depth thermal gradients and the surface temperature go always over 4 °C during the summer, but only the deeper lakes (NIVSUP, LILLET, MOTTA, LEYNIR, ROSSET) show clear thermoclines, while the highest surface temperature measured (nearly 16 °C) was in DJOUAN, the most shallow of the studied lakes.

Oxygen concentration increases during the study period, in particular in the deeper layers, probably because earlier measurements are still affected by oxygen depletion occurring in Winter below ice cover. In August and September, deeper, stratified lakes show maximum oxygen levels (higher than saturation) at the thermocline, which frequently acts as a barrier for algal vertical movements (Hansson 1996). As expected, relative depth (Z_r) resulted important in controlling stratification: considering the importance of maximum depth into account, small deep lakes with $Z_r > 4\%$ shows a greater resistance to wind mixing action (Wetzel & Likens 1991). Z_r exceeds this threshold in all studied lakes but LEITÀ and DJOUAN. In fact, in spite of its relatively large maximum depth (11 m), LEITÀ did not stratify in 2008.

Transparency is another important factor influencing the ecology of alpine lakes: the increase in Secchi depth transparency (Z_S) during the study period can be ascribed to the input of organic and inorganic materials carried to the lakes at snowmelt. We assumed the depth of penetration of 1% of the surface incident light to be 2.7 time Z_S ($Z_{<1\%} = 2.7 \times Z_S$) (Margalef 1983) even if this product is variable from 1.4 to 3 and more, depending on local conditions (Vollenweider 1969), but we used one of the highest values in literature to be cautious in describing photic conditions (Fig. 7). In winter, when snow over ice cover is thick enough, the whole water column can be in the dark.

5.2. Factors influencing water chemistry

The actual chemical composition depends on the interplay of several variables that are unique to each catchment area, including the initial chemical composition of precipitation, the amount and distribution of rain and snowfall (related to its proximity to coastal regions, industry, and climate), the nature of the surrounding catchment (related to topography, geology, soils, vegetation and to the contribution of groundwater), the influence of human activity and land use in the catchment, the influence of biotic community (Newman 1995; Berner & Berner 1996; Feng *et al.* 2001; Albert *et al.* 2002; Lee *et al.* 2008).

The multivariate statistical analysis output highlights both the importance of weathering process and of direct precipitation input: the first PCA axes is linked to weathering process and captures variability of pH and main ions concentrations (SO_4^{2-}, Ca^{2+}, K^+, F^-). PCA axis 2 captures Na^+, Cl^- and TP concentrations and could be interpreted as a component related to evapotraspiration or to distance from the sea (Mosello *et al.* 1991) and thus to precipitation. PCA axis 3 is related to TN, NO_3^-, mainly derived from rain (see the next paragraph), and TOC, originated by biological processes in soils and lakewater. The difference among the PCA axes 1 scores of lakes placed on different geological substrates sustains the importance of weathering; besides, the wider is the watershed, the greater is the amount of rain water that reaches the lakes and alters its chemistry, determining the positive correlation between catchment area (B) and PCA axis 3.

5.3. Acidification and atmospheric deposition

A number of studies confirmed that long-range transport of air-born pollutants, as N compounds and SO_4 = from intensively cultivated or industrial areas, will affect lakes in different remote areas of Europe (Allott *et al.* 1995; Kopáček *et al.* 2000; Evans *et al.* 2001; Wright *et al.* 2005). The emission of the Po Plain in Northern Italy gives an example; Po Plain is one of the most densely populated and industrialised regions in

Europe, from which air masses move towards the subalpine and alpine areas, where most of the precipitation occurs (Mosello *et al.* 2001).

Emission of sulphates and other acidic pollutants from anthropogenic sources results in their deposition on the earth's surface and in the lakes, affecting pH values. Being conservative, alkalinity is best indicator of sensitivity to acidification: values higher than 200 μeq L^{-1} are frequently considered higher enough to buffer lakewater against chronic acidification and acidity pulses (Goldstein & Gherini 1984; Turner *et al.* 1986); in our data set, only 4 samples show alkalinity values lower than this threshold: both samples taken in lake MOTTA , June sample in DRES and August sample in LOSERE. No lake alkalinity value lies below 20 μeq L^{-1}, that Mill & Schindler (1986) consider to be the survival limit for more sensible organisms.

