

**GEOCHEMICAL AND ISOTOPIC INVESTIGATION
OF LAKES IN THE TRENTO PROVINCE (ITALY)**

**ÉTUDE GEOCHIMIQUES ET ISOTOPIQUES DE CERTAINS LACS
DANS LA PROVINCE DE TRENTO (ITALIE)**

**STUDIO GEOCHIMICO ED ISOTOPICO DI ALCUNI LAGHI
NELLA PROVINCIA DI TRENTO (ITALIA)**

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Abstract

We present the geochemical composition and the stable isotope signature ($^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$) of waters sampled from six lakes (Caldonazzo, Levico, Lases, Santa Colomba, Lamar and Santo) located in the Province of Trento. The chemical compositions invariably revealed a $\text{HCO}_3\text{-Ca}$ hydrochemical facies; however slight differences were observed among the lakes, in relation to the lithologies distinguishing each lakes' drainage basin. Elemental ratios and in particular the Rb/Sr provide a discriminative tool to recognize the rocks that have been weathered; for example this ratio is high in water that interacted with volcanic ignimbrites (rhyolites), and low in rocks that interacted with carbonate rocks. Many other trace elements were analyzed, thus providing baseline data, and only arsenic displayed concentrations higher than the legislative threshold defined for drinking water (10 $\mu\text{g/l}$), especially in Lake Levico (10-19 $\mu\text{g/l}$). As concerns the stable isotopes δD and $\delta^{18}\text{O}$, the obtained results approach the meteoric signature for waters sampled during the 2012 winter season. The waters sampled during two summers (2011 and 2012) displayed distinctive trends, reflecting the significant influence of evaporative processes. We emphasize that the annual differences recorded in the isotopic composition of distinct years are plausibly related to temperature changes and type of precipitation that recharged the lakes. In this light, the peculiar isotopic signature recorded in the year 2011 is possibly related to a significant snowy period, which greatly contributed to the lakes' water budget. Interestingly, waters from Lake Santa Colomba were systematically different from all the other samples, possibly due to more effective evaporative processes, or to the involvement of deep underground recharge including fossil waters.

Keywords: lakes, Province of Trento, geochemistry, stable isotopes

Résumé

Cet article résume l'étude géochimique et isotopique ($^{18}\text{O}/^{16}\text{O}$ et $^2\text{H}/^1\text{H}$) des eaux de six lacs (Caldonazzo, Levico, Lases, Santa Colomba, Lamar, et Santo) situées dans

la Province de Trento. Bien que la composition chimique de l'ensemble de ces eaux est toujours caractérisée par un faciès hydro-chimiques carbonate de calcium, des différences ont été observées dans les lacs séparés, par rapport à lithologies distinctes affleurant dans les bassins versants relatifs. Par exemple, le rapport Rb / Sr est élevé dans les lacs du bassin qui se dégagent des roches volcaniques ignimbrite (rhyolites) et faible dans les lacs dans le bassin qui prévaut affleurement de roches carbonatées. De nombreux oligo-éléments ont été analysés pour définir les niveaux de fond de substances potentiellement toxiques (métaux lourds). Parmi ceux-ci, la seule arsenic dépasse parfois la limite de concentration législatif défini pour l'eau potable ($10 \mu\text{g} / \text{l}$), en particulier dans le lac Levico ($10\text{-}19 \mu\text{g} / \text{l}$). Quant à l'analyse isotopique ($\delta\text{D} - \delta^{18}\text{O}$), dans les eaux échantillonnées au cours de la saison de l'hiver 2012 sont les valeurs observées en fonction de la composition de l'eau de pluie, tandis que dans les saisons estivales 2011 et 2012, les valeurs des isotopes diffèrent de celles qui sont typiques de l'eau météorique, suggérant importante phénomènes d'évaporation. Les valeurs qui se trouvent dans différents rente doivent être interprétés en tenant compte du fait que les fractionnements isotopiques sont affectés par la température, mais aussi par le type de précipitations qui contribuent à la recharge. La composition isotopique du lac de Santa Colomba est, cependant, toujours distincte de celle que l'on trouve dans d'autres lacs, peut-être à une plus grande efficacité des processus d'évaporation, ou peut-être en raison de l'implication de la recharge des profond eaux souterraines dans ce lac.

