Tracing recent geochemical sediment properties in subalpine lakes using wavelength-dispersive X-ray fluorescence spectroscopy (XRF): understanding regional patterns of recent lake development

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Abstract

The sedimentary geochemical records of two subalpine lakes (Lake Garda and Lake Ledro) in northern Italy were analyzed and explored using wavelength-dispersive X-ray fluorescence spectroscopy (XRF). The aim of the study was to investigate how human impact and environmental changes have affected the geochemical record of the two lakes and their catchments, in comparison to existing paleolimnological evidence based on biological proxies. Sediment cores were collected from the deepest points of the two basins of Lake Garda (Brenzone and Bardolino) and Lake Ledro, and chronologies were established using radioisotopic dating (^{210}Pb and ^{14}C). In Brenzone, the main basin of Lake Garda, a pronounced shift in elemental composition occurred in the mid-1900s, when major elements (Mg, Al, K) and lithogenic tracers (Ti) start to decrease, while some elements related to redox conditions (Mn, P) and other (contaminant) trace elements (Pb) increase. Bardolino, the shallower and smaller basin of Lake Garda, shows to some extent comparable shifts (Mg, Al, K, Ti, Pb), but some elements show deviating patterns such as those influenced by changing redox (Mn, P). Lake Ledro shows in general higher short-term variability for most elements, even though some features are comparable (Pb) to Brenzone and Bardolino. Overall, the geochemical record reveals a general change in Lake Garda since the mid-1900s, which is in good agreement with the biological records (diatoms, Cladocera, pigments). The differences recorded in the two basins of Lake Garda reflect the effects of local conditions, both related to hydrology and sedimentation patterns. In contrast, the more variable geochemical record of Lake Ledro is mainly affected by human-induced lake-level fluctuations and the effects of the relatively large catchment. This study reveals the importance of the ratio between lake area and catchment area on the lake geochemical records. The sediment records from large and deep lakes seem to be more affected by direct impacts of nutrient enrichment and/or climate change than the changes within the catchment area. On the other hand, small lakes with larger catchment areas are to a larger extent influenced by the modifications occurring in the drainage basin.

Key words: paleolimnology; geochemistry; wavelength-dispersive X-ray fluorescence spectroscopy; Lake Garda; Lake Ledro

Introduction

The structure of today's landscape and the resulting ecosystems are in many areas of Europe a result of a complex interplay between postglacial natural development (e.g. landscape evolution), shifting environmental conditions (e.g. climate) and human impact (e.g. Buentgen et al. 2011). Technological advances within both forestry and agriculture and a growing population have led to a step-by-step increase of human impact on natural ecosystems in a long-term perspective. In order to predict future trajectories of ecosystems, it is essential to understand and quantify the processes that are currently shaping them, and also to examine processes that have been acting over longer time-scales. Whereas extensive monitoring data series are collected to understand present-day conditions and processes, the analysis of paleoecological archives is essential to be able to address the long-term ecosystem development (Smol & Douglas 2007). Lately, paleoecological data have also played an increasingly important role to determine adequate management strategies and restoration targets, both for terrestrial (Valsecchi et al. 2010) and aquatic ecosystems (Bennion et al. 2011).

Lacustrine sediments are a particularly powerful archive to address limnological research questions, because they accumulate material originating from processes operating in the lake water column, in the catchment and in the atmosphere (Haworth & Lund 1984). Furthermore, lake sediments offer the opportunity to analyze both biological remains and geochemical tracers, which allow for a multi-proxy approach to understand long-term environmental change (Engström & Wright 1984; Birks et al. 1996; Bradbury & Dieterich-Rurup 1993). In general, the multi-proxy approach is useful to understand the integrated responses of lake-catchment systems to different stressors (Battarbee 2000). Geochemical proxies provide information on the variety of sediment conditions and diagenetic processes related to the lake itself (Boës et al. 2011), but also its catchment in response to human activity and climate (Last & Smol 2001; Brisset et al. 2013). For example, human activities such as deforestation and agriculture have a strong influence on soil stabilization and erosion, especially in the Mediterranean region (e.g. Garcia-Ruiz et al. 2010), whereas climatic variability plays an important role in both chemical and physical weathering of the catchment area (Vannière et al. 2013). Lake sediments may also provide information about atmospheric contaminants, such as trace metal deposition (Koinig et al. 2003).

A critical issue for multi-proxy studies is the available amount of sediment, which is often limited (Boyle 2000). However, the limitation of sediment availability may be overcome to some extent by using non-destructive methods for geochemical analyses, such as wavelength-dispersive X-ray fluorescence spectroscopy (XRF). XRF of bulk sediment is a rapid, quantitative method to analyze the geochemical composition of sediment (Rydberg 2014). The geochemical matrix can provide information on past productivity (e.g. Si/Al ratios to infer biogenic silica), redox conditions (Fe/Mn ratios), atmospheric pollution (e.g. Pb), human impact (lithogenic elements), climate change and weathering (weathering indices such as K/Al ratios) in the catchment area and in the lake itself (Martin-Puertas et al. 2011).

