Lake Bolsena (Central Italy): an updating study on its water chemistry

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ABSTRACT

In spite of its importance as regards size (volume 9.2 10^6 m^3, max depth 151 m) and as a source of drinking water, Lake Bolsena has not been studied from a hydrochemical point of view since the second half of the 60s, when a group of researchers from the Istituto Italiano di Idrobiologia co-ordinated a complete study of the limnology of the Latium lakes Bolsena, Albano, Vico, and Bracciano. In the following years analyses were performed sporadically; since the 90s, temperature and oxygen profiles and other studies were made by the Associazione Lago di Bolsena. Based on chemical profiles made in 2001-2003, this paper discusses the present chemical composition of Lake Bolsena waters, and compares them with those of other volcanic lakes in Latium (Bracciano, Albano, Nemi and Vico). The paper briefly considers the main factors influencing the water chemistry of Lake Bolsena, the variations observed from the analyses of the 60s, and the main sources of risk to water quality.

Key words: volcanic lakes, hydrochemistry, chemical processes, water renewal time

1. INTRODUCTION

The lake district of Central Italy (Fig. 1), with twelve lakes and a total water volume of 14.8 km^3, is the second most important in Italy after that south of the Alps. The three lakes are Bolsena, Bracciano and Albano, as they comprise respectively 62, 34 and 3% of the total volume of freshwater in the area, with volumes of 9.2, 5.1 and 0.5 km^3 (Tab. 1; Fig. 1). Lakes Vico and Nemi are smaller (0.26 and 0.03 km^3), but are also of interest as they also occupy volcanic basins. These lakes are largely the result of Pleistocene volcanic activity (Barbanti & Carollo 1966; Carollo & Barbanti 1971; Camponeschi & Lombardi 1969); the formation of lakes Bolsena and Bracciano in particular is related to subsidence and caldera formation during the final stages of volcanic activity (Pichler 1970), with direct control by large-scale tectonic processes (Nappi *et al*. 1991; Niessen *et al*. 1993). A complex volcano-tectonic origin for the lake Bolsena and Bracciano basin was suggested by Locardi *et al*. (1976). These two lakes are affected by young regional tectonic activity and do not represent typical caldera lakes (Niessen *et al*. 1993).

The importance and the potential vulnerability of these lakes is enhanced by their location in populous areas, with a great demand for water from agriculture and other civil uses; the waters of Lake Bracciano and Albano (Capelli *et al*. 2000) are already used for drinking supply to the city of Rome (Martini 1985).

There have been several studies of the limnology of the Latium lakes; see Margaritora (1992) for an extended review. A number of biological studies include information on their water chemistry, but this is rather scant and out of date. Most of the chemical data refer to a complete limnological study, with measurements of the main morphometric, physical, chemical and biological characteristics, carried out from the Istituto Italiano di Idrobiologia on lakes Bolsena, Bracciano and Vico between October 1965 and April 1970 (Istituto Italiano di Idrobiologia 1971; Istituto di Ricerca sulle Acque 1974). More recent chemical data were provided by Pagnotta *et al*. (1987), Pagnotta & Rolle (1982), Cioni *et al*. (2003) and Martini *et al*. (1994); however, these were spot studies and did not incorporate any seasonal variation.

Lake Bolsena is the main lake in peninsular Italy as regards water volume (9.2 km^3, Tab. 1). It is located at a height of 305 m, while its watershed has a mean height of 490 m and a maximum height of 690 m a.s.l. (Poggio Torrone), in the north-western part of the watershed. The lake has a circular shape (Fig. 2), of almost uniform width all round the lake. Its catchment has an area of 159 km^2, slightly greater than the area of the lake surface (114 km^2, Tab. 1). Lake Bolsena lies within the Vulsino volcanic district, in which the volcanic activity occurred in alternate effusive and explosive phases from five main centres of emission: Paleobolsena, Bolsena, Montefiascone, Latera and Neobolsena. The geological evolution of the district is very complex, with outcrops of a variety of rocks which are very different both from the petrographical and granulometric points of view, while massive sequences of lava flows, ignimbritic flows, layers of scoriae, lapilli and argillized tuffs can be distinguished. The fluvial and lacustrine alluvial deposits, the latter of which surround the whole perimeter of the lake, are altogether subordinate. The complex of vulcanites containing the lake has good porosity owing to the incoherent pyroclastic rocks and the fissuring of
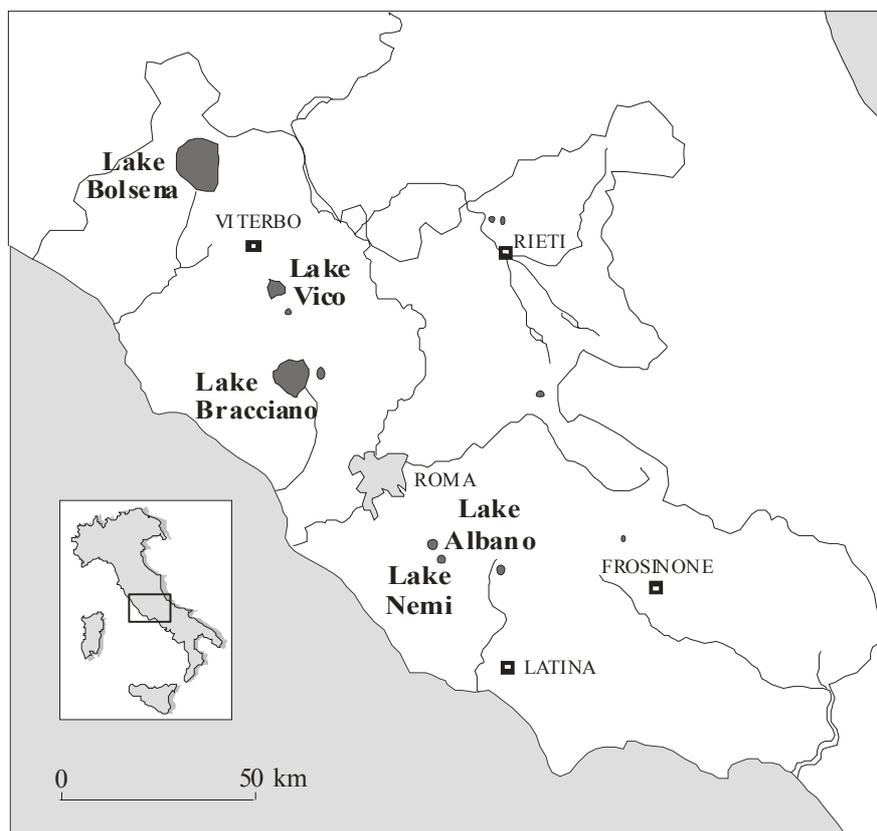
Fig. 1. Location of the main lakes in Central Italy.

