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Recent trends in chloride and sodium concentrations in the deep subalpine lakes (Northern Italy)

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Abstract

A growing concern exists about the effects of chloride (Cl) on freshwater systems. Increasing Cl concentrations have been observed in the last few decades in several rivers and lakes, mainly in northern countries. In Italy, present levels and temporal changes of sodium (Na) and Cl in water bodies have rarely been assessed. Based on long term data for the lakes of the subalpine district in Italy (Maggiore, Lugano, Como, Iseo, Garda), we analyzed trends affecting Cl and Na concentrations during the last 25 years, with the aim of identifying temporal changes and assessing possible causes. An in-depth analysis is presented for Lake Maggiore. Positive temporal Na and Cl trends were evident in all studied lakes, with the trends increasing since early 2000's. Data for Lake Maggiore tributaries showed a clear seasonality (higher values in winter and early spring). The NaCl used as road de-icing agent, together with Cl discharge from wastewater treatment plants, were identified as the main causes for the observed trends.

Chloride concentrations in the lakes are below the threshold limit for reduced water quality and below concentrations known to harm aquatic biota. However, considering the relevance of deep subalpine lakes, representing almost 80 % of the total freshwater volume in Italy, these trends indicate an important chemical change, which warrants further analysis.

Keywords: deep subalpine lakes, water chemistry, long-term trends, NaCl

Introduction

In the recent period, there has been a growing concern about the possible effects of increasing chloride (Cl) concentration in surface waters. High Cl concentration can negatively affect aquatic life as documented in Tuchman et al. 1984, Sanzo and Hecnar 2006, Nielsen et al. 2003, and Karraker et al. 2008. The problem posed by road-salt runoff has been recognised since the 1960s (Bubeck et al. 1971; Sonzogni et al. 1983). Increasing Cl loadings associated with road salting has been observed in several lakes and rivers in Europe and US (Löfgren 2001; Ruth 2003; Thunqvist 2003; Novotny et al. 2008, 2009; Chapra et al. 2009; Corsi et al. 2010). In most cases, the agent used is sodium chloride (NaCl), which is highly soluble and conservative; therefore runoff water can reach surface waters. Furthermore, cationic exchange traps sodium (Na) in the soil, leaving Cl to pass down to the ground water, where it remains (Ramakrishna and Viraraghavan 2005).

A further source of Cl to surface water is wastewater treatment. Sewage treatment plants discharging directly into the lakes or into lake tributaries contribute to the total Cl input. Chloride salts as $AlCl_3$ and $FeCl_3$ are used in municipal wastewater treatment plants for removal of suspended particles and bacteria and to enhance the removal of phosphorus, respectively. In addition to these sources, farming and solid waste incineration also act as Cl inputs to water bodies (Canadian Council of Ministers of the Environment 2011).

Most of the studies on Cl enrichment of lakes and rivers and its effect on water quality have been performed in cold climate regions, where low winter temperature and ice-freezing events lead to an extensive use of de-icing salts (Kaushal et al. 2005; Corsi et al. 2010). Much of the research has also focused on water environments in urban (e.g. Godwin et al. 2003; Ruth 2003) or metropolitan areas (Novotny et al. 2009). Beside the direct effects on the biota, Cl can affect lake water quality by increasing the transport and bioavailability of heavy metals (Backstrom et al. 2004), which are also harmful for aquatic species. Increased Cl or heavy metal concentrations may limit or delay natural mixing events, with depletion of oxygen levels of deep waters (Jones and Jeffrey 1992).

Sodium and Cl represent a minor part of the dissolved ions in surface water bodies in Italy and, to our knowledge, major effects of these ions on water quality of Italian water bodies have never been described. Due to the general absence of evaporitic deposits, natural sources of these ions are atmospheric deposition and weathering of silicate minerals in the catchments. Regarding anthropogenic sources, the main contributors are metabolic waste from civil use and industrial discharge. Thus road salt may be the most relevant source of these ions to surface waters in the northern part of the country, especially in mountain catchments, where urban or industrial discharge are of minor importance.

To our knowledge, temporal changes of Na and Cl concentrations in surface water bodies in Italy have never been assessed, mostly due to the limited availability of long-term data series of these ions. Although long-term series of chemical data for the lakes of the subalpine district (Maggiore, Lugano, Como, Iseo and Garda) exist, monitoring of lakes has been mainly performed with the aim of assessing trends in nutrient concentrations in relation to eutrophication processes (e.g. Salmaso et al. 2007, Salmaso and Mosello, 2010). Large and deep lakes, as those considered in this study, have long water renewal time and show delayed response to changing inputs. For this reason it is particularly important to assess long-term chemical changes in their water and investigate the drivers of these changes.

In this paper, we analyzed long-term series of Na and Cl concentrations in the deep subalpine lakes during 1988-2013. Our hypotheses were that (i) Cl concentrations have increased in the lakes in the last 25 years, and (ii) road salts played a key role in the patterns and variability of Na and Cl concentrations. An in-depth analysis for Lake Maggiore is presented; high frequency lake data and loading data from the main tributaries are discussed.

2. Study lakes and methods

2.1 Study sites

The deep subalpine lakes (DSL) (Maggiore, Lugano, Como, Iseo and Garda, Fig. 1) constitute the most important water district in Italy, located south of the Alps, in one of the most densely populated and highly productive areas of the country. They represent an essential strategic water supply for agriculture, industry, fishing, and potable use and are an important resource for recreation and tourism.

The surface of the drained area (Table 1) is 15,536 km², about 20 % of the whole River Po watershed, the largest and most important river in Italy. From a hydrographic point of view, the outflow of DSL contribute about 40 % of the River Po discharge, because of higher precipitation in their watersheds, due to the orographic effect of the Alps (Salmaso and Mosello 2010). Precipitation shows a gradient from west to east, with the highest value of 1703 mm for the watershed of Lake Maggiore and the lowest (1199 mm) for Lake Garda. This aspect and the ratio between watershed surface/lake volume, account for the differences existing in the hydrology of the five lakes, as highlighted from the theoretical water renewal time, ranging from 26.6 years for Lake Garda, to 4.1-4.5 for lakes Maggiore, Como and Iseo (Table 1).

The importance of DSL is even higher in terms of water volume, which is 121 km³, about 80 % of the total freshwater volume in Italy, including artificial lakes (Marchetti et al. 1992). Their maximum depth, ranging from 251 to 410 m (Lake Iseo and Como, respectively), and specific morphological and climatic conditions, determine the difficulty to reach a full thermal and chemical homogenization of the water every year (oligomixis). In fact, the complete winter

overturn can only occur during particularly cold and windy winters and is therefore a rather uncommon event. For this reason the DSL are classified as holo-oligomictic (Vollenweider 1975; Ambrosetti and Barbanti 1992, 1999). Complete overturn is also prevented by density gradients related to chemical stratification, as it has been the case for several decades in the northern basin of Lake Lugano and in Lake Iseo (Barbieri and Simona 2001; Simona 2003; Leoni et al. 2014). The deepest basin of Lake Lugano constitutes an extreme situation from this point of view: for years it showed meromictic characteristics due to both the morphology of the lake and its chemical and trophic conditions (Barbieri and Polli, 1992). Also in the case of Lake Iseo full overturn did not occur for several years, resulting in anoxia in the deepest water layer (Garibaldi et al. 1999, 2003).

As regards lithology, the major part of the Lake Maggiore basin is composed of metamorphic and igneous rocks (calcareous rocks are present in small amounts only in the eastern part). Lake Lugano watershed is dominated by calcareous rocks, with outcrops of quartziferous porphyries and metamorphic rocks. Igneous and sedimentary rocks prevail in the northern and southern part of the Lake Como watershed, respectively. The southern part of the drainage basins of Lakes Garda, and at a less extent of Lake Iseo, are characterized by the presence of sedimentary rocks with crystalline formations in the most northerly sections (Vollenweider 1965; Bonomi et al. 1979; Ambrosetti and Barbanti 1997).

Population density in the DSL catchments ranges between 82 and 137 inhabitants per km² (Table 1), but it may be higher when tourists are included. For instance, it has been calculated that population density in Lake Maggiore area increases from 114 to 150 inhabitant km² when tourists are included (CIPAIS 2003).

The DSL have been monitored since the 1950s, mainly in the framework of eutrophication studies. Several papers gave a synoptic view of algal nutrients trends and trophic evolution of these lakes (Salmaso et al. 2007, 2014; Salmaso and Mosello 2010). However, major ion concentrations were rarely considered (Vollenweider 1975; Manca et al. 1992).

Due to their long-term series of chemical, biological and ecological data, the DSL have been included in the LTER Europe network (www.lter-europe.net).