In this study, we analyze and explore the geochemical record of two subalpine lakes in northern Italy, i.e. Lake Garda and Lake Ledro. Sediment cores were collected from the deepest points of the two basins of Lake Garda (Brenzone and Bardolino, respectively) and Lake Ledro. The main aim is to investigate how human impacts and environmental change have affected the two lakes and their catchments. Both lakes have been affected by hydroelectrical exploitation since the first half of the 20th century, which may have modified the quality of organic and minerogenic material deposited in the two lakes. Moreover, Lake Ledro is exposed to considerable lake-level fluctuations, which is influenced by the connection of Lake Ledro to Lake Garda by underwater pipes. The catchments of the two lakes are strongly affected by extensive human activities, such as agriculture and forestry, but also increasing activities related to tourism. Because both lakes were previously studied for the long-term ecological development through the analysis of biological proxies (Milan et al. 2015, Tolotti et al. in prep.), a further objective of this study is to compare the geochemical record with the biological information in order to understand the response of the lake-catchment system to external forcings. Except for studies in Lake Ledro on paleohydrology and flood events (Magny et al. 2012; Vannière et al. 2013; Simonneau et al. 2013a), the geochemical records of the two lakes have not yet been studied.

Material and methods

Study site

Lake Garda, located on the southern slope of the Alps, is the largest Italian lake (area = 368 km^2, Vol = 49 km^3, Zmax = 350 m) (Fig.1). Although the catchment area is relatively small (~2350 km^2) compared to the lake surface (ratio of 6:1; Gerletti 1974), its topography ranges from 3556 m (Monte Presanella) down to 65 m a.s.l., with a mean altitude of ~1000 m a.s.l.. The main lake inflow, River Sarca, flows through the siliceous Adamello-Presanella mountain range in the northern part and through sedimentary rocks in the southern part of the catchment (Sauro 1974). A submerged ridge divides the lake into a main western basin (Brenzone, 350 m depth) and a shallower eastern basin (Bardolino, 81 m depth), with

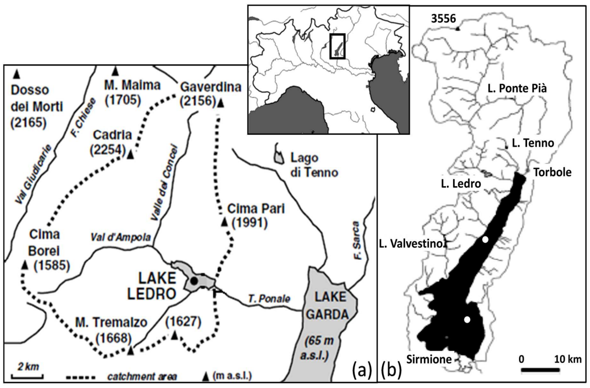

Fig. 1 Geographical setting including catchment for (a) Lake Ledro and (b) Lake Garda. Dots are indicating coring locations.

the latter basin accounting for only 7% of the total lake volume (Salmaso 2010). Since the first half of the 20th century, the River Sarca has been interested by hydroelectrical exploitation, which has affected the lake sedimentation rate (Milan et al. 2015).

Lake Ledro is a smaller lake (area = 3.7 km^2, Vol = 0.08 km^3, Zmax = 49 m) of glacial origin, located very close to the northern extremity of Lake Garda (Fig. 1). The large catchment area (111 km^2) ranges from 2254 m a.s.l. down to 652 m a.s.l.. Previous work on the sediment from Lake Ledro has shown several stages of high flood frequency during the Holocene, which are due to the combined effects of the torrential regime of the two temporary tributaries, Massangla and Pur rivers, the steepness of their valleys and the high ratio between catchment and lake area (30:1 ratio; Vannière et al. 2013; Simonneau et al. 2013a). The outlet Ponale River was responsible for the downcutting of the lake in a morainic dam (Beug 1964).

The two lakes are connected by an underwater pipe located at 25 m depth in Lake Ledro. Water is forced through a pump-storage power plant built on the River Ponale down to Lake Garda, and then the water is pumped back up. The lake-level of Lake Ledro has been regulated for hydroelectricity production since production since AD 1929 (Vannière et al. 2013).

Detailed information concerning biological and chemical data, such as diatom and Cladocera assemblage compositions, subfossil pigment concentrations, and diatom-inferred total phosphorus (DITP) are available in previous limnological and paleolimnological studies by Salmaso (2010), Salmaso & Cerasino (2012) Milan et al. (2015; submitted) and Tolotti (in prep.).

Sediment coring and chronology

A gravity corer (UWITEC, Austria) was used to collect four short sediment cores in Lake Garda: the master cores Bren1-09 and Bar1-11 and the parallel cores Bren2-09 and Bar2-11, respectively, from the deepest point of the Brenzone (Bren) basin (45°42´06´´N, 10°43´30´´E, collected in October 2009) and from the deepest point of the Bardolino (Bar) basin (45°32´58´´N, 10°40´34´´E; collected in January 2011). The same gravity corer was used to collect one master core, Led1-11, from the deepest point of Lake Ledro (45°52'44"N, 10°45'10"E; collected in December 2011). All the cores were vertically extruded and sliced in the laboratory at 0.5 cm intervals from 0 to 30 cm, and at 1 cm intervals from 31 cm down to the core bottom (~54 cm depth for Brenzone, 63 cm for Bardolino and 83 cm for Lake Ledro).