Tab. 1. Main morphometric and hydrological characteristics of Lake Bolsena and other four lakes located in volcanic watershed. Watershed area not including lake surface.

	Level (m a.s.l.)	Watershed area (km²)	Lake area (km²)	Volume (10^6 m³)	Mean depth (m)	Max depth (m)	t_w (years)
Bolsena	305	159.45	113.6	9200	81	151	121
Bracciano	164	89.7	57	5050	88.6	165	137
Albano	293	16	6	464	77	175	48
Vico	510	28.05	12.1	261	21.6	48.5	17
Nemi	316	10.5	1.7	30	19.5	32.4	7

the lava and ignimbritic flows. This gives rise to a volcanic aquifer, supported by a clayey or flyschioid sedimentary substrate, of which Lake Bolsena represents the outcropping part. The aquifer has an area of 350 km², and thus exceeds the area of the watershed, which is 273 km². About 22,000 people live in the watershed, increasing to 35,000 in the summer period, and the sewage reaching the lake was untreated until 1996, after which a pipeline was constructed to convey sewage from the main population centres to a treatment plant located about three km from the lake, along the outflow (Associazione Lago di Bolsena 2003). Further sources of pollution are the fertilisers derived from agricultural runoff. The total amount of N and P applied as fertiliser has been evaluated at 950 and 450 t y⁻¹ respectively (Associazione Lago di Bolsena 2003). The hydro-geological basin is slightly larger than the lake area,

bounded by an impermeable clayey layer formed of marine deposits (Pagano 1998) (Fig. 2). The Bolsena watershed is separated from the main hydrographic watershed of the River Tiber, the main river in Latium, as the lake outlet, the River Marta, drains directly into the Tyrrhenian Sea, with a total drainage basin of 1091 km². The low ratio between total watershed surface and lake volume indicates a low theoretical water renewal time, evaluated at 120 y. However, the real turnover rate is probably greater (discussed below) making the lake more susceptible to pollution and thus demands a higher degree of care in sewage disposal and water use.

The aim of this paper is to update the information on the water chemistry of Lake Bolsena, on the basis of samplings performed from June 2000 to February 2003, comparing the results with those obtained in the sixties and seventies. Limited to the main ion composition, the
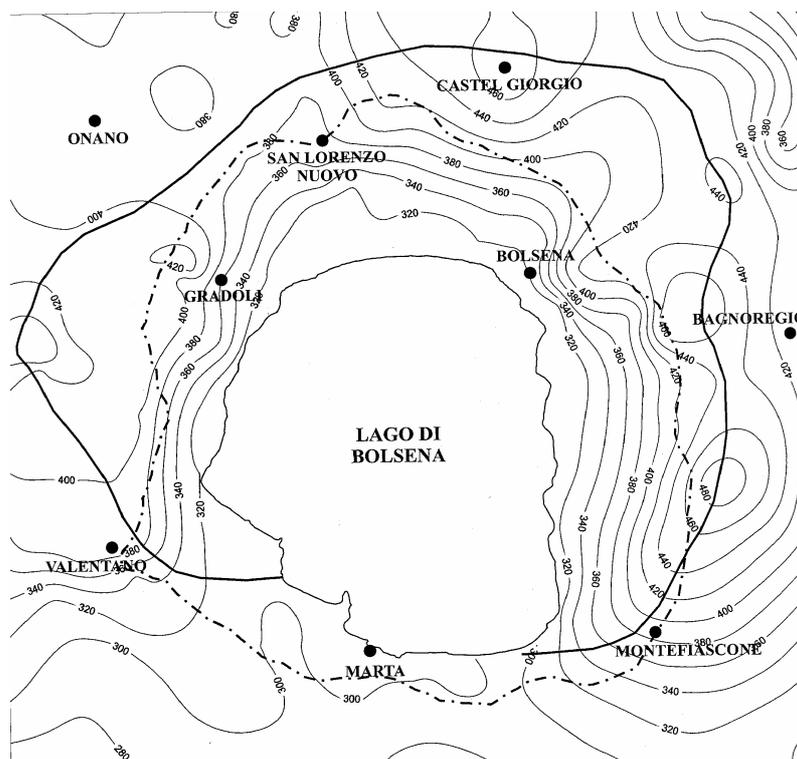
Fig. 2. Lake Bolsena, hydrographic (broken line) and hydrogeological (full line) basins.

comparison will be extended to include the other volcanic lakes of Bracciano, Albano, Nemi and Vico in Central Italy.

2. SAMPLING AND ANALYTICAL METHODS

Lake water samplings were performed in December 2001, April, August 2002, and February 2003 at the following depths: 0, 20 50, 100, 130 m. Unless differently indicated, concentrations used in the text are obtained as average of the values measured at each depth weighted on the volume of the corresponding water layer.

Temperature and oxygen concentration were measured only for the April 2003 sampling, but several profiles are available for the period 1997-2000 (Associazione Lago di Bolsena 2003) and will be discussed in the paper.

Tables 2 and 3 show the chemical variables considered and the analytical methods used, the corresponding limits of detection (LOD) and repeatability at different concentrations, expressed as relative standard deviation (RSD, percent ratio between the standard deviation of 15-25 measurements and the mean value). Details of the analytical methods and the quality assurance/quality control criteria adopted in the laboratory are given by Tartari & Mosello (1997). Metals other than the main ions were measured on the samples taken in August 2002 by ICP-AES (Simultaneous ICP-OES Vista MPX, Varian; Tab. 3) following the methodologies given by U.S. E.P.A. (1994, 1996), ISO 11885 (1996) and A.P.H.A. (1998).

Water chemistry of the lakes Albano, Mergozzo, Maggiore, Lugano, Como, Iseo and Garda, used for the comparison of the inorganic carbon equilibrium with Lake Bolsena, was obtained by analyses performed in the same laboratory with the same analytical methods.