Mots clés: lacs, Province de Trento, géochimique, analyse isotopique

Riassunto

Questo articolo sintetizza lo studio geochimico ed isotopico ($^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$) delle acque di sei laghi (Caldonazzo, Levico, Lases, Santa Colomba, Lamar e Santo) localizzati nella provincia di Trento. Benché la composizione chimica di tutte queste acque sia sempre caratterizzata da una facies idro-chimica carbonato-calcica, differenze sono state osservate nei distinti laghi, in relazione alle distinte litologie affioranti nei relativi bacini di drenaggio. Per esempio il rapporto Rb/Sr risulta elevato nei laghi nel cui bacino affiorano rocce vulcaniche ignimbritiche (rioliti), e basso nei laghi nel cui bacino prevale l'affioramento di rocce carbonatiche. Molti elementi in traccia sono stati analizzati per definire i tenori di fondo di sostanze potenzialmente tossiche (es. i metalli pesanti). Fra questi, il solo arsenico talvolta eccede il limite di concentrazione legislativo definito per le acque potabili ($10 \mu\text{g}/\text{l}$), specialmente nel Lago di Levico ($10\text{-}19 \mu\text{g}/\text{l}$). Per quanto riguarda le analisi isotopiche ($\delta\text{D} - \delta^{18}\text{O}$), nelle acque campionate durante la stagione invernale 2012 si osservano valori conformi alla composizione delle acque meteoriche, mentre nelle stagioni estive 2011 e 2012 i valori isotopici divergono da quelli propri delle acque meteoriche, suggerendo importanti fenomeni evaporativi. I valori che si rinvergono nelle diverse annualità vanno interpretati, tenendo in considerazione che i frazionamenti isotopici sono influenzati dalla temperatura ma anche dalla tipologia di precipitazioni che concorrono alla ricarica. La composizione isotopica del Lago di Santa Colomba è invece sempre distinta da

quella che si rinviene negli altri laghi, forse per una maggior efficienza dei processi evaporativi, o forse per il coinvolgimento di profonde acque fossili nella ricarica di questo lago.

Parole chiave: laghi, Provincia di Trento, geochimica, isotopi stabili

Introduction

This study considered the geochemical composition and the stable isotope signature ($^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$) of water as a tool to obtain information concerning chemical budgets and water fluxes in six lakes located in the Italian Southern Alps of the autonomous Province of Trento (Fig. 1).

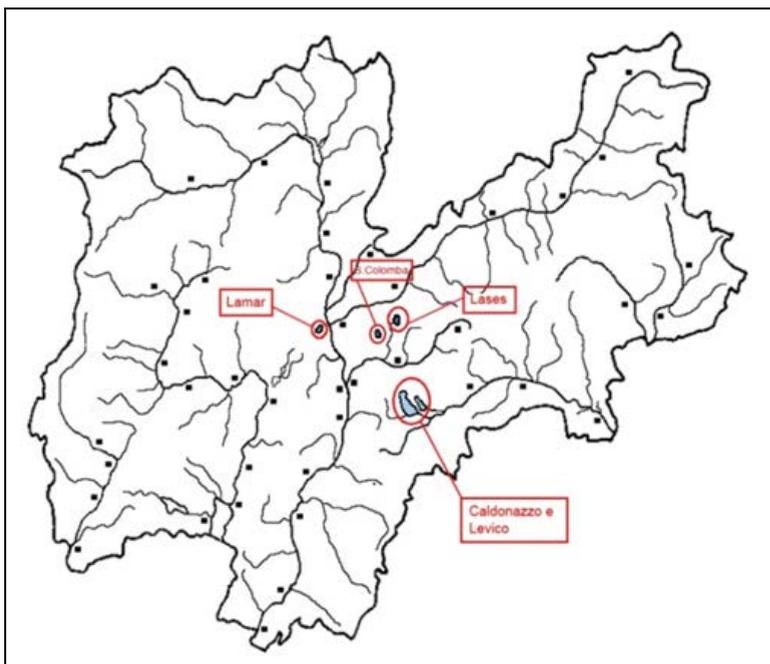


Figure 1
Location of the studied lakes in the Province of Trento (Northern Italy).