The two parallel cores collected from Lake Garda were analyzed for this work, while the master cores Bren1-09 and the Bar1-11 were used for previous paleolimnological studies, including the radiometric dating. The matching between the master and parallel cores, which is based on the water and dry weight percentage depth profiles, exhibited well-resolved fluctuations and comparable peaks. The chronologies of the master cores from Lake Garda and Lake Ledro were established using the CRS dating model (Appleby 2001) on the basis of direct gamma assay radiometric analyses (^{210}Pb, ^{226}Ra, ^{137}Cs and ^{241}Am) conducted at ENSIS Ltd-University College London, UK. The few vegetal remains found in the Brenzone core and in the Ledro core were dated using ^{14}C at the Poznan Radiocarbon Laboratory, Poland.

Geochemical methods

Major and trace elements were measured on 0.2 g of dried and homogenized powder using a Bruker S8 Tiger WD-XRF analyzer equipped with an Rh anticathode X-ray tube. Specific details on the calibrations, accuracy and precision are presented by Rydberg (2014); for most of the elements reported here accuracy is within 10% and analytical precision within 5%. Although a general overview of all the main elements and their subdivision in major groups (i.e. major elements, redox, lithogenic trace and trace elements) are discussed, the study focuses on a series of process-relevant element ratios. In particular the Mn/Fe ratio was used to infer changes in the redox conditions at the three study sites (Brenzone, Bardolino, and Ledro). The Si/Al ratio was used to infer changes in biogenic silica for the comparison with the trends in subfossil diatoms studied by Milan et al. (2015). The Pb enrichment factor (PbEF) was analyzed for all the three cores to outline the atmospheric pollution in this region. The PbEF is calculated using titanium (Ti) as the reference element and the ratio of Pb/Ti in the deepest sediments in each core was used as reference value. Moreover, the Zr/Ti ratio, a proxy for tracking changes in grain size patterns, was considered in order to understand the impact of the construction of dams and power plants on the sediment quality in the two lakes. K/Al was considered as a proxy for mineral matter changes, whereby lower values generally reflect more-weathered mineral matter and higher values less-weathered mineral matter (Kauppila & Salonen 1997). Arbitrary zones were added on the geochemical and biological stratigraphies in order to facilitate core comparisons and to identify the major common changes in each core. Geochemical and biological data were drawn with the software C2 version 1.7.2 (Juggins 2007).

Results

Chronology

The ^{210}Pb dating of the master core from Brenzone basin (Bren1-09) placed the year AD 1896±36 at the depth of 26.75 cm, while the radiocarbon date at the depth 48.5 cm indicated an age of AD 1418±30 (Fig. 2). In the Bardolino master core (Bar1-11) ^{210}Pb analysis set the year AD 1842±30 at the depth of 31.5 cm. The Ledro core was dated with ^{210}Pb back to the year AD 1861±23 at the depth of 27.75 cm, and two radiocarbon dates yielded AD 1689±9 at 82.5 cm and AD 1783±21 at the depth of 38.5 cm, respectively. As the radiocarbon date at 38.5 cm is in good agreement with the ^{210}Pb chronology, the radiocarbon date at 82.5 cm is considered as an outlier. Further details on the radioisotopic dating, as well as the CRS age-depth models and sedimentation rates for the two profundal cores from Lake Garda (Bren1-09 and Bar1-11) and for the Ledro core are available in Milan et al. (2015) and in Tolotti et al. (in prep.), respectively.

General trends of the geochemical records (XRF data)

In the Brenzone core the XRF analyses showed a major change in composition at ~22.5 cm depth and a smaller change in composition at ~40 cm depth (Fig. 3a). In the upper 22.5 cm elements associated with mineral matter, such as Mg, Al, K and Ti, declined by 25–50%. For example, Al declined from values >5% to 2.8–4% and Ti from >2800 µg g^{-1} to 1500–2000 µg g^{-1}. In contrast, the organic matter, Ca, some redox sensitive elements and pollutant indicators all increased. Organic matter, inferred from loss on ignition, increased from 6–12% to 11–27%, as did some elements often associated with organic matter such as Br, which increa-