Table 1 Morphometric and hydrological characteristics of the deep subalpine lakes (DSL) in Northern Italy

Parameter	Unit	Maggiore	Lugano	Como	Iseo	Garda
Lake altitude	m a.s.l.	193	271	198	186	65
Lake area	km ²	213	28	146	62	368
Maximum depth	m	370	288	410	251	350
Mean depth	m	178	171	154	123	133
Volume	km ³	37.5	4.69	22.5	7.57	49.03
Catchment area	km ²	6599	297	4508	1842	2290
Catchment mean altitude	m a.s.l.	1429	786	1569	1272	966
Catchment max altitude	m a.s.l.	3554	2245	4049	4633	3556
Mean outflow discharge	m ³ s ⁻¹	291.3	12	158	58.7	58.4
Renewal time	years	4.1	12.4	4.5	4.1	26.6
Cryptodepression	m	177	17	212	65	285
Population density	inhab km ²	114	137	95	94	94

Fig. 1

Research on Lake Maggiore and Lake Lugano, with catchments shared between Italy and Switzerland, have been carried out more systematically and with greater continuity than for the other lakes since 1978, because of the support of International Commission for the Protection of Waters between Italy and Switzerland (CIPAIS; CNR-ISE 2013). Fourteen tributaries of Lake Maggiore have been systematically sampled since 1978 to evaluate algal nutrients and main ion loadings into the lake (Mosello et al. 2001). Main morphometric characteristics of Lake Maggiore tributaries and their watersheds are presented in Table 2.

Table 2 Main morphometric characteristics of Lake Maggiore tributaries and their watersheds.

Tributaries (acronyms)	Mean altitude (m a.s.l.)	Length (km)	Catchment area (km²)	Area/Length (km)	Annual average discharge (1978-2011) (m³ s⁻¹)
Ticino inlet (Tic)	1720	90.2	1616	17.9	64.69
Verzasca (Ver)	1611	33.3	237	7.1	-
Maggia (Mag)	1550	55.9	926	16.6	-
Cannobino (Can)	1057	27	110	4.1	6.17
San Giovanni (Sgi)	914	17.6	61	3.5	2.29
San Bernardino (Sbe)	1228	29.2	131	4.5	7.02
Toce (Toc)	1570	80.1	1547	19.3	63.16
Strona (Str)	800	28.4	224	7.9	9.71
Erno (Ern)	657	14.5	26	1.8	0.98
Vevera (Vev)	449	13	21	1.6	0.55
Bardello (Bar)	284	23.3	134	5.8	2.78
Boesio (Boe)	501	14.4	45	3.1	1.6
Tresa (Tre)	650	58.2	754	13	22.85
Giona (Gio)	998	14.2	50	3.5	-
Ticino outlet	1283	248 (110 at lake outlet)	6599	26.6	279.27

2.2 Methods and source of data

2.2.1. Chemical data for the DSL

The yearly data used to assess long-term trends in the DSL was derived from synoptic surveys performed by the CNR Institute of Ecosystem Study (CNR ISE). Samplings were performed at the deepest point of each lake, during winter overturn (late February – early March) in the period 1988-2012. Average concentrations of Na and Cl were obtained from 10 to 12 (13 for Lake Maggiore) sampling depths along the water column, weighted by the volume of the respective water layers. Chemical analysis were performed at the hydrochemical laboratory of the CNR ISE in Verbania Pallanza, Italy. Monthly samples of Lake Maggiore and its tributaries were also analyzed at this laboratory.

Data at winter overturn were used for comparison between the sites because in this period of the year the lakes usually reach the maximum water mixing and the highest homogeneity of concentrations along the water column. Even if winter mixing seldom affects the whole water column, as explained above, Na and Cl usually show a high homogeneity within the water column over the seasons, because they are less involved in biogeochemical processes than other solutes and are not affected by hypoxic or anoxic conditions.

Monthly data are also available for lakes Maggiore (since 1988), Iseo (since 1998) and Garda (since 1996), and were used to explore the temporal behavior of Cl concentrations, in particular the presence of thresholds in the time series. Monthly concentrations of Cl in Lake Garda and Lake Iseo were determined at the Istituto Agrario di S. Michele all'Adige, Fondazione E. Mach, and at the Freshwater Ecology laboratory of the Department of Earth and Environmental Sciences of University of Milan-Bicocca, respectively.

Quality controls, both internal and external, were routinely applied in the laboratories involved in the study, such as the regular use of the control charts, the analysis of certified samples and the participation to national and international inter-comparison exercises (e.g. Marchetto et al. 1995, 1999; Mosello et al. 1997). Furthermore, the laboratories involved in long-term studies on the DSL regularly performed inter-calibration exercises since the 1980s, both in the frame of national and European projects and through *-ad hoc* field and laboratory inter-comparisons (e.g. Marchetto 1995, 1999). Trends in Na and Cl concentrations were calculated for each lake by means of the Kendall test and slope estimated with the Sen's method (Sen 1968). The same approach was used to evaluate trends in the annual loads of Na and Cl to Lake Maggiore.

Temporal changes of monthly Cl concentrations in lakes Garda, Maggiore and Iseo were analyzed by stepwise regressions. The Akaike Information Criterion (AIC) was used to compare the quality of the piecewise regression model with respect to the linear one. The piecewise regression allows to identify a breakpoint (a critical or threshold value beyond or below which an effects occurs). The selection of breakpoints was guided by the identification of rapid changes in the smoothing models performed with LOESS techniques (R Core Team 2013).

2.2.2. Lake Maggiore data

Concentrations and chemical loads for Lake Maggiore tributaries have been collated since 1985 within the studies promoted by International Commission for the Protection of Waters between Italy and Switzerland (CIPAIIS).

Sampling has been performed on a monthly basis, or even more frequently in the case of in-depth studies on a few sites (Boggero et al. 1996). Chemical loads have been calculated on a yearly basis using daily water discharge data and monthly concentrations, with the approach described in Rogora et al. (2001).

Owing to the availability of data on chemical loads to Lake Maggiore, a mass budget was calculated for this lake. The aim of this approach was to assess the equilibrium concentrations of Na and Cl in lake water (with respect to external loads) and compare them with present concentrations, to evaluate how far the lake is from a stationary condition.

The area drained by the tributaries represents about 90 % of the watershed; we estimated the load from the remaining undrained area by multiplying its surface for the average load (Meq Cl m⁻² yr⁻¹) from the drained area. The total input to the lake was calculated as the sum of these two contributions (drained + not drained), plus the contribution from atmospheric deposition to the lake surface.

Relationships between input loads and in-lake concentrations were calculated assuming that Na and Cl act as conservative substances, i.e. no loss to atmosphere and sediments, no strong chemical stratification of the lake; in these conditions the approach described in Vollenweider (1975) may be applied. Actually, Na may be incorporated in the soil displacing other cations, and acting as a less conservative substance than Cl (Novotny et al, 2009). However, we assume this effect to be of minor importance in Lake Maggiore catchment, because most of the water flow to the lake is through runoff, thus limiting interaction with soils.

The variation in time of the mass of the substance in water (M_w, eq) was obtained from the sum of the different inputs (i) to the lake minus the mass leaving the lake via the outlet:

$$dM_w/dt = \sum v_i [m_i] - v_w [m_w]$$

where v_i and v_w are the volume of water of input i and the volume leaving the lake, respectively. We assumed in-lake concentration of the considered solute as:

$$[m_w] = [M_w]/V$$

where m_w is the lake water concentration (eq m⁻³) and V the lake volume (m³).

The solution of the above differential equation is:

$$[m_w]_t = [m_w]_{t_0} * e^{-\rho_w(t-t_0)} + I_M/\rho_w * (1 - e^{-\rho_w(t-t_0)})$$

where the indexes t₀ and t indicate the starting and present time, ρ_w is the water theoretical renewal time (yr⁻¹), and I_M is the ratio between the solute load (eq yr⁻¹) and the water volume (m³).

This equation describes the development in time of the concentration for any situation; in the steady state, for t → ∞, the equilibrium concentration becomes:

$$[m_w]_{\infty} = I_M/\rho_w.$$

Annual data for Lake Maggiore were used to calculate the expected concentration of Na and Cl of the lake for two periods: 1984-93 and 2003-2012. These values were compared with the actual concentrations in the lake in the same periods.

For the Lake Maggiore watershed we also estimated the contribution of the different Cl sources, considering inputs from atmospheric deposition, population and road salt.