Atmospheric deposition chemistry was measured at the forest (*Quercus cerris*, *Turkey oak*) station of Monte Rufeno, at 690 m a.s.l, located about 20 km north-east of the lake. Bulk deposition measurements, in the open and throughfall, were performed weekly, following the methods adopted in the Italian National Monitoring Programme of Forest Ecosystems (Mosello *et al.* 2002). The data used in the paper are the mean volume-weighted concentrations for the period January 1998-December 2002. The input to the watershed was calculated using the open field bulk deposition for the lake surface (113.6 km^2) and the throughfall deposition for the land part of the watershed (159.5 km^2). The analytical methods used are the same as those used for the analyses of lake water.

The relationship between pH and bicarbonate at different atmospheric partial pressure of carbon dioxide used to discuss the inorganic carbon equilibrium of the waters is described by Stumm & Morgan (1981). In particular, the stoichiometric approach of the equilibrium of solutes in aqueous carbonate solution has been used, having the effect of simplifying the lake Bolsena waters to a solution of calcium carbonate. The equilibrium constants of inorganic carbon and calcite solubility used, reported by the same text, are corrected for the

Tab. 2. Analytical techniques used, lower detection limit (LOD) and repeatability at different concentrations of some of the analytes (RSD relative standard deviation).

Variable	Method	Units	LOD	Repeatability		References
				Mean	RDS	
pH	Potentiometry					Westcott 1978
Conductivity	Conductometry	$\mu S\ cm^{-1}$	0,5	14.3	1.4	A.P.H.A. 1992
				186.1	0.6	
Alkalinity	Potentiometry	$\mu eq\ l^{-1}$	1	37	5.4	A.P.H.A. 1992, Gran 1952
				179	1.5	
				341	1.7	
Nitrate	Ionic chromatography	$\mu eq\ l^{-1}$	1	14	3.0	A.P.H.A. 1992, Camusso & Polesello 2000a
		$\mu eq\ l^{-1}$		38	1.7	
				104	0.7	
Ammonium	Spectrophotometry	$\mu g\ N\ l^{-1}$	5	63	3.8	Fresenius 1988
		$\mu g\ N\ l^{-1}$		320	3.4	
Total N	Spectrophotometry	$\mu g\ N\ l^{-1}$	100	540	5.6	Valderrama 1981, A.P.H.A. 1992
		$\mu g\ N\ l^{-1}$		1210	3.3	
Reactive P	Spectrophotometry	$\mu g\ P\ l^{-1}$	3	8	12.4	Valderrama 1977
		$\mu g\ P\ l^{-1}$		165	5.3	
		$\mu g\ P\ l^{-1}$		242	1.8	
Reactive silica	Spectrophotometry	$mg\ l^{-1}$	0.02	0.42	7.1	Golterman 1978
		$mg\ l^{-1}$		2.61	1.1	
Sulphate	Ionic chromatography	$\mu eq\ l^{-1}$	2	34	8.2	A.P.H.A. 1992, Camusso & Polesello 2000a
		$\mu eq\ l^{-1}$		58	4.3	
Chloride	Ionic chromatography	$\mu eq\ l^{-1}$	0.5	6	10.0	A.P.H.A. 1992, Camusso & Polesello 2000a
		$\mu eq\ l^{-1}$		9	6.3	
Calcium	Ionic chromatography	$\mu eq\ l^{-1}$	0.5	27	6.3	U.S. E.P.A. 1986, Camusso & Polesello 2000b
		$\mu eq\ l^{-1}$		74	3.6	
Magnesium	Ionic chromatography	$\mu eq\ l^{-1}$	1	9	5.7	U.S. E.P.A. 1986, Camusso & Polesello 2000b
		$\mu eq\ l^{-1}$		58	2.8	
Sodium	Ionic chromatography	$\mu eq\ l^{-1}$	0.5	5	10.0	U.S. E.P.A. 1986, Camusso & Polesello 2000b
		$\mu eq\ l^{-1}$		11	7.9	
Potassium	Ionic chromatography	$\mu eq\ l^{-1}$	0.2	3	13.2	U.S. E.P.A. 1986, Camusso & Polesello 2000b
		$\mu eq\ l^{-1}$		8	7.7	

lake temperature and water ionic strength (the extended Debye-Huckel approach, as the water ionic strength of Lake Bolsena and of the other lakes considered in the comparison have ionic strengths below 10^{-1} M). The presented values of carbon dioxide in atmosphere were assumed to be 355 μatm (Riebesell *et al.* 1993).

Tab. 3. Lower detection limit (LOD), repeatability at different concentrations and Lake Bolsena measured values at the 07/08/02 sampling (units: $\mu g\ l^{-1}$). Ag, Bi, Cd, Co, Cr, In, Pb, Tl, Mo, Be, Ni, Ga concentrations resulted lower than 1 $\mu g\ l^{-1}$.

Variable	LOD	Repeatability		Measured values	
		Mean	RSD	0 m	130 m
Aluminum	7	66	4.2	9	9
Arsenic	6	66	3.6	<6	<6
Boron	4	149	11.1	390	395
Barium	1	66	2.4	35	38
Copper	2	33	3.7	<2	4
Iron	1	165	2.0	<1	25
Manganese	0.1	17	5.4	<0.1	21
Selenium	7	170	3.3	<7	<7
Zinc	0.5	168	1.9	<0.5	20
Lithium	0.7	-	-	42	41
Strontium	0.1	-	-	420	450

3. RESULTS AND DISCUSSION

3.1. Water chemistry

The lake water is characterised by a high ion concentration (mean of 10.77 meq l^{-1} in the February 2003 sampling), with a prevalence of bicarbonate among the anions (38% of the total ion concentration) and sodium among the cations (17%) (Tab. 4). Magnesium, potassium and calcium have approximately the same concentrations, constituting 12, 12 and 10% respectively of the total ion content; chloride and sulphate (8% and 4%) are of minor importance among anions, while nitrate and ammonium are negligible, with regard to ion concentrations. The ion concentration results in a conductivity of 485 $\mu S\ cm^{-1}$ at 20 °C and an ionic strength of 6.75 mmol l^{-1}. pH values range between 8.7 and 8.1 as the mean of the epilimnion and hypolimnion, the lowest value of 7.6 being detected in the bottom waters on December 2001. The mean ion concentrations and conductivity measured in the 2001 and 2002 samplings were not significantly different, ranging between 10.5 and 10.8 meq l^{-1}, 475 and 486 $\mu S\ cm^{-1}$. The lowest and highest conductivity values measured at single depths (475 and 492 $\mu S\ cm^{-1}$) were obtained respectively in the surface and bottom waters on August 2002, as an effect of thermal stratification and the biological processes going on in the thermally separated layers. The differ-

Tab. 4. Concentrations of the main chemical variables measured in epilimnion (0-15 m) and hypolimnion (20-130 m) in Lake Bolsena (χ 20 °C: conductivity at 20 °C; T.alk.: total alkalinity; RP, TP: reactive and total phosphorus; TN: total nitrogen; RSi: reactive silica).