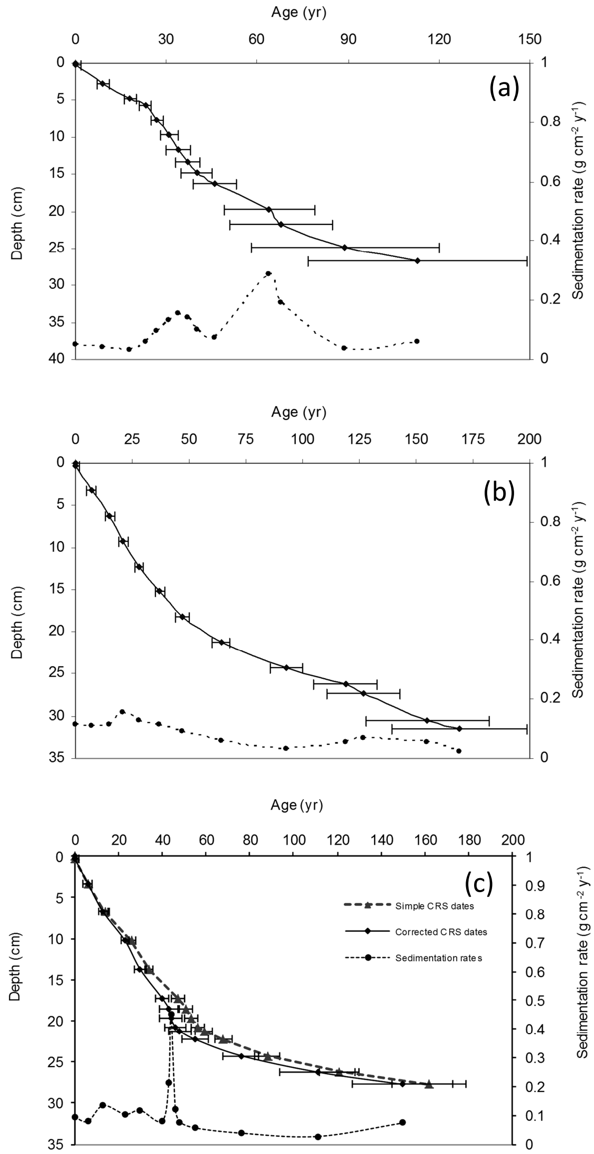

Fig. 2 Radiometric chronology of (a) Bren1-09, (b) Bar1-11 and (c) Ledro1-11. The solid line shows age, while the dashed line indicates sedimentation rate.