A network for the monitoring of atmospheric deposition chemistry has existed in this area since the 1980s (Rogora et al. 2001). In particular, rain chemistry has been analyzed at the sampling station “Pallanza” since 1975 on an event basis. Previous studies showed how deposition data at this site can be considered representative for the whole area of Lake Maggiore watershed (Rogora et al. 2001). Using these data, we calculated the annual input of Cl to Lake Maggiore through atmospheric deposition.

Unfortunately, data on Cl discharge from waste water treatment plants were available only in a very few cases. For this reason, to estimate the input from population, we applied a pro-capita contribution of 8 kg Cl yr⁻¹, as suggested by Muller and Gatcher (2012) for the Lake Constance area. Human population data (including number of tourists) were taken from CIPAIS (2003).

To estimate the input of Cl from road salt, we used the following data:

- for the Swiss part of the Lake Maggiore watershed: total amount of road salt used in winter months on annual basis on the roads of the Canton Ticino area; these data were provided by the Canton Ticino authority, Territorial Department;
- for the Italian part of the watershed: average amount of road salt used in winter per km of road; these data were provided by ANAS s.p.a., which is the national authority responsible for the management of roads of national interest. The density of roads at a Province level were taken from <http://www.aci.it/laci/studi-e-ricerche/dati-e-statistiche.html>. This approach allowed just a rough estimation of the salt amounts; the maintenance of the roads is done mostly by municipality or province, but data on the real amounts applied each year cannot be obtained.

3. Results

3.1 Trends in the DSL

The ionic composition of the lakes averaged for two periods, 1990-1992 and 2010-2012, is shown in Table 3. For Lake Lugano, only data for 1993 were available for the same suite of variables; data of Na concentrations were lacking before 1998. The total ion concentrations increased in all the lakes during the recent period, ranging between 4 % (Lake Garda) and 7 % (Lake Iseo). Variations of electrical conductivity are in agreement with the greater ion concentration. The increase in absolute value is mostly due to Ca and HCO₃ ions, but the rate of Na and Cl increase is the highest among all ions, ranging from 10 to 26 % in the case of Na and from 21 to 39 % for Cl. The Na:Cl ratio (on an equivalent basis) in all lakes was over one during both periods, but decreasing in 2010-12 (Table 3).

Table 3 Ionic balance, pH and electrical conductivity of the study lakes in 1990-92 and 2010-12 and % change between the two periods. * refers to one sampling only, in 1993.

lake period	Unit	Maggiore			Lugano			Como			Iseo			Garda		
		1990-92	2010-12	%	1990-92	2010-12	%	1990-92	2010-12	%	1990-92	2010-12	%	1990-92	2010-12	%
Ca	µeq L ⁻¹	1080	1110	3	1824*	1908	5	1244	1258	1	2146	2344	9	1637	1700	4
Mg	µeq L ⁻¹	296	305	5	752*	776	3	451	471	4	658	690	5	687	707	3
Na	µeq L ⁻¹	104	132	26	-	124		126	141	12	121	133	10	150	180	20
K	µeq L ⁻¹	38	39			31		36	35		29	33		25	28	
HCO ₃	µeq L ⁻¹	774	833	8	2395	2466	3	1177	1237	5	1872	2036	9	2095	2172	4
Cl	µeq L ⁻¹	59	83	39	63*	83	32	66	82	24	70	87	24	131	159	21
SO ₄	µeq L ⁻¹	617	617	0	258*	242	-6	526	537	2	1045	1029	-1	236	234	-1
NO ₃	µeq L ⁻¹	57	60	4	13	14	6	61	60	0	58	51	-12	22	26	18
Σ Ions	µeq L ⁻¹	3025	3179	5	-	5644		3687	3821	4	5999	6403	7	4983	5206	4
Na:Cl ratio		1.76	1.59	-10	-	1.49		1.92	1.73	-10	1.73	1.52		1.15	1.13	-2
pH		7.38	7.37		7.77	7.70		7.57	7.59		7.78	7.71		8.09	8.10	
Cond. at 20°C	µS cm ⁻¹	146	151	4	234	239	2	169	174	3	268	277	4	214	222	4

The increase of Na and Cl in the DSL from 1988 to 2012 is examined in greater details in Fig. 2 and Table 4. The trends of Cl were highly significant in all the lakes ($p < 0.001$), with slope varying between 0.8 and 1.5 µeq L⁻¹ yr⁻¹. Sodium also increased in all the lakes but at a lesser extent in Lake Iseo ($p < 0.05$). The relative increase was greater for Cl with respect to Na (Tab. 3) because initial Na concentrations were higher (100-150 µeq L⁻¹ in the early 1990s). On the other hand, the rate of increase over the whole period showed very similar slopes for Na and Cl, ranging between 0.3 and 1.6 µeq L⁻¹ yr⁻¹ (Tab. 4). Lake Garda shows the highest rate of increase (1.51 and 1.57 µeq L⁻¹ yr⁻¹ for Cl and Na respectively). This lake is also characterized by the highest absolute concentrations of the two ions.

Fig. 2

Table 4 Level of significance of Cl and Na trends according to the Kendall test and rate of increase (Sen's slope) of Cl and Na concentrations in the period 1988-2012 (1998-2012 for Lake Lugano) (***) $p < 0.001$; ** $p < 0.01$; * $p < 0.05$.

Lake	p	Cl µeq L ⁻¹ yr ⁻¹	p	Na µeq L ⁻¹ yr ⁻¹
Maggiore	***	1.23	***	1.41
Lugano	***	0.80	**	0.88
Como	***	0.76	**	0.69
Iseo	***	0.83	*	0.33
Garda	***	1.51	***	1.57

The rate of Cl increase in lakes Garda, Maggiore and Iseo were additionally analyzed on a monthly basis (Fig. 3). The smoothing of the data (LOESS) revealed a breakpoint in the mid-2001 for both lakes, Maggiore and Garda. This common threshold was confirmed by the computations of piecewise regressions. The piecewise models were significantly different (ANOVA, $P < 0.01$) and better (AIC, Maggiore, 1257 vs. 1567; Garda, 893 vs. 927) than the simple linear model. On the other hand, the linear model was not significantly different by the stepwise model in the case of Lake Iseo.

After June 2001 the rate of Cl increase in lakes Maggiore and Garda was around $2.07 \mu\text{eq L}^{-1} \text{yr}^{-1}$ and $2.41 \mu\text{eq L}^{-1} \text{yr}^{-1}$, respectively. Before the rate of increase in the two lakes was 3 to 4 times lower ($0.74 \mu\text{eq L}^{-1} \text{yr}^{-1}$, Maggiore; $0.48 \mu\text{eq L}^{-1} \text{yr}^{-1}$, Garda). The rate of increase in Lake Iseo over the whole period was $1.15 \mu\text{eq L}^{-1} \text{yr}^{-1}$.

Fig. 3

3.2 In-depth analysis for Lake Maggiore

The annual loads of Na and Cl from the tributaries of Lake Maggiore (draining altogether about 90% of the watershed) and the total input to the lake are shown in Table 5. Because loads are affected by a high interannual variability, related to hydrology, we compared average values for a five-year period: 1987-1991 and 2008-2012. Data are expressed both as total amount (Meq yr^{-1}) and as contribution for square meter ($\text{meq m}^{-2} \text{yr}^{-1}$), which makes comparing different watersheds easier. In the majority of the rivers, an increase in the loads of both Na and Cl occurred. The overall increase (from the area drained by the tributaries) between the two periods was 56 % for Cl and 17 % for Na.

Table 5 Annual input of Na and Cl to Lake Maggiore from the different tributaries. Mean values of 5-year periods.

Tributaries	Watershed area km^2	Na (Meq yr^{-1})		Na ($\text{meq m}^{-2} \text{yr}^{-1}$)			Cl (Meq yr^{-1})		Cl ($\text{meq m}^{-2} \text{yr}^{-1}$)		
		1987- 1991	2008- 2012	1987- 1991	2008- 2012	% change	1987- 1991	2008- 2012	1987- 1991	2008- 2012	% change
Ticino Inlet	1616	183	244	113	151	33	106	210	66	130	98
Maggia	926	65	120	70	129	84	33	71	35	77	119
Verzasca	237	9	29	36	124	242	9	19	40	82	106
Cannobino	110	8	21	77	188	144	4	13	32	117	262
San Giovanni	61	8	10	139	170	23	3	5	50	85	71
San Bernardino	131	40	13	306	103	-66	8	5	62	41	-34
Toce	1547	159	167	103	108	5	82	105	53	68	28
Strona	223	41	48	184	217	18	15	29	66	130	98
Erno	26	9	11	335	431	29	1	11	53	414	680
Vevera	21	4	1	167	66	-60	2	3	111	142	27
Bardello	134	111	97	824	724	-12	64	67	479	497	4
Boesio	45	110	59	2429	1296	-47	53	38	1157	828	-28
Tresa	754	206	294	273	390	43	134	225	178	298	67
Giona	50	5	8	109	159	46	2	4	42	89	113
Total (measured)	5882	958	1124	163	191	17	517	805	88	137	56

It should be highlighted that the amount of precipitation in the Lake Maggiore area did not show any trend, and the same holds for water discharges of the main tributaries (CNR-ISE 2013). Consequently, the increasing loads of Na and Cl from the rivers to the lake cannot be ascribed to hydrological factors but to the increase of concentrations.