Consistently, the minimum pH value is 6.95 (MOTTA), far from the limit of 6.0, under which damaging effects for organisms are often detectable (Raddum e Fjellheim 1984; Schindler *et al.* 1985; Mills & Schindler 1986), and far from high acidification value of 5.3, corresponding to which aluminium compounds toxicity adds up to the low pH toxic effects (Wright 1983).

As expected, pH generally shows its lower annual values at snowmelt, with the input of acidifying compounds (as NO_3) retained in the melting ice or snow (Camarero *et al.* 1995), and increases during the ice-free period. Our studied lakes can be considered as not affected by acidification, if compared with the data collected by Marchetto *et al.* (1995) during a four-year study (1988-1991) carried out in the Central Alps (Italy, Switzerland and Austria), where 68% of 413 alpine lakes had alkalinity values of less than 200 μeq L^{-1} and 36% of less than 50 μeq L^{-1}.

In spite of this, it is important to consider the role of watershed in setting the buffer capacity of lakes: in the areas covered by acidic rocks, some small watershed could host little buffered lakes and, on the other hand, it is sufficient that a marginal part of the catchment area may be covered by soluble basic rocks to cause high alkalinity levels (Mosello *et al.* 1991; Kamenik *et al.* 2001); this remark suggests not to generalize the obtained results as representative of the whole Park area, but to consider seriously the clear connection between lithology and hydrochemistry highlighted in the results. As an example, Giussani (1986) recorded very low alkalinity and pH levels (respectively 20 μeq L^{-1} and 5.86) in Lake Muanda (Soana Valley, in the south east of Gran Paradiso National Park), where rock lithology is acidic and the lakes are more directly exposed to the flux of pollutants originated in the industrial area around Turin.

Rogora *et al.* (2006) found a widespread decrease in the acidity of precipitation in the last 15-20 years as a consequence of the reduced emission of S compounds. In effect, European sulphur dioxide emissions increased after 1950, reaching their peak in the 1970s. According to emission control measures, gradual reductions took place in most of Western Europe during the 1980s (Mylona 1996; Tait & Thaler 2000). Thus, it is possible that the most sensitive among the studied lakes have been interested by acidification during the past, when sulphur emissions were higher than today.

Giussani *et al.* (1986), in a large surveys of Alpine lakes, measured pH values in LEITÀ and ROSSET, recording values of 7.8 and 7.7, respectively, slightly lower than the present values of 8.2 and 8.1, even if these lakes, because of their high alkalinity, show good acid neutralization capacity. More sensitive lakes could than have experienced larger effects.

The decreased sulphate deposition is consistent with the measured SO_4^{2-} concentration in the studied lakes: SO_4^{2-} levels are low and we find some strong correlations between SO_4^{2-} and other variables linked to weathering processes; as a consequence, the most of SO_4^{2-} content in the lakes can be attributed to weathering of rocks and soils bearing sulphur minerals, contrary to what occurs in a lot of lakes, where sulphate contents are almost of anthropic and marine origin; for example this is unlike the situation in Scandinavia, where acidification of lakes on a regional basis corresponds closely with the sulphur deposition pattern (Wright & Henriksen 1978; Neary & Dillon 1988).

On the contrary, studying the atmospheric input of N compounds in excess of the environmental retention capacity, Mosello *et al.* (2006) found that nitrate concentrations in rain have not dropped in the Alpine region, and ammonium has decreased significantly only in the Austrian sampling sites, still determining an increase in total nitrogen (TN) deposition. The two main factors influencing the final N concentration are atmospheric N deposition rates and the type of watershed which can determine both the share of nitrate in the pool of total N and its concentrations by soil and vegetation retention process (Kopàček 2000). Concentrations of N compounds can be used as an index of the impact of human settlement on remote lakes: when lakes are subject to low N input (<1 kg N ha^{-1} y^{-1}) nitrate (NO_3^-) concentrations are usually below the detection limit and organic nitrogen (ON) accounts for a substantial proportion of the total nitrogen (TN) content (Hedin *et al.* 1995; Kaushal & Lewis 2003; Rogora *et al.* 2008).