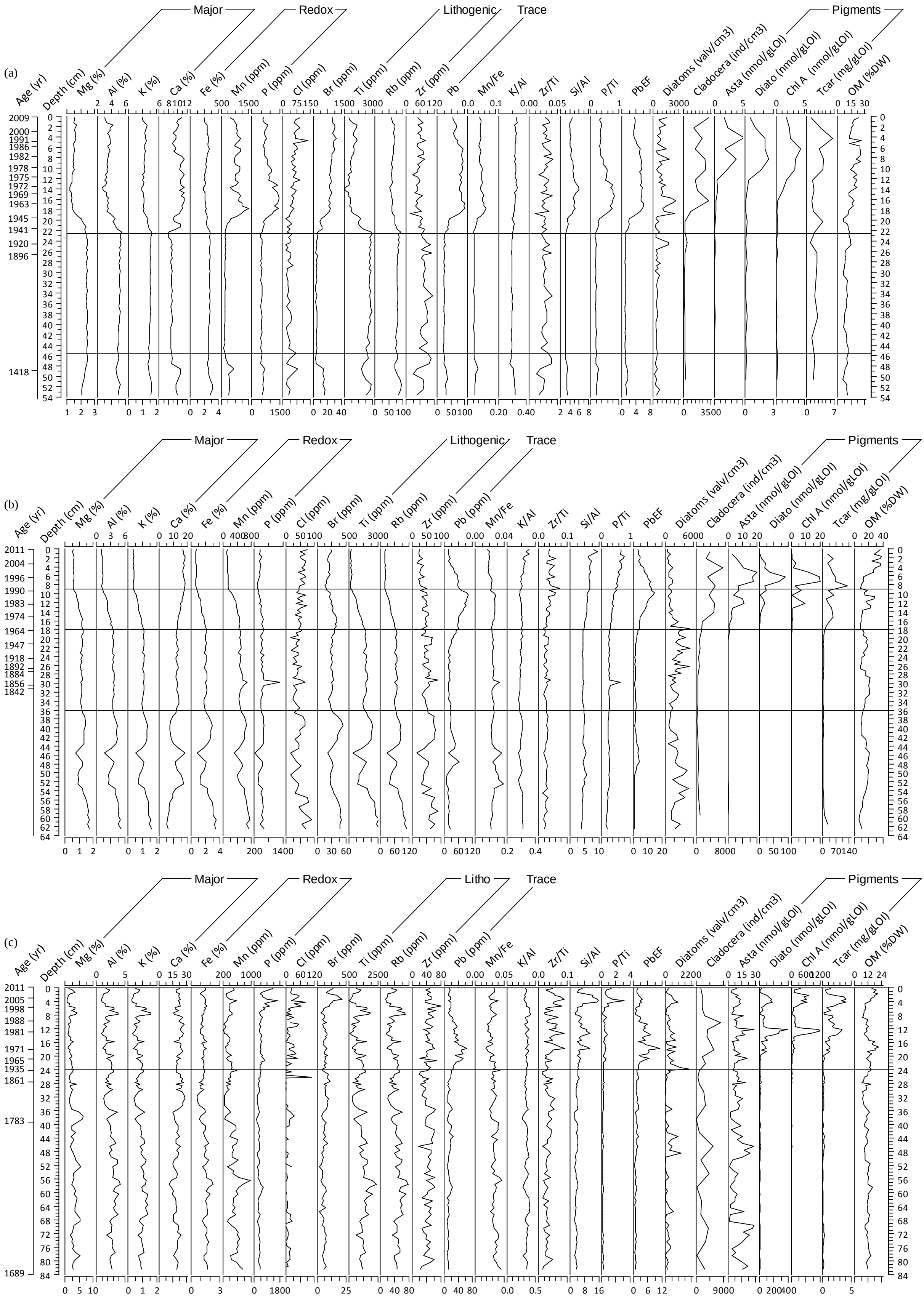

Fig. 3 Selected geochemical and biological profiles for (a) Bren2-09, (b) Bar2-11 and (c) Ledro1-11. PbEF: Pb enrichment factors; Diatoms: diatom concentration; Cladocera: Cladocera concentration; Asta: astaxanthin; Diato: diatoxhantin; Chl A: chlorophyll *a*; Tcar: total carotenoids; OM: organic matter.

sed from ≤6 µg g^{-1} to 20–30 µg g^{-1}, and Cl, which increased from 40 µg g^{-1} to more than 100 µg g^{-1}. Calcium increased from about 8.5% to 10–11%, which we inferred as being $CaCO_3$, and trace metals increase, such as Pb from <30 µg g^{-1} to 60–100 µg g^{-1}. P, Mn and S all increased, although they exhibit peaks at different depths. The change in composition was clearly expressed in changes in elemental ratios, which indicated changes in redox (increase in Mn/Fe), quality of mineral matter (increase in K/Al), increase in nutrients (increased P/Ti) and biogenic Si (increased Si/Al), and increasing pollution (increasing PbEF). The change in composition below 40 cm was less distinct and not as cohesive amongst element groups. Instead, the main changes were in elemental ratios with slight increases in Si/Al, P/Ti, Fe/Mn, K/Al and PbEF.

Even though changes in sediment composition are not as pronounced in the Bardolino core (Fig. 3b), some slight variations in the elements trends were observed along the entire core. The first period, covering the uppermost 9 cm, exhibited constant values for almost all the elements. Mg, Al and K showed values ≤1%, while Ca remained around 17% and Ti around 650 µg g^{-1}. Mn and P remained stable around 140 and 450 µg g^{-1}, respectively. Organic matter in the Bardolino basin varied cyclically through the whole profile from 10% to 30%, registering higher values (24–38%) in this uppermost section. Bromine varies from 20 to 50 µg g^{-1} mainly inverse to organic matter, but also increases in the upper section from 18 to 30 µg g^{-1}. Cl mainly varies in similar fashion as Br (but with greater analytical noise), but Cl shows an increasing trend (~45 to 75 µg g^{-1}) already from about 18 cm depth (c. early 1960s). Trace metals exhibited a decrease in values after the peak recorded at different depths between 9 and 18 cm, e.g. Pb decreased from 60% at the beginning of the section to 25% at the core surface. PbEF presents the same trend as Pb concentrations along the entire core. Mn/Fe showed a weak decrease, while K/Al presented the same value (0.3) for the entire core and Zr/Ti values fluctuated around 0.04. Si/Al ratios increased already after ~18 cm (1960s) from 4 up to 10 at the beginning of the 21st century. The opposite trend was recorded for P/Ti, which decreased after ~18 cm (c. 1960s) from 4 to 1.5. Between 9 and 18 cm all the major and other lithogenic elements registered a decrease of 40%–50% of the values recorded below 18 cm, and show the same trends as Br and Cl. The trend for Ca, however, is inverse to the other major elements such as Mg and Al. Calcium increased from 12–14% in the interval 18–35 cm to 16–18% in the top 9 cm. Zr/Ti showed also a slight increase. Zn, Pb and PbEF show peak values at 10 cm depth, whereas the peak for Cu is somewhat deeper (15 cm). Constant values were recorded for all the elements and the ratios between 18–36 cm. Compared to the other elements, which exhibited higher values in this section, trace metals showed very low concentrations; for example, Pb had values around 20 µg g^{-1}. Below 36 cm all the elements and the elemental ratios showed a series of synchronous variations, in particular between 39 and 54 cm.

The core collected from Lake Ledro showed continuous oscillations and no significant trends in all the different elements (Fig. 3c). Mg and Al fluctuated around 2.5%, while Ca oscillated around 21% and Mn around 430 µg g^{-1}. P and P/Ti ratios exhibited stable values below ~25 and 20 cm, respectively (c. 1920s and 1950s), where after these showed a slight increase and a peak at ~4 cm (beginning of the 21st century). In the same period Br recorded also a peak. Ti values oscillated around 1400 µg g^{-1} but with a generally declining trend until ~24 cm (c. 1940s), when they decrease around 1000 µg g^{-1}. Trace metals did not show significant changes, except for Pb, which showed the same trend as in Lake Garda. Pb, as well as PbEF, increased in values during the first half of the 20^{th} century until the peak at ~17 cm (c. 1970s). As observed for the single elements, almost all the ratios showed fluctuating trends. In particular Zr/Ti showed an increase in the fluctuation frequency after ~24 cm (the 1930–1940s). Among the ratios, Si/Al exhibited a different trend compared to the other ratios. The steady trend was interrupted by a rapid increase in values at 17, 13 and 4 cm (in early 1970s, 1980s and at the beginning of the 20^{th} century, respectively).

