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Water and dissolved gas geochemistry of the monomictic Paterno sinkhole (central Italy)

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ABSTRACT

This paper describes the chemical and isotope features of water and dissolved gases from lake Paterno (max. depth 54 m), a sinkhole located in the NE sector of the S. Vittorino plain (Rieti, Central Italy), where evidences of past and present hydrothermal activity exists. In winter (February 2011) lake Paterno waters were almost completely mixed, whereas in summer time (July 2011) thermal and chemical stratifications established. During the stratification period, water and dissolved gas chemistry along the vertical water column were mainly controlled by biological processes, such as methanogenesis, sulfate-reduction, calcite precipitation, denitrification, and NH_4 *and* H_2 *production. Reducing conditions at the interface between the bottom sediments and the anoxic waters are responsible for the relatively high concentrations of dissolved iron (Fe) and manganese (Mn), likely present in their reduced oxidation state. Minerogenic and biogenic products were recognized at the lake bottom even during the winter sampling. At relatively shallow depth the distribution of* CH_4 *and* CO_2 *was controlled by methanotrophic bacteria and photosynthesis, respectively. The carbon isotope signature of* CO_2 *indicates a significant contribution of deep-originated inorganic* CO_2 *that is related to the hydrothermal system feeding the* CO_2*-rich mineralized springs discharging in the surrounding areas of lake Paterno. The seasonal lake stratification likely controls the vertical and horizontal distribution of fish populations in the different periods of the year.*

Key words: monomictic lake, sinkhole, lake Paterno, water lake chemistry, dissolved gas chemistry.

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INTRODUCTION

The term sinkhole was introduced by Fairbridge (1968) to indicate a sub-circular depression formed by the collapse of small subterranean karst cavities. Genetic classifications for sinkholes related to karst processes have recently been proposed (*e.g.* Williams, 2003; Neuendorf *et al.*, 2005; Waltham *et al.*, 2005), allowing to distinguish sinkholes produced by i) dissolutional lowering of the ground surface and ii) subsurface karstification. Sinkholes were classified on the basis of i) genetic processes (*i.e.* collapse, suffusion or sagging) and ii) type of collapsing material (bedrock, cover or caprock) (Gutierrez *et al.*, 2008). In the Italian literature, sinkhole often stands for collapse phenomena not directly linked to karst dissolution, such as those caused by both anthropogenic activities and deep piping processes due to the presence of carbonate bedrock buried under a thick sedimentary cover (Ciotoli *et al.*, 2001; Salvati and Sasowsky, 2002; Nisio, 2003; Nisio *et al.*, 2005, 2007; Caramanna *et al.*, 2008). A significant percentage of sinkholes in Italy (≈38%) hosts lakes or ponds (Nisio *et al.*, 2007). In the Latium region (central Italy), 34 zones prone to sinkhole formation through deep piping processes are recognized and include 163 active, filled and buried sinkholes (Caramanna *et al.*, 2008). Among these zones, the S. Vittorino Plain (eastern Latium) is characterized by the presence of at least 35 sinkholes with diameters from a few to 200 m. The origin of sinkholes in this area is mainly related to deep piping processes caused by CO_2- and H_2S-rich fluid upwelling along fracture-fault systems (Caramanna *et al.*, 2008). The presence of hydrothermal fluids at depth of a lake resembles the situation at Nyos-type maar lakes, prone to stratification and gas accumulation at depth, which can eventually be liberated by lake overturn (Kling *et al.*, 1987; Kusakabe *et al.*, 2000).

Lake Paterno is located in the NE sector of the San Vittorino Plain (Fig. 1), has a sub-circular shape and a maximum diameter of about 190 m. This lake, indicated by Marco Terenzio Varrone (116- 27 B.C.) as the *Umbilicus Italiae*, is the biggest active sinkhole in the San Vittorino Plain. It is known since pre-Roman Age, because of the presence of a small floating island, which was possibly consisting of carbonate incrustations lying on tree branches and trunks, where religious ceremonies were celebrated (Persichetti, 1893, 1910; Aliotta, 1982; Marinelli, 1995).

This paper examines the distribution of chemical (major, minor and trace compounds) and isotope compositions of water and dissolved gases along the vertical water column of the lake sampled in winter (February) and summer (July) 2011. The main aim of this study is to investigate the processes, such as i) water-rock interactions, ii) biological activity and iii) external fluid inputs, likely controlling the seasonal evolution of the water and dissolved gas chemistry.