A more detailed analysis was performed on monthly Cl concentrations for six lake tributaries (Ticino, Maggia, Verzasca, Tresa, Toce, Cannobino), which contributed 80 % of the total Cl load to the lake. These river catchments are affected by varying levels of urbanization, in terms both of population density and the presence of roads and paved surfaces. River Tresa, the outlet of Lake Lugano, is affected by effluents from treatment plants that discharge into some of Lake Lugano's tributaries. Rivers Maggia, Ticino and Toce are less affected by anthropogenic impact, and have a significant portion of their catchment occupied by mountains. Verzasca and Cannobino are less impacted rivers, with a very low population density and limited presence of roads in the catchments.

Upward trends of Cl concentrations affected all the tributaries (Fig. 4), with a steeper slope for rivers Tresa and Ticino. The tendency towards higher concentration is particularly evident in the recent period (since 2000-2001). The highest values are recorded in River Tresa (mainly between 150 and $250 \mu\text{eq L}^{-1}$); being a lake outlet, this river has a more consistent concentrations with respect to the other tributaries. The lowest concentrations (mostly below $50 \mu\text{eq L}^{-1}$) characterize rivers Maggia, Verzasca and Cannobino. When considering the distribution of concentrations in the different months, a seasonal pattern is evident for rivers Ticino and Toce, with the highest average concentrations in winter and early spring. Maximum concentrations occurred in winter months, also in the case of the other rivers; this is particularly evident for River Cannobino, where concentrations above $80 \mu\text{eq L}^{-1}$ are detected from December through April (Fig. 4).

Fig. 4

Sodium concentrations (not shown) showed a very similar pattern with respect to Cl, with positive trends and maxima mainly occurring in early spring and winter; concentrations of the two ions were indeed highly correlated in all the rivers (r between 0.85 and 0.95).

The seasonality of Cl concentrations in the major tributaries has effects also on the upper water layer of Lake Maggiore. In Figure 5 the monthly concentrations of Cl in the epilimnion of the lake are compared with the average values in the water column: the highest concentrations in surface water regularly occurred in late spring (May-June). This pattern seems to be particularly evident in the last number of years (2005-2012; Fig. 5).

Fig. 5

Assuming that both ions act as conservative substances, and using the mass-balance approach described in the methods, we evaluated how far from the expected values the present concentrations of Na and Cl are in Lake Maggiore (Table 6). Using the measured loads for the periods 1987-1991 and 2008-2012, we calculated that the expected Na concentrations in the lake should be 112 and 141 $\mu\text{eq L}^{-1}$, vs measured values of 100 and 131 $\mu\text{eq L}^{-1}$. The respective values for Cl are 64 and 100 $\mu\text{eq L}^{-1}$, vs 55 and 80 $\mu\text{eq L}^{-1}$.

Table 6 Temporal changes of loads and in-lake concentrations: comparison between actual concentrations and expected values on the basis of loads to Lake Maggiore. Calculation details in the text.

parameter	Symbol	Unit	Na		Cl	
			1987-1991	2008-2012	1987-1991	2008-2012
Present lake concentration	[mw]	$\mu\text{eq L}^{-1}$	100	131	55	80
Total in lake mass	Mw	10^6 eq	3763	4928	2053	3011
Annual load	Lin	10^6 eq yr^{-1}	988	1244	555	879
Output	Lout	10^6 eq yr^{-1}	900	1358	536	920
Loading (per unit volume)	IM	$\text{eq m}^{-3} \text{ yr}^{-1}$	0.026	0.033	0.015	0.023
Lake concentration at equilibrium	[mw] $_{\infty}$	meq L^{-1}	112	141	64	100
In-lake retention		%	9	-9	3	-5

4. Discussion

4.1 Long-term trends

All lakes demonstrated coherent positive trends of Na and Cl, with steeper slopes in recent years, particularly evident in lakes Maggiore and Garda (Fig. 2, Fig. 3).

Lake Garda showed a distinct pattern with respect to the other lakes: both the absolute values and the rate of increase were higher. Lake Garda also manifested the lowest Na:Cl ratio with respect to the other sites (1.1 compared to 1.5-1.7, respectively; Table 3). The higher concentrations in that lake may be partly due to the different lithology of the catchment, which is mainly composed of more soluble sedimentary rocks (Vollenweider 1965, Bonomi et al. 1979). Furthermore, it has been estimated that groundwater inputs may be relevant in the hydrological balance of this lake (Decet and Salmaso 1997). In the southern lake area and catchment, many karstic areas are present, whereas a number of springs are characterized by thermal waters, suggesting a possible contribution of aquifers to Cl inputs to the lake. For example, chloride concentrations in the thermal waters at the Sirmione peninsula (southern basin) are around 910 mg L^{-1} (Balderer et al. 2007).

The rate of Cl increase in the studied lakes was lower compared to that reported in other studies on large lakes: in Lake Constance, for instance, the second largest lake in Europe, Cl increased by a factor of 2.4 in the last 40 years, reaching the present level of 5.5 mg L^{-1} (155 $\mu\text{eq L}^{-1}$) (Muller and Gatcher 2012). The authors estimated a 45 % contribution of road salts to the observed increase of Cl concentration; the remaining fraction can be attributed to wastewater, farming and incineration of solid wastes (Muller and Gatcher 2012). At the North Basin of Lake Biwa, Cl ion concentration has been continuously increasing from 7.4 to 9.9 mg L^{-1} (from 209 to 279 $\mu\text{eq L}^{-1}$) over a 20-year period (Aota et al. 2003). In the Great Lakes, Cl increased exponentially over the first six decades of the 20th century—the increase was dramatic especially in Lakes Erie and Huron, where concentrations in the 1970s reached 26 and 29 mg L^{-1} (733 and 818 $\mu\text{eq L}^{-1}$), respectively (Chapra et al., 2009). A mass-balance model applied to these lakes showed that improvements in the last three decades of the 20th century were mainly attributed to industrial controls. However, recently published data revealed concentrations continue to rise despite industrial controls: these trends can be partly attributable to increased loadings that occurred in the past (Chapra et al. 2009).

Several factors may account for a delay in the response of in lake concentrations to changing loads. In the case of Lake Constance, for instance, the imbalance between total Cl imports to the catchment and its loss via tributaries was explained by Cl retention in soil and groundwater compartments (Muller and Gatcher 2012). Other studies highlight the

role of water residence time in the transient storage of Cl in groundwater (Bastviken et al., 2006; Kincaid and Findlay 2009).

Long residence times are a distinctive feature of the studied lakes, this may result in a considerable delayed response of Cl levels in lake water with respect to changing inputs. The observed patterns of Na and Cl concentrations in Lake Maggiore, for instance, and the values relative to its tributaries, clearly indicated that lakes are not in a steady-state condition with respect to external loads. The comparison of in lake concentrations to those which could be expected on the basis of present loads, showed a difference of 10 and 19 $\mu\text{eq L}^{-1}$ for Na and Cl, respectively, i.e. 8 and 24% of the present concentrations (Table 6). Most likely we should expect a further increase of Na and Cl concentrations in this lake, even assuming that the loads will be maintained at the present levels. Considering similar characteristics and common trends observed in the DSL, this condition could be expected for other lakes too: concentrations in the DSL are probably still adjusting with respect to external loads. Even in the scenario of a load decrease or stabilization, concentrations may increase further in the next years.

4.2 Possible sources of Cl

An assessment of the main sources of Cl to lake and river water was performed for the catchment of Lake Maggiore. The analysis was limited to Cl, because Na and Cl showed similar temporal patterns in the lake and in the main tributaries; furthermore, for Na a relevant contribution may be from weathering of silicate minerals, while for Cl essentially all the inputs can be ascribed to anthropogenic sources.