Comparison of the geochemical records with biological proxies

Considering the diatom concentration (number of diatom valves g^{-1}DW) in the Brenzone core (Fig. 3a) it is evident that an increase in values began already at the end of the 19^{th} century. Even if the peak of Si/Al was to some extent delayed compared to the peak in diatom concentration, the two proxies exhibit the same trend. Cladocera concentration increased after the 1940s from 200 ind cm^{-3} to more than 3000 ind cm^{-3}. On the other hand subfossil pigments presented stable and very low values until the 1970s. After that period they showed an increase, reaching their maximum value in early 1990s (except for diatoxanthin, which peaked a bit earlier in the 1980s).

Biological proxies in the Bardolino core showed higher concentrations compared to those in Brenzone (Fig. 3b). As observed for geochemical elements, also the biological proxies showed a change in the late 1960s. The diatom concentration decreased drastically from 5000 valves g^{-1}DW to less than 1000 valves g^{-1}DW, showing an opposite trend compared to the Si/Al ratio. On the other hand Cladocera increased until the peak (7000 ind cm^{-3}) at the beginning of the 20^{th} century. As observed in the Brenzone core, subfossil pigments increased slightly only after the 1970s, while a rapid change in the concentrations was observed after the mid-1990s, in concomitance with the return to constant values in the geochemical data.

Biological proxies in the Ledro core showed the highest concentrations as compared to those collected from Lake Garda (Fig. 3c). Diatoms showed a peak of about 2000 valves g^{-1}DW in late 1930s, which was not observed in the Si/Al ratio. On the other hand, other high values shown by Si/Al ratio are also reflected by diatom concentrations. According to pigment data, Cladocera presented continuous fluctuations without a significant trend, as highlighted also by astaxanthin, which is considered as a proxy for invertebrates. As already observed in the two Garda cores, the subfossil pigments increased in concentrations only after the late 1960s, showing high values during the 1980s and at the beginning of the 20^{th} century.

Discussion

The different radiometric dating approaches indicate that the two cores collected from the two basins of Lake Garda cover a period of ~700 years (Milan et al. 2015). The core collected from Lake Ledro, which was longer compared to the Garda ones, represented only the last ~300 years. Comparisons of some of the geochemical proxies indicate good coherence for the age-depth models for the past 150 years, but also suggest some uncertainties in the pre-AD 1850 ages. Given that the significant changes in geochemistry and biology occur over the past c. 100 years, this does not affect the chronology of changes for the main period of interest. The comparison of the PbEF profiles could particularly be useful as a tool to further develop the age-depth models for older sections. For example, the slight increase in PbEF toward the base of the Brenzone core (48.5–53.5 cm) is at a similar depth to an increase in the Bardolino core (44.5–54.5 cm). If these increases in PbEF are considered synchronous then also a low value in Fe/Mn in both cores (48.5 cm in Brenzone, 44.5 cm in Bardolino) would be synchronous. If the ^{210}Pb ages are run in Clam 2.2 (Blaauw 2010) and the one ^{14}C date for Brenzone is excluded, the age-depth models suggest a late-17th century date for the increase in PbEF in both cores at about 50 cm. This would coincide with an increase in Pb during AD 1660–1720 in the Monte Rosa ice record (Schwikowski et al. 2004). This would imply that the ^{14}C date in Bardolino leads to a possible overestimation of the sedimentation rate in the age-depth model. In Lake Ledro PbEF preceded by 50–70 years the ^{210}Pb age at the depth of 38.5 cm and postponed for 300 years the core bottom. The discrepancy between the different methods and between the two lakes were probably related to the many floods events occurred in Lake Ledro causing an irregular transport of material into the lake, which in turn altered the sedimentation rate.

The geochemical analysis reveals an overall change in Lake Garda since the mid-1900s. At the same time there are a few differences recorded in the two basins, reflecting the effects of local impacts on each of them. In contrast, the geochemical analysis of Lake Ledro's sediment record shows continuous fluctuations along the entire core, which could probably be related to the influence of the large catchment area on the lake system. Lead concentrations are useful to assess the impact of pollution on the two lakes. Similar Pb patterns are observed in the three cores, reflecting the typical trend recorded in the Alpine region that reflects mainly larger scale atmospheric deposition in northern Italy/southern Alps (Schwikowski et al. 2004; Rogora et al. 2006; Thevenon et al. 2011). After the early 20th century, both lakes showed an increase in Pb content due primarily to the use of lead additives in gasoline. After the Pb peak during the 1970s–1980s, the concentrations decreased due to the ban of lead additives and increasing emission controls (e.g. UN-ECE Convention on Long-Range Transport of Atmospheric Pollutants). One difference among the cores, however, is that higher values for Pb are recorded in the Bardolino basin. In fact, the southern border of Lake Garda is located near the Po plain, which is Italy's most industrialized and populated region (Rogora et al. 2006). In addition, the spheroidal carbonaceous particles (SCP) analysis in the sediment of European mountain lakes identified Central Europe as the most industrialized region from the beginning of the 20th century (Rose et al. 1999). Like Pb, SCP, which originate from fossil fuel combustion, are used as a proxy for the atmospheric deposition from industrial sources (Rose 2001). Overall, the increase in Pb records in all the three cores at the end of the 20th century could be the effect of regional atmospheric pollution patterns, in combination with local contributions (mainly petrol Pb).