The geochemical composition of lake water is controlled mainly by three mechanisms: recharge, reactions of rock weathering and dissolution, and evaporation-precipitation processes. According to the dominant mechanism, lake water shows a characteristic chemical composition.

The isotopic composition of oxygen and hydrogen of meteoric water (expressed as $\delta^{18}\text{O}$ and δD) is related to (temperature-dependent) fractionation processes occurring during the hydrological cycle, and each geographic site displays a specific precipitation composition, a fingerprint related to the latitude, altitude, distance from the sea and orographic influences, but is also affected by seasonal variations (Clark and Fritz, 1997). Then, the isotopic fingerprint can be potentially affected by subsequent evaporation processes that are effective especially in

summer (Gat, 1995; Rozanski et al., 2000; Froehlich et al., 2005; Kebede et al., 2009).

On the other hand, the chemical composition of the dissolved components is related to a) the specific lithologies outcropping in the area; b) the effectiveness of the weathering processes, which in turn are related to the existing climatic conditions; and c) anthropogenic activities that superimpose the natural geochemical signature.

This contribution presents data on the following lakes: Caldonazzo, Levico, Lases, Santa Colomba, Lamar and Santo, which were sampled in summer 2011, summer 2012 and winter 2012. Results should be considered as an instantaneous “snapshot” to be compared with the existing data (Flaim et al., 2013; Perini et al., 2009) and possibly with future investigations to provide a geochemical hydro-archive useful to understand possible environmental evolutions.

Study approach

Study sites

We studied two large lowland lakes (L. Levico and L. Caldonazzo) and four small mid-altitude lakes (L. Santa Colomba, L. Lases, L. Lamar and L. Santo) characterized by different hydrological regimes. The drainage basins of these lakes are characterized by extremely heterogeneous lithologies, as the area includes Paleozoic metamorphic and igneous rocks as well as Mesozoic carbonate sediments, all of which were variously folded and faulted during the Alpine orogenic cycle. These rocks have been partially covered by Quaternary deposits and variously molded by exogenous processes, including glacial activity. Geological and geomorphological features, as well as climatological constraints of the area, influence the current water budget and the heat distribution, in turn influencing chemical, physical and biological processes of the studied lakes that are strictly related to these characteristics.

Lakes Caldonazzo and Levico in the northern part of the Valsugana valley are mainly located on Hercynian metamorphic rocks (mainly phyllites) within basins dammed by alluvial fans; Lake Lases, in the Cembra Valley, sets on Permian rhyolitic ignimbrites and is dammed by moraine deposits; Lakes Lamar and Santo are located in a glacial basin dammed by alluvial fans in an area exclusively characterized by Mesozoic carbonate rocks. Lake Santa Colomba is a small lake that doesn't display surface tributaries; it is located on Mount Calisio, surrounded by rhyolitic ignimbrites, marls and limestone, peculiarly crossed by tectonic discontinuities.

Sampling and in situ analyses

Water sampling was carried out during three different campaigns: summer 2011, summer 2012 and winter 2012, but the winter sampling of Lakes Santa Colomba and Santo was complicated by ice-cover. Water samples were taken at the central site, over the deepest part of each lake. Lakes Levico, Caldonazzo and Lases were sampled in two different sites in order to detect possible chemical-isotopic

variations within the lake. The coordinates of the sampling sites were registered with a portable GPS Magellan Platinum. The water was filtered in the field with 0.45 µm filters and stored in: (1) two 50 mL polyethylene bottles, one for anions determination, and the other for analysis of δ¹⁸O-δD stable isotopes; (2) one 50 mL polyethylene 50 bottle in which the sample was acidified and stabilized with concentrated Suprapur HNO₃ for the analysis of cations and trace elements. Temperature, pH and electric conductivity were measured *in situ* with EC TEST 11 (OAKLON INSTRUMENTS) and HI 9813-5 (HANNA INSTRUMENTS) probes. Alkalinity was determined *in situ* with HI 3811 alkalinity kit (HANNA INSTRUMENTS).