Geological and hydrological settings of the study area

San Vittorino Plain, located in the Velino watershed, 20 km east of the town of Rieti, is a triangular-shaped intramontane depression, with a total surface of 7 km^2, bordered by direct and transtensive faults (Ciotoli *et al.*, 1998, 2001; Centamore and Nisio, 2003; Centamore *et al.*, 2004). The valley is mainly filled by Pleistocene and Upper-Holocene fluvial deposits with a maximum thickness of 170 m and placed over a faulted calcareous sequence (Nisio, 2003). The main tectonic structures are represented by the Anzio-Ancona and the Olevano-Micciani lines and by the Fiamignano-Micciani and the Cerquara-Piedimozza faults (Centamore *et al.*, 2009). In the valley, several thermal and mineral springs (*e.g.* Cotilia sulfur spring), areas of anomalous soil degassing, as well as travertine deposits testifying past and present hydrothermal activity, are present (Brancaccio *et al.*, 1988; Faccenna *et al.*, 1993; Ciotoli *et al.*, 2001; Minissale *et al.*, 2002; Nisio, 2003). The spatial distribution of the San Vittorino sinkholes, mainly located in the northern sector of the plain, is strongly controlled by the NNW-trending and SW-dipping Fiamignano-Micciani fault (Faccenna *et al.*, 1993; Capelli *et al.*, 2000; Bersani and Castellano, 2002; Nisio, 2003, 2008; Annunziatellis *et al.*, 2004; Nisio *et al.* 2007) (Fig. 1). West of the Fiamignano-Micciani fault, a few collapse events are recorded (Faccenna *et al.*, 1993; Ciotoli *et al.*, 1998; Centamore *et al.*, 2002, 2004). The spatial distribution of the sinkholes suggests that their formation is mainly related to the collapsed sector of the Mt. Paterno block, whose structural setting favors the development of confined aquifers (Centamore *et al.*, 2009). Several sinking events

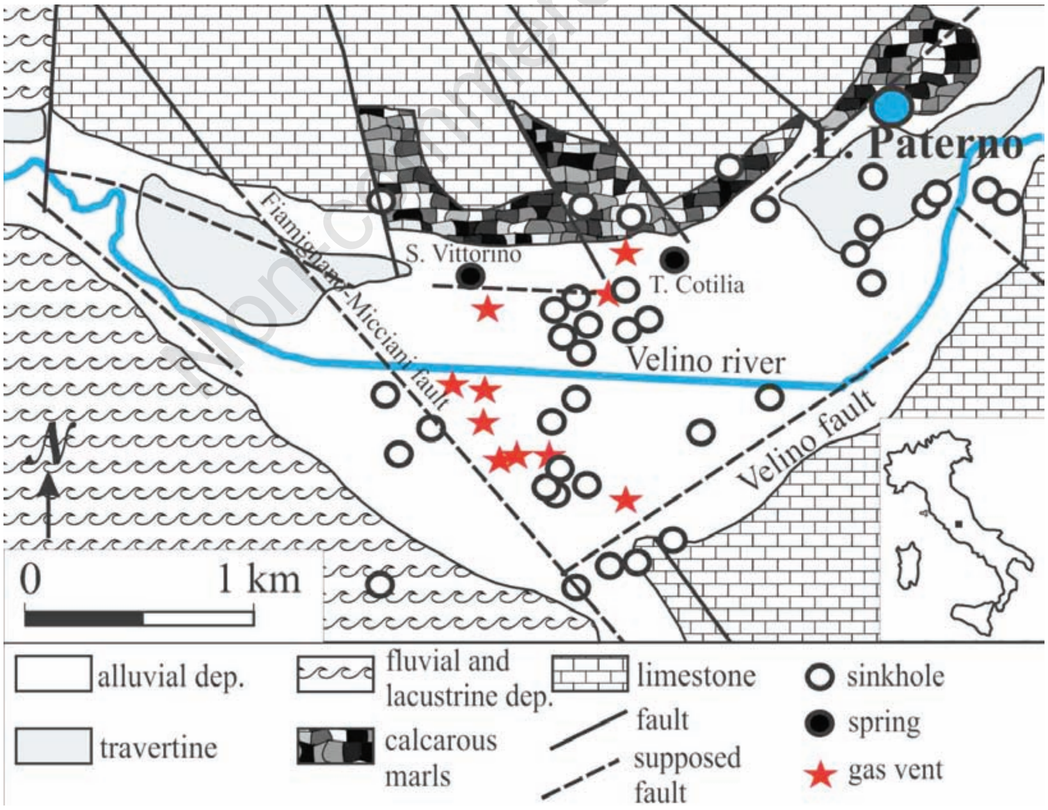

Fig. 1. Geological schematic map of San Vittorino plain and location of lake Paterno and San Vittorino (SV) and Terme Cotilia (TC) mineral springs.

have occurred in this area during historical times, the first one being recorded in 1703 following an earthquake that damaged the San Vittorino church built between 1604 and 1614 (Annunziatellis *et al.*, 2004). Between 1770 and 1850, five sinkholes formed (Riccardi, 1951; Capelli *et al.*, 2000; Bersani and Castellano, 2002). In 1886, three depressions with diameters from 5 to 60 m formed in the Sciamagutta area (Catenacci, 1992), whilst in 1915, after the Avezzano earthquake, the Pozzo Gustavo, well-like cavity opened (Michetti *et al.*, 1994). Small sinkholes also formed during the last two decades, the latest being opened in September 2003 (Annunziatellis *et al.*, 2004). In the past century, several sinkholes also reactivated (Riccardi, 1951), including that of lake Paterno whose maximum depth in 1915, 15 days after the Marsica earthquake, passed from 37.7 to 45.2 m (Crema, 1924); a further deepening occurred in the 1950s, when the lake achieved the present depth of 54 m.