The negative correlation between the PCA axis 3, representing a gradient in nitrogen concentration, and LC confirms the importance of catchment in N soil retention process: N retention capacity of alpine sparse vegetation is lower than in prairies or forests. In the studied lakes, TN average level ranges between 0.08 and 0.35 mg L^{-1}, mainly accounted by inorganic nitrogen, in particular nitrate (up to 75% and 69%, respectively).

For comparison, a set of 35 alpine lakes, sampled in the Central Italian Alps (Ossola and Sesia Valleys, Piedmont region at an altitude between 1900 and 2700 m a.s.l.) in late summer, shows distinctly higher TN levels, ranging between 0.17 and 0.63 mg N L^{-1} (Rogora *et al.* 2003). But consistently with PNGP area, in the Central Alps, NO_3^- represents up to 70% of the total N content. High deposition values in that area results from combined effect of high amount of precipitation (Frei & Schär 1998) and N deposition among the highest in Europe (Rogora *et al.* 2001), originated by human activities in the Po Plain, bordering the alpine rim (Rogora *et al.* 2006).

However, seasonal patterns in water chemistry can be relevant (Tait & Thaler 2000) and, as described in the results, NO_3^- decreases from 0.20 to 0.16 (seasonal average values) during the study period and some differences are noticeable if we just compare data collected in early and late Summer, in the latter NO_3^- contribution to TN significantly decreases in a significant way (p <0.05) in all lakes but LILLET, MOTTA, NERODJ and LEYNIR, with an average contribution reduced from 69% to 59%.

Comparing data from Gran Paradiso National Park with data from remote mountain regions with low N deposition rates allows to consider long range anthropogenic impact.

Serra da Estrela is the main mountain area of Portugal and 16 lakes, located above the local tree line (between 1500 and 1800 m a.s.l.) were sampled in 1994-1995 to investigate their water chemistry in relation to atmospheric inputs (Boavida & Gliwicz 1996); no relevant emission source lie along the main trajectories of the air masses reaching this region and atmospheric deposition showed concentrations of IN (from 0.07 to 0.35 mg N L^{-1} as the sum of ammonium and nitrate) lower than the values commonly found for the Alps (0.8-1.0 mg N L^{-1}, Rogora *et al.* 2006). Considering an average precipitation amount of 2000 mm, N deposition in the Serra da Estrela should vary between 1.5 and 7 kg N ha^{-1} y^{-1}, compared to about 15 kg N ha^{-1} in Central Alps. Lakes in the Serra da Estrela showed TN concentrations comparable to those in the Gran Paradiso area (0.24 and 0.32 mg N L^{-1} as median and average value, respectively) but NO_3^- levels in this area are markedly lower, representing ON almost 90% of TN.

Moreover, examining data from non-European mountain areas, where N deposition rates are appreciably lower, it is possible to notice corresponding lower TN concentration: in 18 Andine lakes in northern Patagonia, low TN values (average value: 0.17 mg L^{-1}) are linked to low N deposition rate ranging between 0.7 and 1.0 kg N ha^{-1} y^{-1} and in 31 lakes in the Sagarmatha National Park (Khumbu-Himal region, Nepal), TN mean value in 1991-97 was 0.24 mg L^{-1} and N deposition rate was 0.3 kg N ha^{-1} y^{-1} (Tartari *et al.* 1998). ON dominated in both the Andine and Himalayan lakes, representing about 80% of the TN content of lake water.

TN levels of Gran Paradiso lakes are comparable with data collected in pristine areas slightly affected by N deposition, but the high relative contribution of IN to TN anyhow suggests that the area is interested by long range nitrogen transport.