Major ions, trace elements and isotopes analyses

Analyses were carried out at the Department of Physics and Earth Sciences of The University of Ferrara. Major cations and trace elements were detected with inductively coupled plasma mass spectrometry (ICP-MS) with the X Series (Thermo-Scientific) spectrometer. Major anions were determined by ion chromatography using DIONEX ICS-1000 equipped with a self-sampler. The ¹⁸O/¹⁶O and ²H/¹H of water were determined by laser absorption spectrometry using the CRDS LOS GATOS LWIA 24d isotopic analyzer. Certificated standards were periodically used to calibrate measurements and to verify analytical precision and accuracy.

Results

In situ parameters

Physico-chemical parameters measured *in situ* are reported in Table 1. The temperatures of summer 2011 were slightly lower than those of summer 2012; the lowest temperatures were obviously recorded in winter 2012.

Table 1. *Physical and chemical parameters measured in situ.*

Lakes	Summer 2011			Summer 2012			Winter 2012		
	T (°C)	pH	Ec (µS/cm)	T (°C)	pH	Ec (µS/cm)	T (°C)	pH	Ec (µS/cm)
<i>Levico</i>	25.8	8.6	280	26.5	8.6	290	5.9	7.9	315
<i>Caldonazzo</i>	25.1	9.0	280	26.3	8.8	315	6.6	8.1	360
<i>Lases</i>	22.5	8.6	190	24.6	8.7	200	4.8	8.0	225
<i>S.Colomba</i>	24.0	8.8	220	24.4	8.7	240	0.8	7.5	220
<i>Santo</i>	20.6	8.5	280	23.7	8.4	330	-	-	360
<i>Lamar</i>	-	-	-	22.9	8.3	300	7.0	8.0	-

The pH values ranged from 8.3 to 9.0 for the summer 2011, from 8.3 to 8.8 for the summer 2012 and from 7.5 to 8.1 for winter 2012, reflecting lower algal activity in winter. Caldonazzo showed the highest values of pH in all the sampling seasons. The electric conductivity ranged from 190 to 280 µS/cm for summer 2011, from 200 to 320 µS/cm for summer 2012 and from 220 to 360 µS/cm for winter 2012.

Conductivity increased during the cold season in all lakes except L. Santa Colomba. Possibly, during winter time the lower algal activity allows a greater amount of ions in solution.

Major and trace element compositions

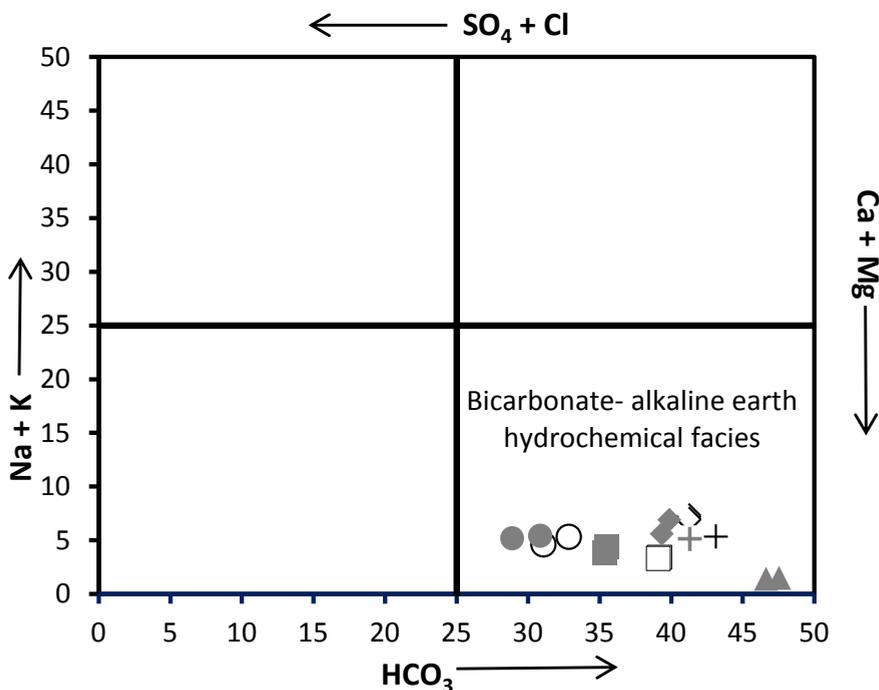
Chemical analyses of lakes are presented in Table 2. A preliminary observation revealed that Total Dissolved Solids (TDS) decreased with altitude, reflecting the length of the path flows of water to the lakes.