The Mn/Fe ratio is used in this study to assess the historical redox conditions in the two basins of Lake Garda and in Lake Ledro. Brenzone exhibited a change in the redox condition after the 1960s. The higher ratios after 1960 suggest more-oxygenated bottom water (Naeher et al. 2013), which agrees with the limnological information recorded during the monitoring period (Salmaso & Mosello 2010). Before the 1960's the Mn/Fe ratios were lower, indicating that the sediment was anoxic (Koinig et al. 2003). No information on O_2 at the lake bottom are available from before the monitoring period. However, in Milan et al. (2015), the 430:410 spectrophotometric absorbance ratios suggested a pronounced pigment degradation, due to the combined effects of the great depth of the Brenzone basin, which enhances the pigments degradation rate (Leavitt 1993), and the oxygenated conditions in the bottom water (Guilizzoni et al. 1992). Therefore the anoxic conditions indicated by the Mn/Fe ratios could refer only to the sediment-water interface and not to the bottom water. The redox conditions did not change in Bardolino as observed in Brenzone, with only a slight decrease in the Mn/Fe ratios recorded after the 1990s. The lower ratios could indicate a change in redox conditions, and in fact reduced oxygen concentration in the Bardolino bottom water were recorded at the beginning of the 1990s (Salmaso et al. 1994). A different trend was observed in Lake Ledro. Although anoxic conditions were registered during the 1970s–1980s and the seasonal oxygen depletion was recorded at sediment-water interface (Boscaini et al. 2012), no particular changes in redox conditions were observed (or at least preserved) in this sediment core.

Moreover, the Mn/Fe ratios were also considered as a possible proxy for lake productivity. In the Brenzone basin the ratios suggest an increase in aquatic production, corroborating previous results based on diatom-based inferences and pigments analysis (Milan et al. 2015). In fact algal biovolume data show a continuous increase since AD 1996 with a dominance of chlorophytes, diatoms and cyanobacteria (Salmaso 2010). An opposite trend was observed in the Bardolino basin suggesting a decrease in aquatic production, while previous limnological and paleolimnological data showed an increase in the phytoplankton biovolume during the past few decades (Milan et al. 2015; Salmaso 2002). For comparison, a geochemical study on a sediment core collected in Lake Bourget revealed a period of oxygen depletion as a consequence of the increase in organic matter production during the eutrophication period (Giguet-Covex et al. 2010).

Both lakes were previously analyzed for their diatom assemblage compositions. Thus biogenic silica, as inferred by changes in Si/Al, was used to infer changes in the total diatom production (Peinerud et al. 2001). In the three studied cores, Si/Al ratios suggest an increase in deposited biogenic silica from the beginning of the 1960s. The diatom concentrations of the Brenzone core increased in the sample following the first increase in the ratio. In the Bardolino basin an opposite trend was observed between diatoms and Si/Al ratios, which could be related to changes in the diatom assemblage composition after the 1960s. Larger diatoms, such as *Tabellaria flocculosa* (Roth) Kützing, *Stephanodiscus neoastraea* Håkansson & Hickel and *Aulacoseira granulata* (Ehrenberg) Simonsen, replaced the smaller and much more abundant diatom taxa, which characterized the bottom part of the sediment core (Milan et al. 2015). In Lake Ledro, Si/Al ratios followed the diatom concentration trend only after the 1960s, and showed in particular the same pattern as the large colonial pennate diatoms. Higher values of the Si/Al ratios corresponded to higher concentrations of this diatom group. Before the 1960s, the unicellular Centrales dominated the diatom assemblages. Although the diatom concentration revealed higher values between 44 and 48 cm and a peak in the 1940s (Tolotti et al. in prep.), Si/Al ratios were not affected by these higher concentrations. In Lake

Kutsasjärvi the lack of correlation between diatoms and Si/Al concentrations was explained with the variations in Si content in the different diatom taxa (Peinerud et al. 2001). In fact the sole count of the valves without regard to the diatom cell sizes could alter the Si/Al ratios and make an erroneous estimate of the diatom productivity.

The overall change in Si/Al ratios in both lakes agree with the previous observations based on diatoms and pigment analysis, which suggested a change in diatom assemblage composition and an increase in lake productivity after the 1960s (Milan et al. 2015; Tolotti et al. in prep.). An increase in lake productivity and nutrient enrichment was also estimated through P/Ti ratios (Engstrom et al. 1985), which show an increase in both Garda basins since the 1960s. Total phosphorus concentrations inferred by diatoms (DITP) confirmed a nutrient enrichment after the 1960s, while diatom concentrations and subfossil pigments supported the resulting increase in lake productivity (Milan et al. 2015). In Lake Ledro the P/Ti ratios confirm the nutrients increase after the 1960s (Tolotti et al. in prep.). In addition the high diatom concentrations and subfossil pigments concentrations at the beginning of the 21st century confirmed the high lake productivity suggested by the peak in P/Ti ratio.