	Depth (m)	pH	χ°C (μS cm^{-1})	N-NH$_4$ (μeq l^{-1})	Ca (μeq l^{-1})	Mg (μeq l^{-1})	Na (μeq l^{-1})	K (μeq l^{-1})	T.Alc. (μeq l^{-1})	Cl (μeq l^{-1})	SO$_4$ (μeq l^{-1})	N-NO$_3$ (μeq l^{-1})	RP (μg l^{-1})	TP (μg l^{-1})	TN (mg l^{-1})	RSi (mg l^{-1})
07/08/2002	0	8.73	475	0	878	1209	1926	1243	4007	838	406	1	2	7	0.16	0.02
	20	8.46	484	1	993	1217	1909	1238	4098	823	398	1	4	13	0.36	0.14
	50	8.15	486	1	993	1217	1917	1253	4095	826	406	8	1	10	043	0.52
	100	8.08	486	0	993	1209	1904	1233	4082	826	412	8	13	15	0.39	0.71
	130	7.80	492	2	1023	1209	1904	1200	4135	835	404	14	32	38	0.72	1.91
25/02/2003	0	8.20	483	0	1043	1283	1874	1238	4106	815	408	8	6	10	0.27	0.58
	20	8.24	484	0	1043	1291	1874	1230	4105	818	396	8	7	13	0.24	0.57
	50	8.23	485	0	1043	1283	1874	1230	4105	815	404	8	9	13	0.32	0.57
	100	8.20	487	0	1043	1283	1878	1259	4105	835	400	8	8	13	0.30	0.57
	130	8.22	486	1	1043	1291	1891	1253	4098	821	410	8	11	17	0.45	0.58

ence is mostly due to calcium and alkalinity, as no relevant differences were detected in the case of the remaining main ions.

At the overturn (February 2003) nitrate was the main form of inorganic nitrogen present in the lake, with a concentration of about 110 μg N l^{-1}; ammonium shows values below 10 μg N l^{-1}, while the value of TN is about 300 μg N l^{-1}, indicating an important presence of organic nitrogen. Reactive and total phosphorus show mean values of 8 and 13 μg P l^{-1}, with slightly higher values in the deepest waters. Reactive silica concentration was 0.57 mg Si l^{-1}. Compared to water during the overturn, the nutrient elements were depleted during thermal stratification due to increased primary production and sedimentation. When overturn occurred the nutrient levels in the upper waters were replenished by mixing with the nutrient replete deeper waters. Peak values of 32 and 38 μg P l^{-1} for reactive and total phosphorus were measured at 130 m in August 2002. These values, considered together with those of ammonium (30 μg N l^{-1}) and nitrate (190 μg N l^{-1}), do not indicate, on this date, a situation of marked oxygen depletion or anoxia. Measurements of other chemical variables made in summer 2002 (Tab. 3) show low concentrations of strontium (420 and 450 μg l^{-1} at 0 and 130 m, respectively), lithium (42 and 41 μg l^{-1}) and barium (35 and 38 μg l^{-1}), while iron and manganese, below the LOD at the surface, increase to 25 and 21 μg l^{-1} in the hypolimnion; values for several other trace metals are below the LOD (Tab. 3). The values of boron (390-395 μg l^{-1}) are of interest as they are high compared with those of natural waters in the absence of urban pollution (Tartari & Camusso 1988). Boron is frequently present in hydrothermal waters as a result of volcanic activity (Arnorsson & Andresdottir 1995); values up to milligrams per litre were measured in a series of volcanic springs in the area of the volcano Etna (Parello *et al.* 2001).

3.2. Processes affecting lake water chemistry

Weathering in the watershed is considered the primary process regulating the concentrations of alkalinity, calcium, magnesium, sodium and potassium. This con-

clusion is supported by the close similarities between the ion balance of Lake Bolsena and those of the other four lakes (Bracciano, Albano, Vico, Nemi) located in watersheds with the same geo-lithology (Fig. 3). Ion concentrations, from the highest to the lowest, occurred in the following order:

$$HCO_3 > Na > Ca, Mg, K > Cl > SO_4 > NO_3$$

By way of comparison, the ion composition of the lakes in the southern Alpine district, including the major Italian lakes Garda, Maggiore, Como and Iseo (Manca *et al.* 1992), is as follows:

$$Ca, HCO_3 > SO_4, Mg > Na, K, NO_3, Cl$$

Bicarbonate concentrations are the main ion species contributing to total alkalinity (TA), as evaluated from the inorganic carbon speciation, taking into account temperature and ionic strength (e.g. Stumm & Morgan 1981). At the highest pH value of 8.7, measured in the epilimnion in August 2002 (Tab. 4), the percentage of H_2CO_3* (carbonic acid and hydrated carbon dioxide), HCO_3^- and $CO_3^=$ was 0, 98, 2% of the total inorganic carbon concentration (4.0 mmol l^{-1}); at the lowest pH of 7.6 values were 6, 94, 0% of the CT concentration (4.3 mmol l^{-1}).