Table 2. Major and trace element analyses of lake waters expressed as mg/l. A more complete set of trace element analyses including Al, Fe, Mn, Ni, Cu, Zn, Se, Cd, Sb, Pb, U can be provided upon request to the corresponding Author (bncglc@unife.it); n.d.= not detected; n.a.= not analysed.

Lakes	Summer 2012					
	F	Cl	NO ₃	SO ₄	HCO ₃	Ca
<i>Levico</i>	0.4–0.76	7.4–7.7	1.2 – 1.7	41-42	90-105	29-32
<i>Caldonazzo</i>	0.18–0.21	7.5–7.8	0.14-0.15	27-28	117-118	30-34
<i>Lases</i>	0.12–0.21	4.8 – 5.1	0.8–1.3	8.9–9.1	74-78	28-34
<i>S.Colomba</i>	0.08	11.0	n.d.	1.6	100	31
<i>Santo</i>	0.06	2.5	2.8	5.1	150	41
<i>Lamar</i>	0.06	2.0	2.4	4.8	185	37
Winter 2012						
	F	Cl	NO ₃	SO ₄	HCO ₃	Ca
<i>Levico</i>	0.64–0.74	6.9–7.0	1.8–1.9	40-45	99-102	40 - 47
<i>Caldonazzo</i>	0.18–0.19	7.0–7.1	0.9–1.1	25-26	150-153	43 - 46
<i>Lases</i>	0.11–0.12	4.3–4.6	1.9–2.1	8.5-8.6	75-84	27 - 31
<i>S.Colomba</i>	0.06	7.3	0.3	2.9	88	25
<i>Lamar</i>	0.06	2.6	3.8	4.5	165	n.a.
Summer 2012						
	Mg	Na	K	Rb	Sr	As
<i>Levico</i>	7.0–7.4	4.7–5.0	1.3–1.9	0.001	0.08–0.09	0.014–0.019
<i>Caldonazzo</i>	21.2–21.3	5.8–6.3	1.5–1.7	0.001	0.07–0.08	0.008–0.009
<i>Lases</i>	3.0–3.7	5.0–5.5	1.0–1.4	0.004	0.11–0.14	0.007–0.008
<i>S.Colomba</i>	13.5	6.5	0.8	0.002	0.06	0.005
<i>Santo</i>	13.5	1.9	0.4	n.d.	0.13	0.012
<i>Lamar</i>	15.4	2.0	0.5	0.001	0.12	0.010
Winter 2012						
	Mg	Na	K	Rb	Sr	As
<i>Levico</i>	8.7-8.9	6.1-6.4	1.7–1.8	0.001	0.09-0.10	0.013-0.018
<i>Caldonazzo</i>	19.9–21.2	5.4-5.7	1.2–2.2	0.001	0.07–0.08	0.008-0.012
<i>Lases</i>	2.9 – 3.0	5.6-5.7	1.0-1,5	0.003	0.11-0.12	0.008-0,009
<i>S.Colomba</i>	9.0	4.8	1,0	0.003	0.042	0.005
<i>Lamar</i>	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

More detailed insights on the lake dynamics were obtained by the elaboration of the analytical data. The notional Gibbs diagram showed that all waters have intermediate values of TDS and low Na/(Na+Ca) ratios, suggesting that geochemistry is mainly controlled by weathering processes. The Langelier-Ludwig classification diagram (Fig. 2) showed that the hydrochemical facies of all the studied lake waters was HCO₃-Ca. Seasonally, there were slight chemical variations in the different lakes.