The fraction of Cl inputs to Lake Maggiore and the DSL that can be attributed to atmospheric deposition is low, due to the distance of the lakes from the sea. An estimate of about 10 $\mu\text{eq L}^{-1}$ of Na and Cl average concentrations measured in rain water at Pallanza sampling station (Lake Maggiore), on the lake shore, was done thanks to the existing long-term data on atmospheric deposition chemistry in the lake catchment (Rogora et al. 2006). The annual deposition of these ions, calculated from the product of concentrations and precipitation amounts, ranged between 15 and 20 $\text{meq m}^{-2} \text{yr}^{-1}$ (Fig. 6). The input of Cl via atmospheric deposition accounted for 13 % of the total Cl input to Lake Maggiore (Table 7) with the atmospheric load decreasing in the last decade (Fig. 6). Therefore, atmospheric deposition cannot be responsible for the positive trends of Na and Cl in the lake.

Fig. 6

Table 7 Estimated inputs of Cl (in Meq yr^{-1}) to Lake Maggiore from population, road salt and atmospheric deposition, compared to the measured load (from the tributaries)

Estimated loads	Meq yr⁻¹	%
Population (including touristic presence)	198	23
Roadsalt	380	43
Deposition	115	13
Total	693	79
Measured load	878	-

It should also be highlighted that the precipitation amount in the Lake Maggiore area did not show any trend, and the same holds for water discharges of the main tributaries (CNR-ISE 2013). Consequently, the increasing loads of Na and Cl from the rivers to the lake cannot be ascribed to hydrological factors but to the increase of concentrations.

The catchment of Lake Maggiore, as well as those of the other DSL, have a steep altitudinal gradient and are occupied by mountains for a significant part of their total area, as revealed by their mean and maximum altitude (Table 1). For this reason, farming is limited to small areas and the inputs of Cl from fertilizers, such as potassium carbonate, is most probably of minor importance. Unfortunately, the lack of published data on this subject prevents any evaluation of the contribution of agricultural practice to Cl inputs.

The Cl load from the population to Lake Maggiore, calculated on the basis of population density in the catchment and a pro-capita contribution of 8 kg Cl yr^{-1} , was about 200 Meq yr^{-1} (Table 7), which represents 23 % of the total load of Cl to the lake. This estimate was done considering the total population i.e. including tourist presence; the fraction of input which could be attributed to tourism is 53 Meq yr^{-1} , i.e. 6 % of the total input to the lake.

The input of Cl from road salt, calculated on the basis of the amount used in the winter months by the authorities responsible for road maintenance, proved to be the most important in the case of Lake Maggiore. When compared to the total Cl load to the lake, road salt contribution represents more than 40 % of this value. This contribution is probably overestimated, because not all the salt applied on the roads is immediately leached to surface water, but may be stored in groundwater. However, as stated before, groundwater input is probably of minor importance in the Lake Maggiore watershed, as well as in the tributary catchments, with respect to runoff.

Other results of our analysis confirmed the importance that the use of NaCl as a deicing agent may have in the observed trends. First of all, beside the positive trend of Na and Cl concentrations in time, the DSL also showed a

decrease in the Na:Cl ratio. This ratio should decrease in the case of an input of Na and Cl in a 1:1 ratio, as could be the case for road salt inputs. In fact, in pristine conditions, and in absence of mineral Cl in the watersheds, the main source of Cl to surface water is atmospheric deposition, where the Na:Cl ratio is close to 0.9-1.0 (i.e. the value in sea spray), while sodium may be leached from silicate minerals.

Several tributaries of Lake Maggiore were affected by industrial pollution in the past, but their conditions improved in the recent period, due to waste and sewage water treatment plants installation and modernization (CNR ISE 2013). On the other hand, almost all the tributaries showed an increase in Na and Cl loads and concentrations and this has become more intense since 2000 (Fig. 4). A seasonal pattern of concentrations is observed in the major tributaries of Lake Maggiore, with a prevalence of higher values in winter and early spring. This pattern is more evident in those rivers with steep catchment slope, where runoff prevailed over infiltration, contributing to winter/spring peaks. Furthermore, peaks of Na and Cl in these rivers mostly occurred in the same samples, suggesting NaCl dissolution as the main cause.

Altogether, population, road salt and deposition account for approximately 80 % of the total Cl input to Lake Maggiore. The remaining 20 % can be attributed to other sources, such as fertilizers, industrial discharge, and weathering.

Our analysis allowed an estimation of the main contributors to Cl levels in lake water. The analysis performed at a catchment level lead to the hypothesis that the use of NaCl as a road de-icing agent during winter may have contributed in a relevant way to the positive trends of Na and Cl in this lake. Indeed the contribution from road salt may have become increasingly important in time, due to a lack of specific regulations about the amounts to be used and procedures for salt spreading; this may also explain the accelerating trend in lake concentrations in recent times (after 2001). Unfortunately, no historical data were available to assess any possible trend in the amount of salt used in the DSL area. In general, the lack of historical data on the different Cl sources (apart from deposition), prevent us from identifying with certainty the factor responsible for the increase in concentrations.

It should also be noted that the assessment of Cl sources and their importance in catchment loads was performed for Lake Maggiore only. In the catchments of the other lakes the situation may be different and sources of Cl other than road salt could be prevalent. The DSL showed coherent temporal patterns of Cl, with a tendency towards a steeper increase in the recent period, more evident in lakes Maggiore and Garda. The reasons for that could be different for the various lakes. Population densities in the catchments of the DSL are quite similar (Table 1) and displayed only a slight increase in the last three decades (<http://www.demo.istat.it>). However, considerable touristic presence may be very important in the DSL catchments, especially in summer and on lakeshore areas. For instance the number of tourists/visitors has increased steadily in the area of Lake Garda, particularly in the last two decades (Lake Garda Community 2013). Consequently, the contribution from domestic sewage could have possibly contributed for a fraction of the increasing trend. Groundwater inputs should also be taken into account, particularly in the case of Lake Garda: Cl stored in the groundwater compartments and successively delivered to the lake may have contributed to the enhanced rate of increase in recent times.

Conclusions

Results considered in this paper clearly show positive trends of Na and Cl concentrations in the most important lakes in Italy during the last 25 years. Despite their different geographic and morphometric features, synchronous trends were observed in all the lakes, especially for Cl. An in-depth analysis performed for the watershed of Lake Maggiore demonstrated the important role that NaCl used as road de-icing agent is likely to have in the observed changes. However, changes in the population density, including an increase of tourists, may also have been important, especially for the other lakes.

Present concentrations of Na and Cl in the DSL are well below the recommended limits for drinking water, according to the European regulations (250 mg L⁻¹; Directive 98/83/EC, 1998) and are also below risk limits at which no adverse effects on ecosystems are to be expected (e.g. 94 mg L⁻¹, according to RIVM, 2008). However, considering the relevant volume of water of the DSL, these trends indicate an important chemical change in the lakes.

The increase of Na and Cl in the DSL is an example of a long-term, continuous chemical variation, occurring in important freshwater bodies in Italy and warrants further investigation. These changes of clearly anthropogenic origin, are indeed in contrast with the principles of the Water Framework Directive, which recommends restoring or maintaining both the chemical and ecological status of water as close as possible to their reference conditions.

To address this problem in a proper way, the actual amount of NaCl used as a de-icing agent in winter should be quantified and monitored at the watershed scale. More, specific rules about salt use that take into account the different climatological and ecological conditions of the considered Regions (e.g in the Alps, or plain areas) should be adopted and be part of the regional water policy.

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Ethical statement

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Conflict of Interest: the authors declare that they have no conflict of interest.

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Figure captions

Fig. 1 Location of the deep subalpine lakes (DSL) in the catchment of the River Po, in Northern Italy (above) and watershed of Lake Maggiore with the main tributaries (below); acronyms refer to Table 2. The white area of the catchment is in Switzerland. The triangle shows the location of the atmospheric deposition sampling station in Pallanza

Fig. 2 Long-term trends of Cl (a) and Na (b) concentrations in the DSL. Average values on the water column at winter overturn

Fig. 3 Long term temporal development of Cl (a) from 1988 to 2013 in Lake Maggiore, (b) from 1996 to 2013 in Lake Garda, and (c) from 1998 to 2013 in Lake Iseo. Monthly measurements smoothed using LOESS models (dashed line)

Fig. 4 Long-term trends (left panels) and distribution in the various months (right panels) of Cl monthly concentrations in six Lake Maggiore tributaries (contributing together to 80 % of the Cl load to the lake). Acronyms refer to Table 2

Fig. 5 Cl concentrations in Lake Maggiore water layer 0-15 m compared with whole lake concentrations (0-360 m)

Fig. 6 Long-term trends of Na and Cl atmospheric deposition in the station of Pallanza, on the shore of Lake Maggiore