A second process contributing to lake water chemistry is the contribution of atmospheric deposition of ions to the watershed and lake surface. This was evaluated using the data collected in the permanent forest plot of Monte Rufeno (Fig. 1) about 20 km north-east of the lake. The effect on the lake concentrations of the atmospheric input of ions (Tab. 5) was evaluated assuming the ions behaved conservatively (i.e. no exchange of mass between water and sediments) at steady state conditions (Vollenweider 1975):

$$[m_w] = I_m / r_w$$

where $[m_w]$ is the concentration of the solute m in water (eq m^{-3}), Im is the load of the solute m divided by the lake volume (eq m^{-3} y^{-1}), r_w is the flushing coefficient (y^{-1}). The ratio between calculated and measured concentrations gives a rough estimation the potential
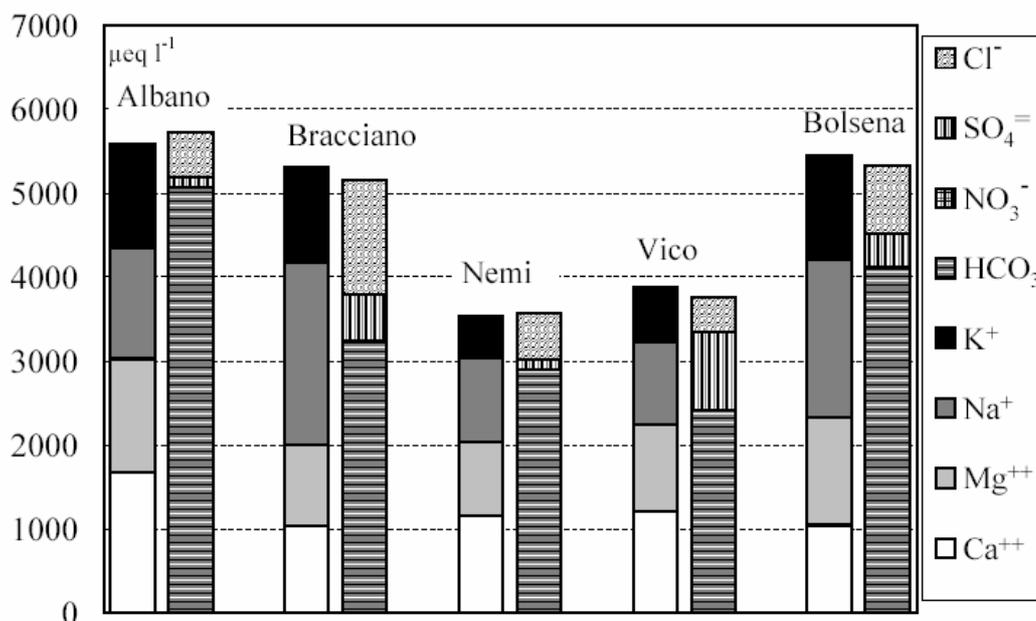
Fig. 3. Ion balance of five lakes located in volcanic watersheds.

Tab. 5. Mean (1998-2002) atmospheric load of ions to Lake Bolsena, in-lake calculated ion concentration in relation to water flushing rate and of in lake measured concentrations.

	Units	H	NH$_4$	Ca	Mg	Na	K	TA	SO$_4$	NO$_3$	Cl
bulk open field	meq m^{-3} y^{-1}	4	20	77	21	67	7	39	46	30	73
throughfall	meq m^{-3} y^{-1}	3	16	85	41	99	43	47	53	39	113
load to the watershed	meq m^{-3} y^{-1}	4	18	81	33	86	28	44	50	35	96
lake calculated conc.	meq m^{-3}	0.02	0.11	0.49	0.20	0.52	0.17	0.27	0.30	0.21	0.58
lake measured conc.	meq m^{-3}	0.00	0.01	1.04	1.29	1.88	1.24	4.10	0.40	0.01	0.82
calculated/measured	-	-	-	10.75	0.47	0.16	0.28	0.14	0.06	0.75	26.76	0.71

role of atmospheric deposition in contributing to the in-lake concentrations. The ratio is relatively high in the case of sulphate and chloride (0.75 and 0.71 respectively); it is lower, but still significantly high in the case of calcium (values). The highest ratio for nitrogen compounds (value) indicates that atmospheric deposition is also an important source of this element. On the other hand it must be said that nitrogen is not a 'conservative' element, in the watershed, it is taken up during vegetative growth, in lake water it can be metabolised by phytoplankton and segregated in the sediments or released to the atmosphere by denitrification processes (Rabalais 2002). The remaining ions show lower, less significant values indicating a main role of weathering processes in determining lake concentrations.

Biological processes are important in determining seasonal variations of chemical compounds in lake waters (García-Ruiz et al. 2000). Previous studies show lower nitrate, silica, reactive and total phosphorus concentrations in the epilimnion in summer compared to the values at the overturn (Istituto Italiano di Idrobiologia 1971). The settling of autochthonous and allochthonous

organic material and their subsequent breakdown results in higher nitrate, total nitrogen, and silicate concentrations in the hypolimnion, as well as oxygen depletion which resulted in anoxic conditions below a depth of 120 m in the late autumn.

A further result of primary production is the formation of calcite in the epilimnion. This is a result of carbon dioxide uptake and an increase in pH, which results in higher concentrations of carbonate and so reaching calcite saturation (Koschel 1997). The calcite values of August 2002 sampling show an oversaturation of the upper 20 m of water, with ratios between ion activity product and calcite saturation ranging from 8 (surface) to 3 (20 m). Calcite oversaturation is a frequent condition of lake waters in summer, but does not necessarily lead to calcite precipitation: phytoplankton typology, mainly the presence of nanoplankton and picoplankton, seems to be fundamental in calcite precipitation (Kurtz 2000; Hartley et al. 1995; Thompson et al. 1997). In Lake Bolsena, calcium and alkalinity values measured in August 2002, compared with those at the overturn (Tab. 4), do not exclude the formation of calcite in the epilimnion, although it is likely that a portion of the set-
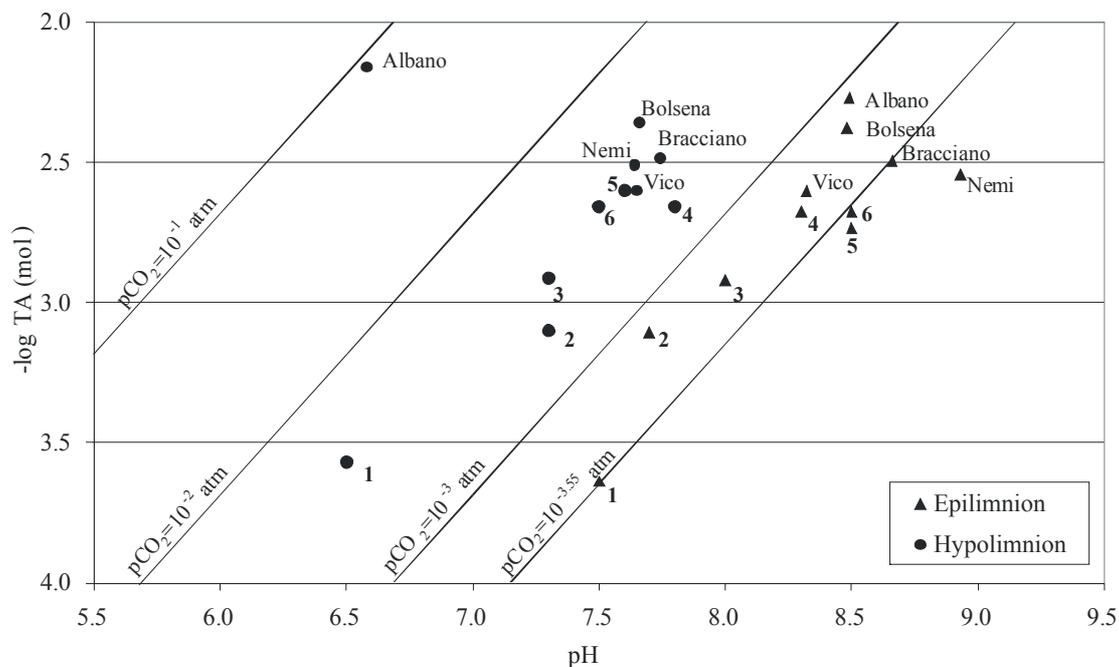
Fig. 4. Relationship between pH and total alkalinity in water of the surface and deep waters of the five Latium lakes compared with those of deep southern alpine lakes Mergozzo (1), Maggiore (2), Como (3), Garda (4), Lugano (5) and Iseo (6) at the summer stratification. The lines indicate the equilibrium values for the dissolution of calcite at different values of partial pressure of CO_2 (atm).