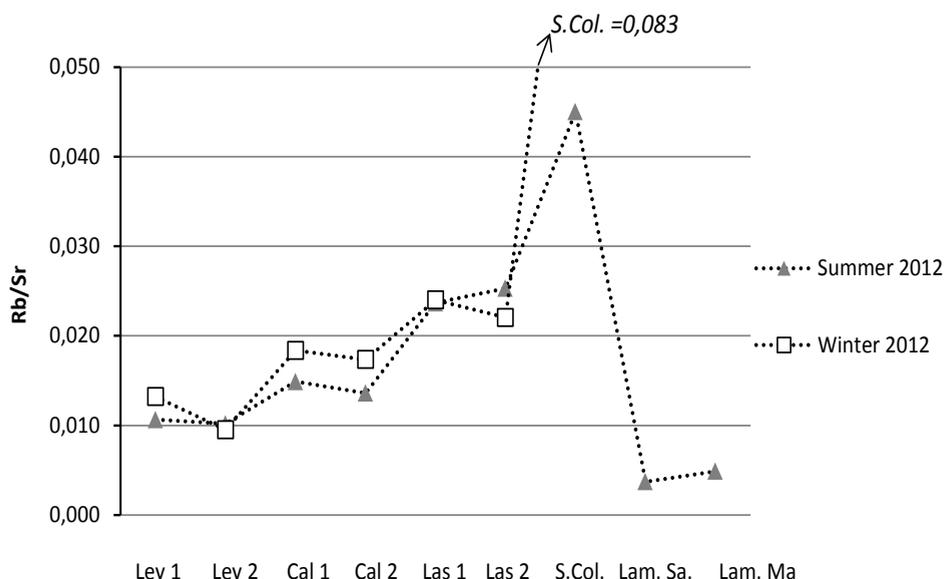
Figure 2. Langelier-Ludwig classification diagram useful to define the hydrogeochemical facies of the studied waters; x axis = $[HCO_3 / (HCO_3 + SO_4 + Cl)] * 50$, y axis = $[Na + K / (Na + K + Ca + Mg)] * 50$, starting from compositions expressed as milliequivalents per liter. Symbols: Caldonazzo, squares; Levico, circles; Lases, diamonds; Lamar and Santo, triangles; Santa Colomba, crosses. grey symbols refer to the summer 2012; empty symbols refer to the winter 2012.



Lakes Lamar and Santo showed the highest concentrations of calcium and bicarbonates in agreement with the dolomitic rocks that characterize their basin. Lake Levico was the richest in sulphate (>40 mg/l) due to the thermal springs characterizing its drainage basin and/or to the presence of sulphides (pyrite) in the local lithologies. Nitrate levels never exceeded the legislative threshold defined for drinking water (50 mg/l) and were higher during the winter season. This was plausibly related to a) nitrate dissolved in the rain b) subsequent surface runoff

from the surrounding agricultural lands and c) lower algal activity during winter. Many trace elements were analyzed in order to define backgrounds of potentially toxic compounds. Only arsenic episodically displayed concentrations exceeding the thresholds defined for drinking water, in particular in Lake Levico (As = 10-19 µg/l). However, although these arsenic concentrations exceeded the legislative threshold for potable water (10 µg/l), they were not due to anthropogenic contamination but related to the above-mentioned presence of thermal springs and/or to As-bearing sulphides in the local lithologies. Emphasis is given to the use of elemental ratios in order to characterize the nature of the rocks outcropping in the drainage basin of each lake. For example, the elemental ratio between rubidium and strontium effectively discriminates the lithologies that mainly interact with water (Fig. 3). Rb/Sr ratio was higher for the lakes located in ignimbric volcanic rocks (Lakes Lases and Santa Colomba), lower in the Lakes Lamar and Santo located in carbonatic rocks, and intermediate L. Levico and L. Caldonazzo, mainly lying on metamorphic lithologies.

Figure 3 – The rubidium/strontium ratio is influenced by the outcropping lithologies. It is high in Lakes Lases (Las 1, Las 2) and Santa Colomba (S.Col.) that reflect interactions with ignimbrite volcanic rocks (rhyolites), whereas it is low in Lakes Lamar and Santo (Lam. Sa., Lam. Ma) that interacted exclusively with carbonate rocks. It is intermediate in Lakes Caldonazzo (Cal 1, Cal 2) and Levico (Lev 1, Lev 2).