Another consequence of nutrient enrichment, derived from anthropogenic disturbance, was an increase in Cl concentrations. In fact a recent study on deep subalpine lakes revealed an increase in lake-water Cl concentrations since AD 1988 as an effect of population growth and a tourism boom (Rogora et al. 2015). In the sediment geochemical analysis the Cl content was mainly a function of organic matter, therefore the slight increase in Cl in all the studied lakes since the 1960s should be interpreted carefully. However these Cl increases could be related to the nutrient enrichment in both lakes. In fact Rogora et al. (2015) attributed the shift in lake-water Cl concentrations to an increased touristic activity in the catchment area of Lake Garda, which raised the Cl discharge derived from wastewater treatment. In addition, Cl stored in the groundwater has been delivered to the lake, increasing once again the lake-water Cl concentration. In Lake Ledro the Cl content was more variable and noisy, preventing a trustworthy interpretation of the data.

Since the 1930s, both lakes were affected by hydropower establishment. Zr/Ti ratios were considered as a proxy for changes in grain size and, as well as an indicator of the origin of the material deposited in the two lakes before and after this anthropogenic impact. Even though the River Sarca was strongly impacted by the establishment of dams and power plants, we do not observe a shift in Zr/Ti ratios in the Brenzone basin. No important changes were observed in the grain-size patterns since the hydropower establishment, despite a peak in sedimentation rate in the early 1940s. On the other hand, K/Al ratios indicate a variation in the quality of the mineral matter after the 1940s, which could be related to these activities. An increase in K/Al ratios would suggest an increase in less-weathered mineral matter, which is less depleted in more labile elements such as K. The same trend was observed in the mineral content determined by dry weight (Milan et al. 2015), supporting the K/Al pattern. In contrast, the Bardolino basin showed a weak change in Zr/Ti ratios after the 1960s, which was not related to the hydropower establishment, possibly because of the longer distance from River Sarca and the presence of an underwater ridge, which limits the amount of mineral material coming across the lake and the deep basin. A different trend was observed for Zr/Ti ratios in Lake Ledro, where the fluctuations recorded since the 1940 appeared to be influenced by the lake-level regulation. Mineral matter quality, indicated by K/Al ratios, showed no significant changes after that period, whereas Rb concentrations showed a comparable trend as observed for Zr/Ti ratios. A study on Lake Majeur highlighted that changes in Rb content depended on the lake-level regulation during the hydroelectric activity (Simonneau et al. 2013b), supporting the observations in the core of Lake Ledro. On the other hand, K/Al registered a change in the mineral matter quality during the flood events.

The previous paleolimnological study based on biological data (Milan et al. 2015) highlighted a comparable temporal evolution of the reconstructed TP patterns in both basins of Lake Garda, but identified at the same time particular ecological responses at each site. The Brenzone basin appeared more suitable for the reconstruction of long-term trophic evolution, while the Bardolino basin was more suitable to understand the effect of local ecological dynamics and ecotone disturbances (Milan et al. 2015). Lake Ledro, despite the large number of flood events and the lake-level regulations, showed similar nutrient dynamics as observed in Lake Garda (Tolotti et al. in prep.). Both lakes reflect the same long-term ecological evolution recorded in other Alpine lakes, in particular large, deep lakes (Marchetto et al. 2004; Berthon et al. 2013; Wessels et al. 1999). Overall, the geochemical analyses are coherent with the results based on biological proxies, indicating a common response to human and climate impacts, especially in the context of nutrient enrichment after the 1960s. However, as already indicated by the biological proxies, the XRF data confirm also the influence of local factors on the individual basins, which are to some extent related to the size and hydrological properties of each basin. For example, the smaller Bardolino basin and Lake Ledro indicate a response, albeit weak, to some minor events (e.g. changes in primary production, lake-level regulations), whereas the larger Brenzone basin appears to be more resilient.

The impact of hydroelectric exploitation was only visible in the sediments of Lake Ledro. In particular, the continuous fluctuations in the element concentrations and ratios could be explained with the lake-level regulations, which affected the lake since AD 1929. The deep basin of Lake Garda (Brenzone) showed only minor changes in the elements associated with mineral matter, which cannot explicitly be related to human activities on the River Sarca. This study revealed the importance of the ratio between lake and catchment area on the lake geochemical dynamics. The study of biological and geochemical proxies showed that large and deep lakes, including their sediment records, seem to be more affected by direct impacts of nutrient enrichment and/or climate change than the changes in the catchment area. On the other hand, small lakes with larger catchment areas are to a larger extent influenced by the modifications occurring in the drainage basin. In fact both biological and geochemical data highlighted the importance of hydrological and land-use changes in flood events, which in turn affected the lake dynamics.

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