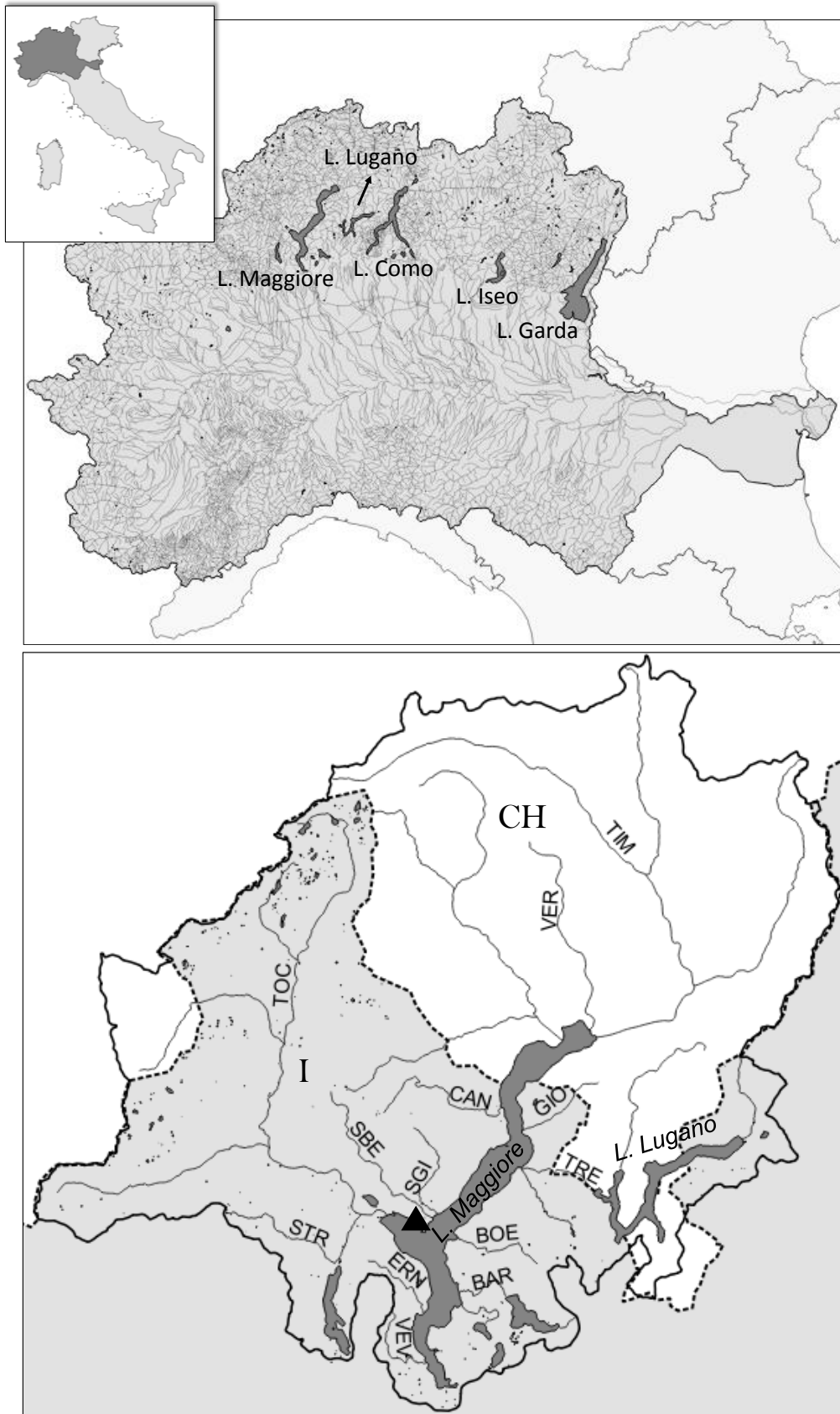


Fig. 1

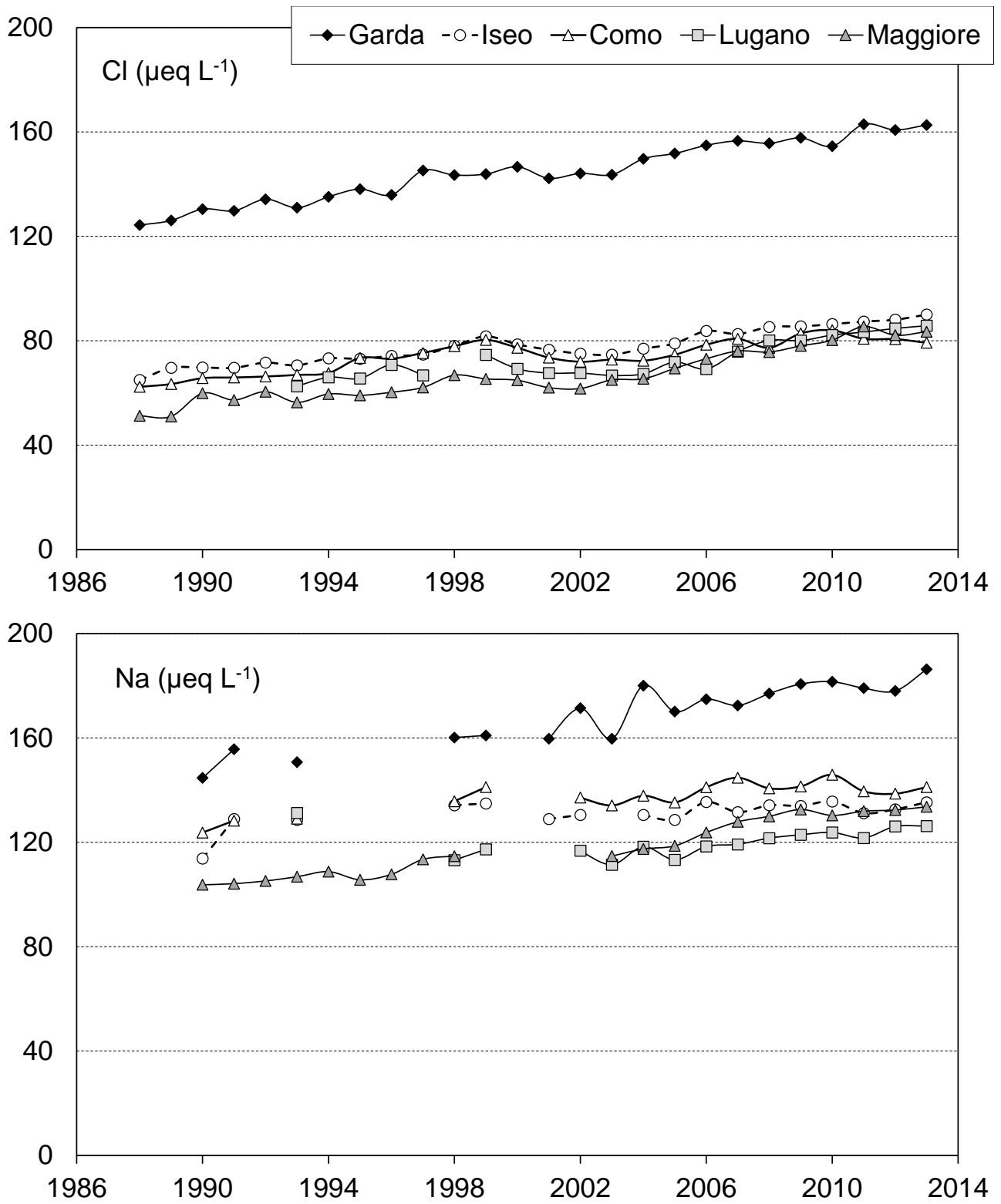


Fig. 2

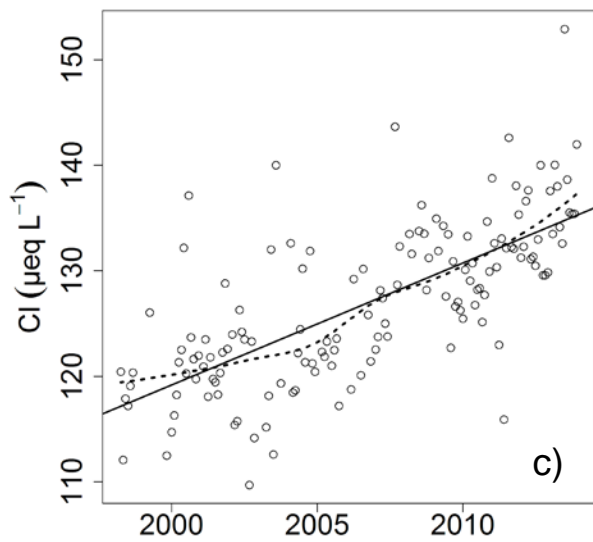
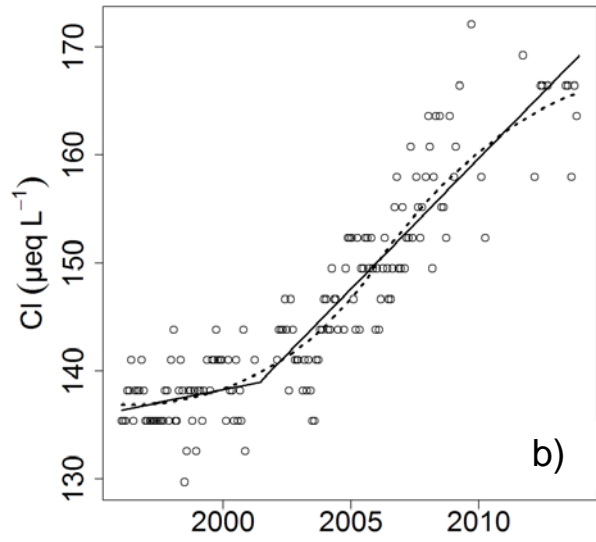
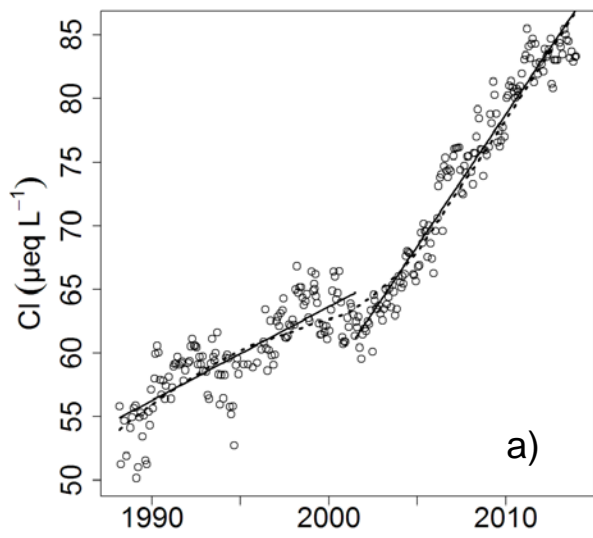


Fig. 3

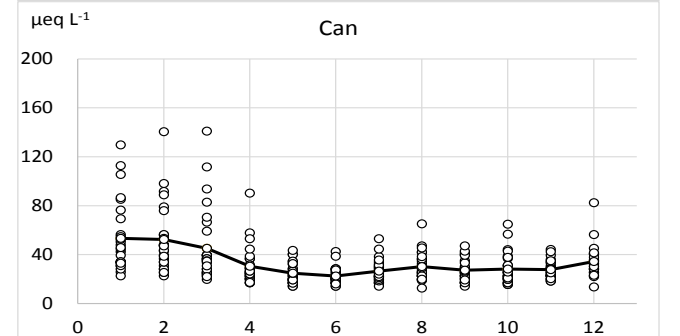
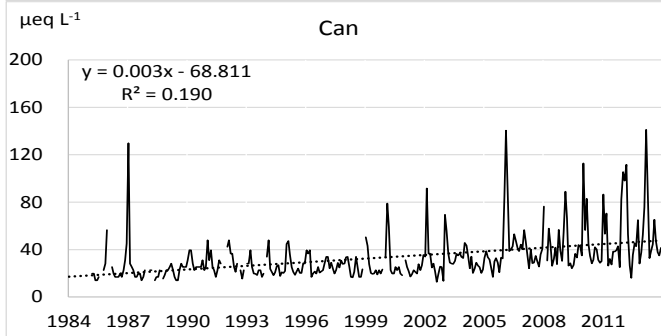
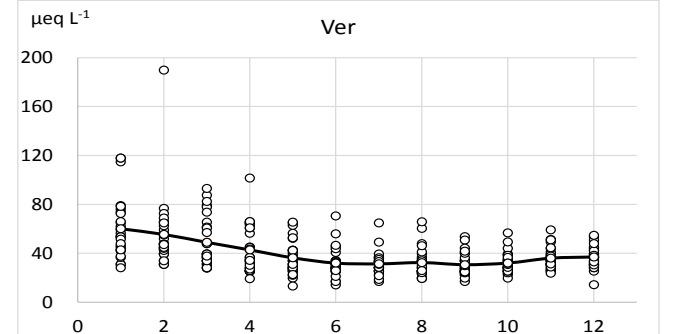