tling crystals is re-dissolved in the deeper waters due to higher carbon dioxide concentrations. In some volcanic lakes, which accumulate gases rich in CO_2 and other carbon components, such as CH_4, can reach such high levels of oversaturation as to produce catastrophic gas exsolution, as occurred in the Cameroon lakes Nyos and Monoun (Sigurdsson *et al.* 1987, Giggenbach 1990). Here, evidence seem to suggest that the higher CO_2 concentration in the deep waters of Lake Bolsena appears to be the result of organic matter degradation rather than volcanic activity. The absence of CO_2 oversaturation is highlighted by the relationship between pH and TA (Fig. 4) in the surface and deep waters of the five lakes considered, compared with the deep lakes of the southern slope of alpine area. On the other hand, CO_2 oversaturation is present in the deep waters of Lake Albano (Martini 1994; Cioni 2003). The source of this CO_2 has been attributed external fluids entering the lake derived from magmatic activity, deciphered using the ratio $^3He/^4He$ (Funiciello *et al.* 2002). This could also explain the low pH value of the hypolimnic waters of Lake Albano, in comparison with those of other deep lakes (Fig. 4), even though, fortunately, the values are not so high as to cause alarm (Cioni *et al.* 2003).

Other important processes affecting the seasonal variations of water chemistry are the development and the breakdown of thermal stratification which has major implications on the biological modification of the lake water. Temperature and oxygen profiles available for Lake Bolsena in the study of the early 60s and since the 90s (Fig. 5) show that Lake Bolsena is monomictic,

reaching the overturn in January/February. Thermal stratification starts in April and ends in December, with the highest epilimnion temperatures (24-26 °C) reached in July/ August. Profiles show that there is marked oxygen depletion in the water layer below 50 m and a condition of anoxia at the end of the autumn, confined to the water layers below 110 m.