Isotopes

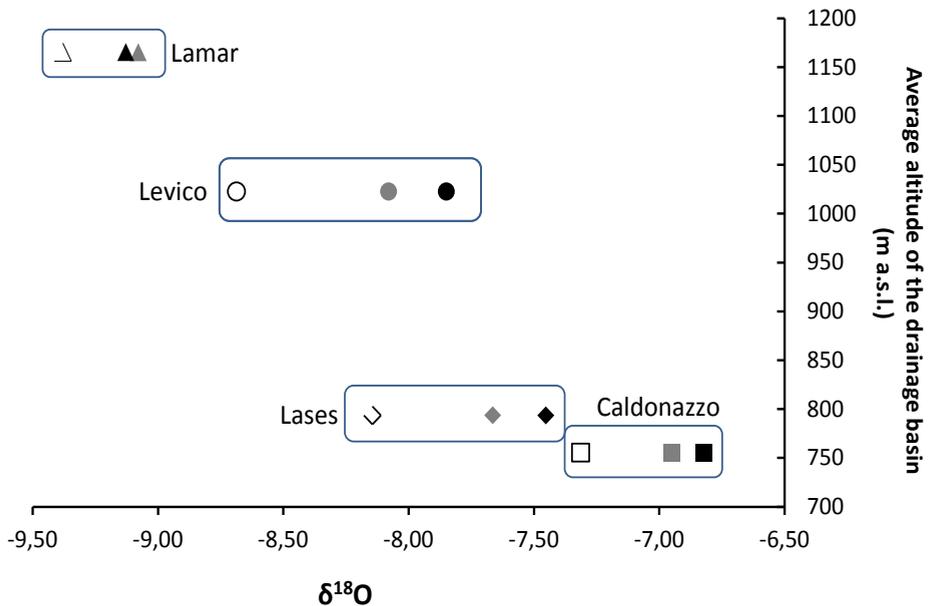
The isotopic δD - $\delta^{18}O$ compositions of the studied lake waters were measured and reported in Table 3.

Table 3. Oxygen and hydrogen isotopic analyses expressed as δ units respect to SMOW (Standard Mean Oceanic Water); n.a. = not analysed.

Lakes	Summer 2011		Summer 2012		Winter 2012	
	$\delta^{18}\text{O}$	δD	$\delta^{18}\text{O}$	δD	$\delta^{18}\text{O}$	δD
<i>Levico</i>	-8.0	-67.8	-7.7	-55.8	-8.5	-59.0
<i>Caldonazzo</i>	-6.9	-62.4	-6.8	-50.9	-7.4	-53.4
<i>Lases</i>	-7.6	-66.6	-7.4	-53.7	-8.1	-60.4
<i>S.Colomba</i>	-3.9	-53.4	-3.5	-37.9	-7.1	-55.5
<i>Santo</i>	-9.1	-75.5	-8.6	-62.4	n.a	n.a
<i>Lamar</i>	n.a	n.a	-9.1	-64.0	-9.4	-66.9

A comparison with existing data (Flaim et al., 2013 and references therein) showed for Lakes Levico, Caldonazzo, Lases and Lamar reasonable agreement, whereas no reference exists for Lake Santa Colomba. Comparing the isotopic fingerprint of specific lakes, we observed a good relation between the isotopic compositions and the average altitude of the drainage basin of each lake (Fig. 4).

Figure 4 – The oxygen isotopic composition of water of the studied lakes expressed as $\delta^{18}\text{O}$ values were progressively more negative for lakes characterized by higher altitude of the drainage basin (average altitude of the catchment areas were calculated with Google Earth). Symbols: Caldonazzo, squares; Levico, circles; Lases, diamonds; Lamar and Santo, triangles; black symbols refer to the summer 2011; grey symbols refer to the summer 2012; empty (white) symbols refer to the winter 2012. Lake Santa Colomba that did not follow the observed trend is not plotted (see text for further explanation).



In particular, the isotopic compositions were progressively lighter (i.e. more negative δD - $\delta^{18}O$) for the lakes characterized by higher altitude of the catchment. Lake Santa Colomba represented an exception, because the isotopic composition of its water deviated from the trend seen in the other lakes. The isotopic results were also reported in the notional δD vs $\delta^{18}O$ diagrams (Fig. 5) where the compositions of the studied lakes were compared with the global meteoric line proposed by Craig (1961) and the meteoric line proposed for northern Italy by Longinelli and Selmo (2003).