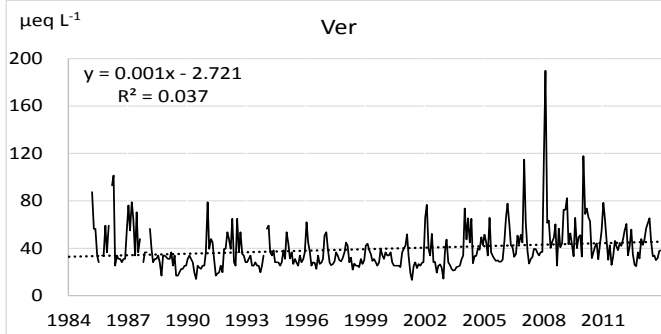
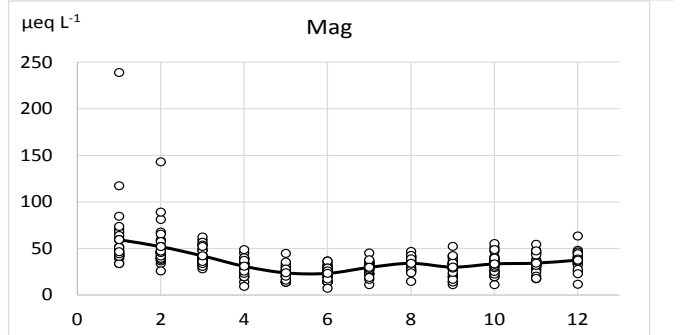
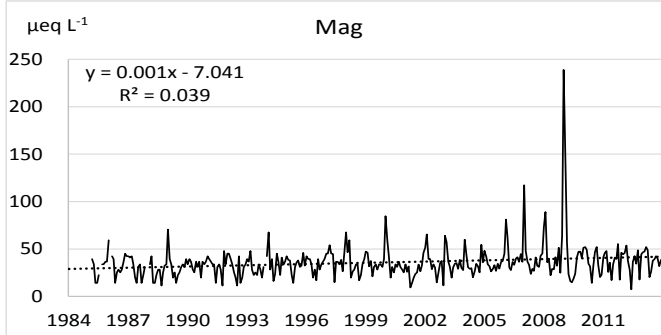
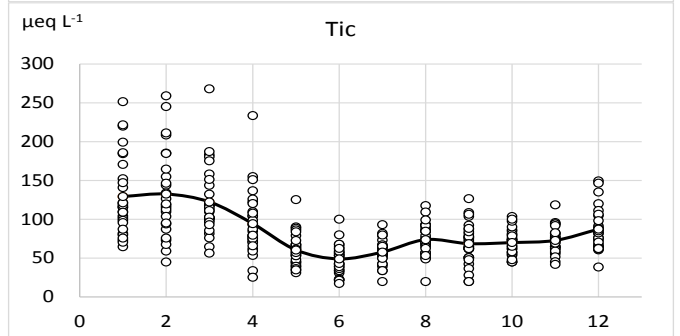
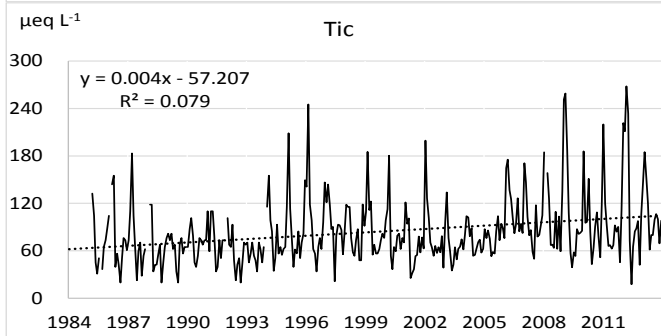
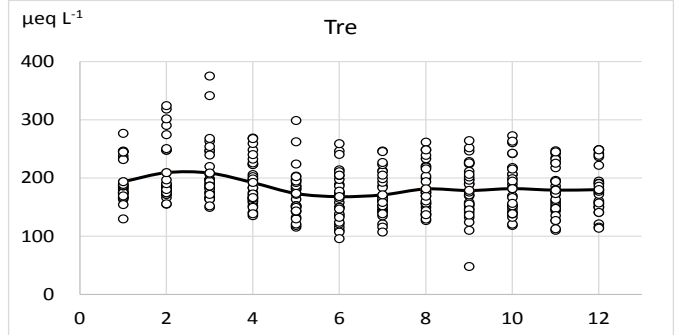
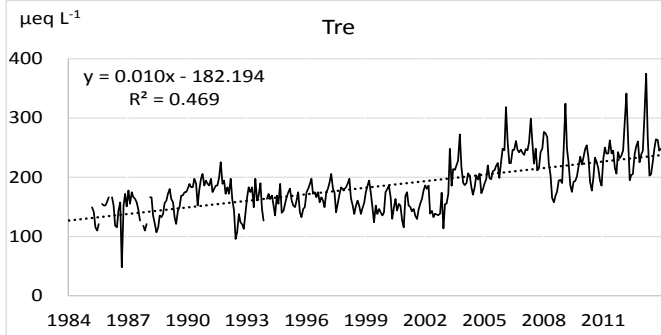
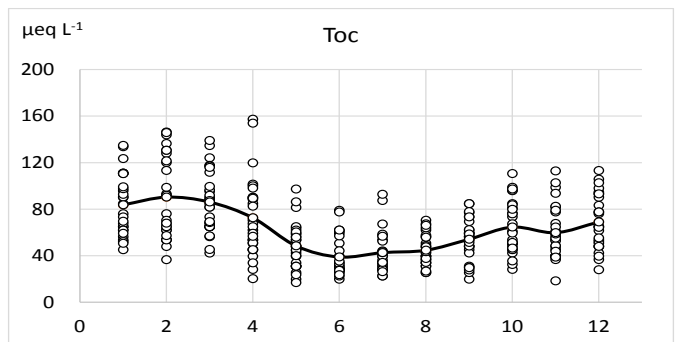
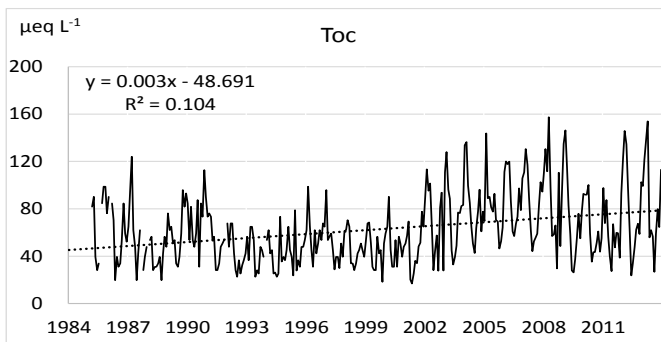