3.3. *Long term evolution of water chemistry, hydrology and temperature*

The comparison of these results with those obtained in the period 1966-1970 (Gerletti 1967; Istituto Italiano di Idrobiologia 1971) does not highlight any major differences in the ionic balance (Fig. 6), in spite of the different analytical techniques used. On the other hand, reactive P concentrations at the end of thermal stratification (Tab. 4) are slightly higher than those measured in the 60s; a marked oxygen deficit was also detected in this part of the season, with anoxia in the deepest water, combined with higher concentrations of ammonium. The data collected in this study indicates that the lake is mesotrophic with a slight increase in trophic level compared to that found in the previous study. This increase is also confirmed by palaeolimnological studies, which pointed out higher algal pigment and biogenic silica in the upper sediments (Masaferro 1994; Lami *et al.* 1994). On the other hand, marked variations were observed in the winter temperature of the lake water, from 1969 to 1998, there was a mean increase in the water temperature from 7.4 to 8.4 °C (Ambrosetti *et al.* 2003).
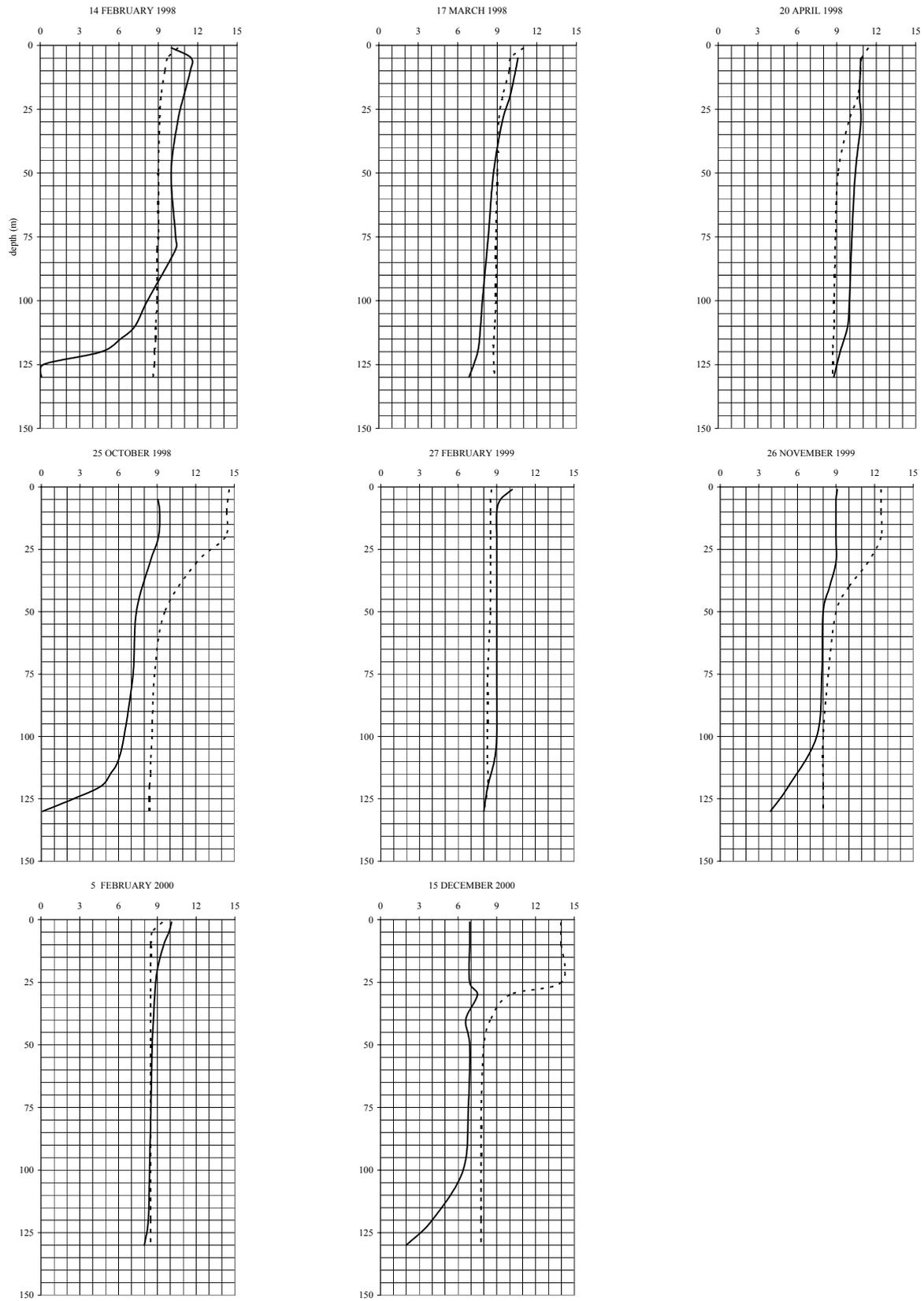
Fig. 5. Vertical profiles of temperature (°C, broken line) and oxygen (mg l^{-1}, full line) at selected dates in Lake Bolsena.
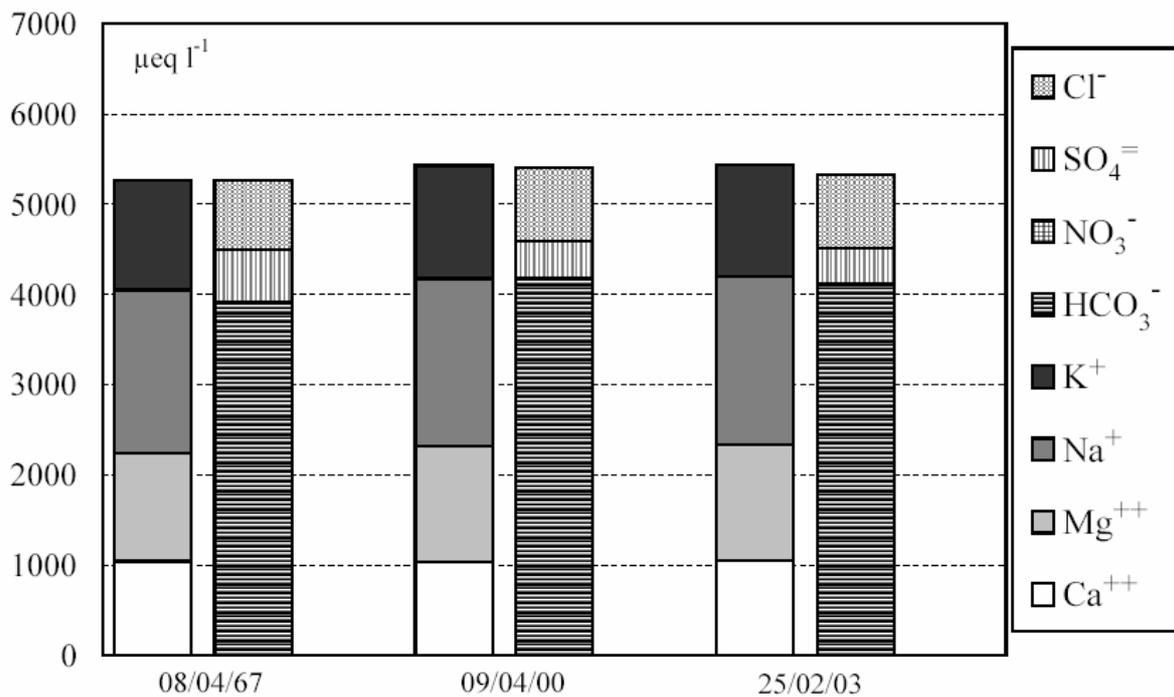
Fig. 6. Comparison of recent and 60s ion concentrations of Lake Bolsena.

In the case of the summer temperature, the increase in the same period was even higher, reaching 34%. As a consequence, thermal stability, defined as the need to homogenise the thermally stratified lake to homothermy in adiabatic conditions, increased from 151 J m^{-2} to 589 J m^{-2}.

A further worrying variation from the 60s has become apparent for the hydrology of the lake. Due to the tapping of underground water for irrigation and domestic use the extraction of water increased from around 5 to 30 10^6 m^3 y^{-1} during the period 1960-2000 (Pagano *et al.* 1998; Dragoni 1998). There has also been a slight decrease in the quantity of precipitation over the last four decades (Fig. 7), while the air temperature has increased by about one degree Celsius over approximately the last hundred years (Dragoni & Gnucci 2002). As a consequence, the outflow discharge has decreased from about 100 to 25 10^6 m^3 y^{-1}, and the lake level has fallen markedly (Fig. 7). The theoretical water renewal time has therefore increased from about 100 to 400 y (Associazione Lago di Bolsena 2003).

Variations occurring in the thermal stability of the water and hydrology, considered together with the considerable maximum depth of the lake, suggest that there may be warming potential for the establishment of meromictic conditions. However, this scenario appears very unlikely, due to the large surface area of the lake, the absence of surrounding mountains, and the high winds of the area. Nevertheless, the relevant variations occurring in the lake thermal structure indicate an increasing susceptibility of the lake to eutrophication and to other types of pollution.

4. CONCLUSIONS

The area which includes Lake Bolsena and its watershed is exceptionally rich in natural and economic resources, as it is located in one of the most historic parts of Europe with a great deal to offer in terms of high quality tourism. However, the data emerging from this study regarding the quality of the water of the lake and its tributaries highlight the extreme fragility of the area's hydrological system.