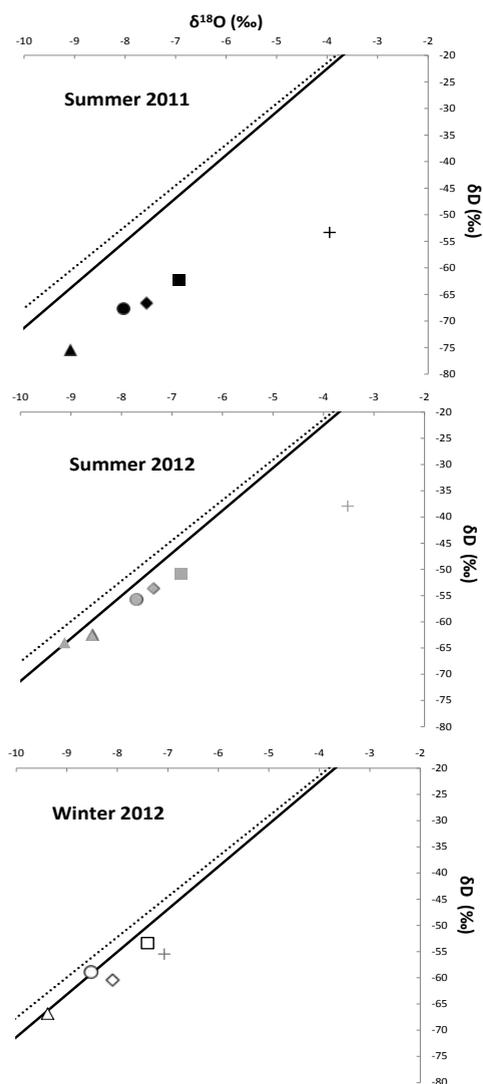


Figure 5

$\delta^{18}O$ vs δD diagrams reporting the water composition of the studied lakes compared to the global meteoric water line (black line; Craig, 1961) and the Northern Italy meteoric water line (dotted line; Longinelli and Selmo, 2003).

Symbols:

Caldonazzo, squares;

Levico, circles;

Lases, diamonds;

Lamar and Santo, triangles;

Santa Colomba, crosses.

While the water of the studied lakes sampled during the winter 2012 approached the above mentioned meteoric lines, the water sampled during the summer periods were aligned along distinctive linear trends, reflecting the significant influence of evaporative processes. We emphasize that the annual differences recorded in the isotopic composition of distinct years are plausibly related to regional and local climatic changes and type of precipitation (rain or snow) that recharged the lakes (Gat et al., 2001). In this light, the peculiar isotopic signature recorded in the year 2011 was possibly related to a significant snowy period, which greatly contributed to the lakes' water budget.

It has to be noted that Lake Santa Colomba systematically diverged from all the observed trends; considering that this lake is characterized by a) absence of surface water inflows and outflows, which limit water circulation and b) higher TDS during summer season, we suspect that this isotopic fingerprint is the result of more effective evaporative processes. An alternative (speculative) hypothesis implies that Santa Colomba is fed by deep fossil water having an isotopic composition different from the current-day meteoric components that upraise along the tectonic discontinuities observed in the area.

As concerns the relationship between isotopic composition and concentration of the dissolved ions, it is interesting to note that a reliable negative correlation was observed between nitrate concentrations (mg/l) and the δ values; this occurred because a high amount of precipitation tends to lower the δ values and increases the nitrate concentrations, mainly as result of soil leaching. Moreover, with higher temperatures algal activity increases (metabolizing nitrates) and the δ values increase as a result of evaporation. A good positive correlation is observed between chlorides (mg/l) and the δ values, possibly due to evaporation processes that ultimately lead to an increase of the concentration of chlorides in water and to higher δ values.

Conclusion

Summarizing, this geochemical and isotopic study contributes to a better understanding of the hydrodynamics of the studied lakes and increases the scarce isotopic database. The recording of similar data can be considered as a “hydro-archive” useful to define geochemical backgrounds and to evaluate ongoing environmental changes (Zuppi and Sacchi, 2004), and therefore should be integrated and implemented by future studies. The data also suggest that the isotopic fingerprints of lake water are influenced by both regional climatic changes and micro-climatic variations that have to be considered at the scale of the single drainage basins.

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