Fig. 4

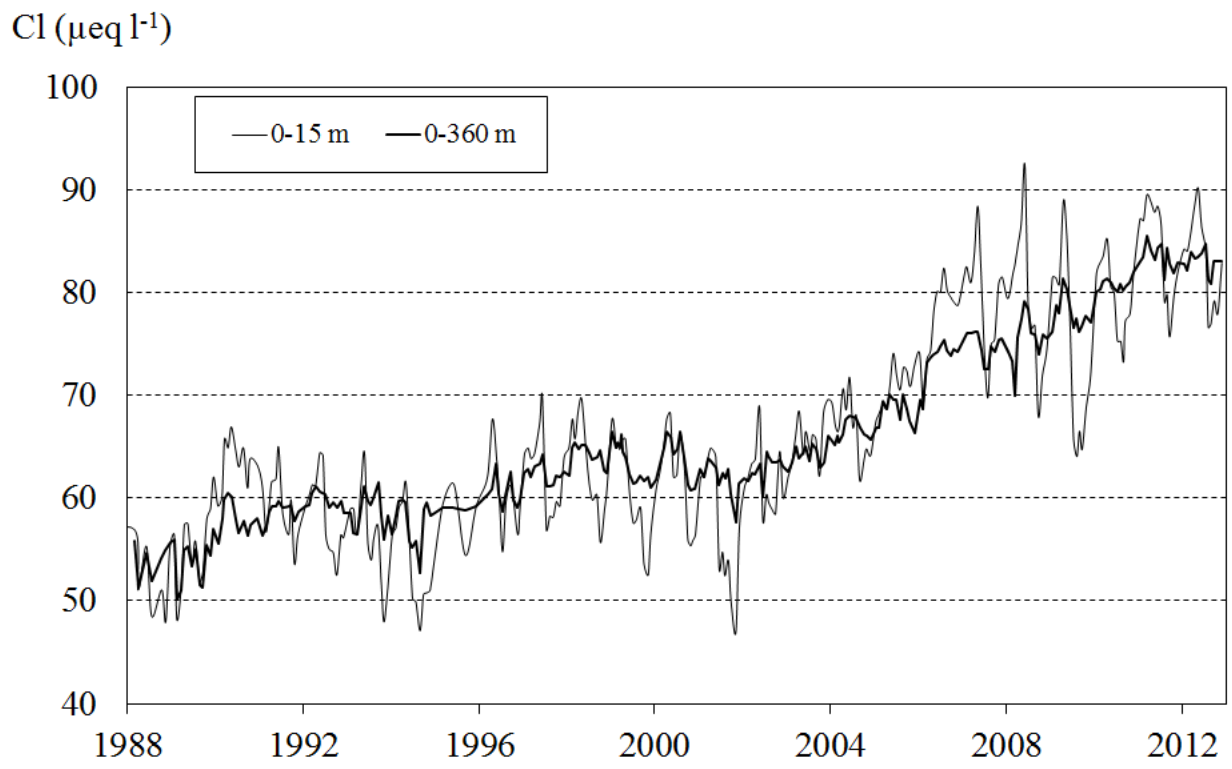


Fig. 5

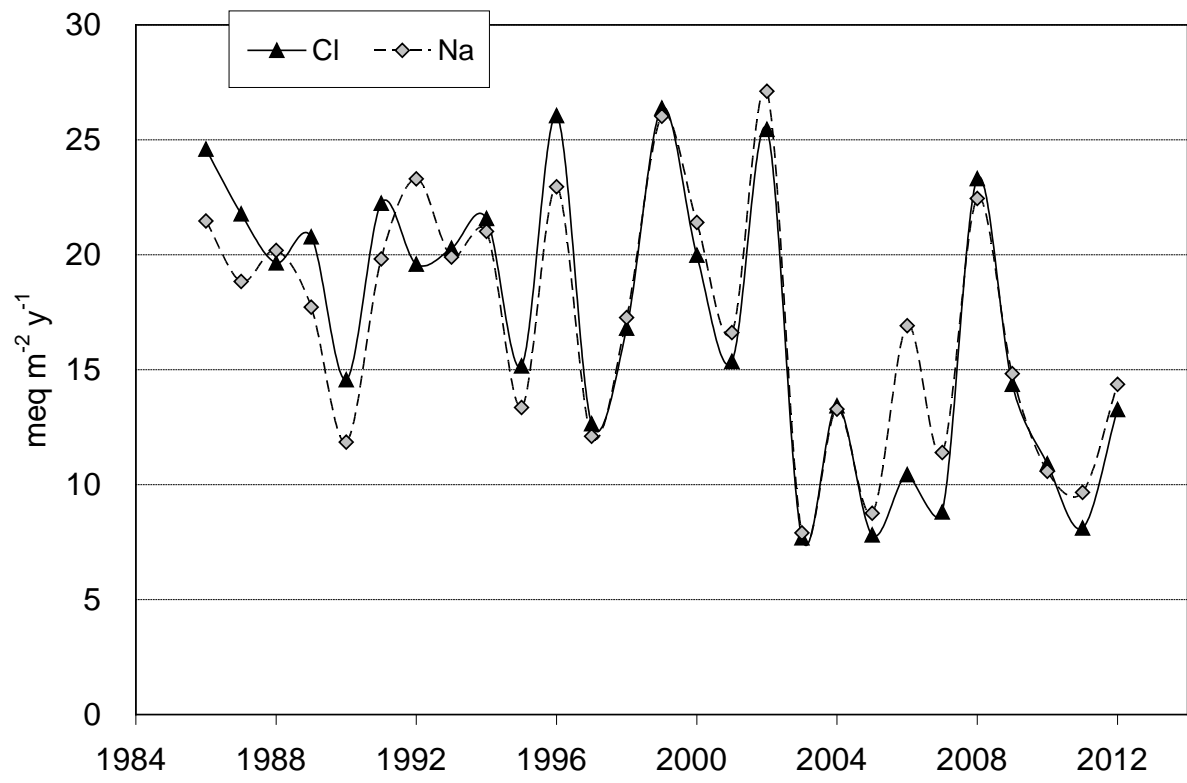


Fig. 6