Due to the origins of its basin, the catchment of Lake Bolsena is very small compared to both the surface area of the lake and its volume. Also, the hydrogeological basin covers a small area, this means that the lake water chemistry depends to a marked extent on inputs from the atmosphere, as is clear from a comparison between the chemistry of the atmospheric depositions and that of the lake, possibly made more evident in light of the longer theoretical water renewal time. The variables which are mostly dependent on atmospheric inputs are nitrogen, chloride, and sulphate; the in-lake concentrations of nitrogen are however, highly dependent on uptake from catchment and on biological processes in the lake water. In contrast, weathering in the watershed is the dominant process in determining concentrations of bicarbonate, calcium, magnesium, sodium and potassium. The prevalence of volcanic rocks together with the impact of atmospheric deposition gives rise to a characteristic ionic spectrum in which bicarbonate dominates the anions, and Na, Mg, and K and Ca, are
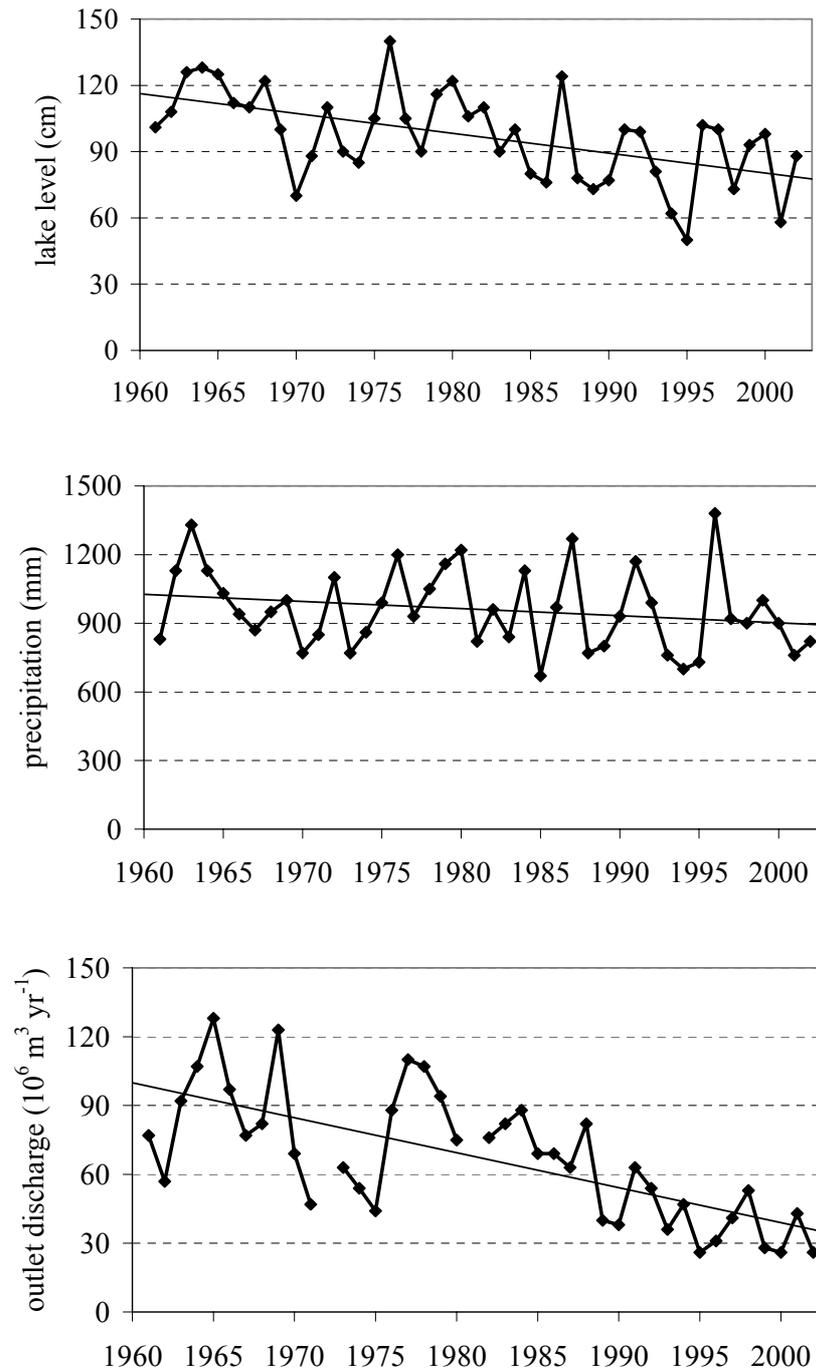
Fig. 7. Annual amount of precipitation in the station of Acquapendente, decrease of the Lake Bolsena outflow discharge and of the water level.

almost equal in importance. This composition is evident in the other four lakes used for comparative purposes, all four of which are fed from watersheds with volcanic rocks.

The present phosphorus concentrations in Lake Bolsena, along with the seasonal oxygen variations, show that the deepest zone of the lake is in a mesotrophic condition. However, due to the large surface area of the lake, more detailed investigations of the shoreline water must be made, as locally different situations, caused by point discharges (illegal or agricultural), cannot be ruled out. The sewage collector around the lake prevents domestic sewage from reaching the lake water, and has indisputably had a crucial role in limiting the eutrophication processes of which the lake was at risk in the 70s and 80s, when the water quality had deteriorated. Nev-

ertheless, as the drainage system is mixed, collecting sewage together with run-off water, a portion of the clean water which used to reach the lake is now prevented from doing so. To get round this drawback and enable some of this water to reach the lake, a new drainage system would have to be constructed to separate the clean water from the sewage.

While this study is primarily aimed at investigating the chemistry of the lake, we must also emphasise the necessity for researching hydrological aspects. Due to its natural characteristics, Lake Bolsena had a very long renewal time, and every time water is removed from the lake this situation is aggravated. The use of water for agricultural purposes or for drinking removes precious water from the lake, increasing its susceptibility to eutrophication and lengthening the time required for recovery from episodes of pollution. Additional to this excessive exploitation of the water in the watershed there is also the increasing surface and atmospheric temperatures, which accentuate the phenomenon of evaporation, leading to further destabilisation of the lake ecosystem. Therefore it is necessity for all ongoing or planned economic activities in the watershed to take into account of all the issues connected with the use of water, so as to stop the removal of water from the lake which has been increasing for thirty years and which risks inflicting irreversible damage on the lake water quality.

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