Finally, the 12 Gran Paradiso studied lakes seem to be well preserved by acidification risk and this works in advantage of researchers who aim to stand out other chemical or ecological dynamics and local or global impacts; as a matter of facts acidification and other environmental threats will interact according to complex and site specific way (Wright & Schindler 1995; Schindler *et al.* 1996; Yan *et al.* 1996; Sommaruga-Wograth *et al.* 1997) generating additional complexity. In spite of this, little can be said about long range pollutants as heavy metals and POPs: the relative low detected TN concentration is not necessarily a synonym of a soft impact of long range pollutants, being the final nitrogen concentration dependent from retention process (closely related to catchment characteristics) (Rzychon & Worsztynowicz 2008) besides N deposition rates; moreover the dominance of IN on ON highlight that the lakes are interested by N deposition and probably by long range transport of pollutants produced in the urbanized area surrounding the massif.

5.4. Nutrients

TP concentration in Gran Paradiso lakes (1-13 μg L^{-1}, mean level = 4 μg L^{-1}) is an index of oligotrophic and ultraoligotrophic conditions (Wetzel 2001) and is consistent with data collected in the other mountain regions in Europe (2-7 μg L^{-1}; Psenner 1989; Marchetto *et al.* 1994; Camarero *et al.* 1995; Mosello *et al.* 1995; Skjelkvåle & Wright 1998; Kopàček *et al.* 2000; Cantonati *et al.* 2002), North America (2.5-15 μg L^{-1}; Schlinder 2000), South America (Rogora *et al.* 2006) and Asia (Tartari *et al.* 1998; Lacoul & Freedman 2005).

According to Redfield's ratio, in most of Gran Paradiso lakes, phosphorus is the phytoplankton growth limiting element, assuming a key role in biological processes and food-web dynamics; this determines that almost all the phosphorus in pelagic water is probably present as organic phosphorus in living or dead biomasses, due to a strong P uptake competition.

As discussed above, atmospheric N deposition enhances nitrate concentrations of lake water, but data collected in a variety of different habitats show that catchment features control total N concentration and the relative proportion of different N compounds (Marchetto *et al.* 1994; Kopàček 2000).

In Northern Italy, atmospheric deposition is an important source of nitrogen compounds. Even in remote sites in the Alps, nitrogen load can reach values as high as 14 kg ha^{-1} y^{-1} (Mosello *et al.* 1999). Episodic deposition of Saharan dust in Southern Europe can produce relevant input of particulate phosphorus to remote watershed, leading to an increase of algal productivity in remote lakes (Reche *et al*. 2009). These episodes have also been recorded in the Alps (Rogora *et al*. 2004), but the amount of phosphorus carried on an annual basis is relatively low.

In high mountain lakes in the Alps, TN:TP ratio generally reflects higher nitrate concentrations than in other kind of lakes (Rogora *et al*. 2008), due to the low N retention capacity of alpine sparse vegetation by comparison with prairies or forests (Marchetto *et al*. 1994; Kopàček 2000) and this is consistent with the high TN:TP ratio values calculated in the studied lakes. Moreover different rates in vegetation uptake are highlighted by strong relation between land cover and TN:TP ratio, with lower TN:TP ratios in watershed is dominated by forest, with high N retention power, and the lowest when it is dominated by bare rocks and glacier, with lower N retention power (Marchetto *et al*. 1994).

6. CONCLUSIONS

Our data show that the effects of the long-range transport of atmospheric pollutants in high mountain lakes in the Western part of the Gran Paradiso National Park is by far less significant than in Alpine lakes in the Central Alps. They could therefore usefully be used as control sites when studying the long term evolution of Alpine lakes to pollutants and their recovery. The low impact of human activity in these lakes, make them important as reference sites for comparing their relatively undisturbed biota with recovery lakes in other Alpine districts.

For this reasons, our data support the opportunity to carry out wider hydrobiological studies to pursue the National Park conservational goals, in order to be able to effectively protect these sensitive ecosystems. In particular, further studies are needed to identify the ecological impact of other human disturbance, such as fish introduction, hydropower exploitation of upstream streams and climate change.

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