METHODS

Water and dissolved gas sampling

Water and dissolved gas sampling was carried out during two field campaigns in February and July 2011 along vertical profiles from the lake surface to the bottom at regular intervals of 5 m, at a site corresponding to the deepest point of the lake. Water and dissolved gas sampling was carried out using a Rilsan® tube (6 mm in diameter). Once one end of the Rilsan® tube was lowered to the chosen depth, water was pumped up to the surface by means of a 150 mL glass syringe connected to the other end of the tube via a three way valve, and transferred into the storage containers (Tassi *et al.*, 2004, 2009). Following this procedure, the sampling was carried out from the lake surface to the bottom. Water and dissolved gases were collected after the displacement of a water volume at least twice the inner volume of the tube (0.0283 dm^3 m^{-1}) (Tassi *et al.*, 2004).

One filtered (0.45 μm) and two filtered-acidified (with ultrapure HCl and ultrapure HNO_3, respectively) water samples were collected in polyethylene bottles for the analysis of anions, cations and trace species. A fourth water aliquot was collected in glass bottles and few tens of milligrams of $HgCl_2$ were added for the determination of oxygen and hydrogen (in water) and carbon (dissolved inorganic carbon, DIC) isotopes. For the two mineral springs discharging close to lake Paterno (SV, San Vittorino – TC, Terme di Cotilia), the filtered, the filtered-(HCl)acidified and the glass bottles aliquots were collected.

Dissolved gases were collected into one-way, pre-evacuated 250 mL glass vials equipped with a Teflon stopcock (Chiodini, 1996; Caliro *et al.*, 2008; Tassi *et al.*, 2008). The gas vial was connected to the Rilsan® tube through a three-way valve, avoiding possible air contamination by filling the connection with lake water. Then, the stopcock was opened to partly fill (75% of the total volume) the gas vial with water. Part of the gas stored in the sampling flask headspace was transferred into pre-evacuated 10 mL glass flasks equipped with a Teflon stopcock. This aliquot was used for the analyses of the $^{13}C/^{12}C$ ratios of dissolved CO_2 ($\delta^{13}C\text{-}CO_{2STRIP}$) and the $^{13}C/^{12}C$ and $^{2}H/^{1}H$ ratios of CH_4 ($\delta^{13}C\text{-}CH_4$ and $\delta D\text{-}CH_4$, respectively).

Field measurements and analytical methods

Temperature (T, in °C), pH, dissolved oxygen (O_2 in mg L^{-1}), and electrical conductivity (EC in mS cm^{-1}) were measured along the vertical profile were measured using a Hydrolab multiparameter probe (Idroprobe) equipped with a data logger for data storage. The nominal precisions are as follows: depth=±0.05 m; T=±0.03°C; O_2=±0.05 mg L^{-1} EC=±0.01 mS cm^{-1}, pH=±0.02. Alkalinity was measured by acidimetric titration (HCl 0.01 N) in the field. The analytical error for alkalinity analysis was ≤2%.

The main anions (Cl^-, SO_4^{2-}, NO_3^-, Br^- and F^-) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+ and Li^+) of water samples were analyzed by ion-chromatography (IC) (Metrohm 761 and Metrohm 861, respectively). Trace elements (Al, As, B, Ba, Cd, Cs, Cu, Fe, Mn, Mo, Ni, P, Pb, Rb, Sb, Sc, Si, Sr, U, V, and Zn) were analyzed at the Acme Laboratories of Vancouver (Canada) by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) with a Perkin-Elmer ELAN 6600 spectrometer. The analytical errors for IC and ICP-MS were ≤5 and ≤10%, respectively.

The $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios (expressed as $\delta^{18}O\text{-}H_2O$ and $\delta D\text{-}H_2O$ ‰ V-SMOW, respectively) were determined with a Finningan Delta Plus XL mass spectrometer according to standard protocols. Water samples were equilibrated with CO_2 for the analysis of the $\delta^{18}O\text{-}H_2O$ values (Epstein and Mayeda, 1953). The $\delta D\text{-}H_2O$ values were measured on H_2 obtained after the reaction of 10 μL of water with metallic zinc at 500°C, following the analytical procedure proposed by Coleman *et al.* (1982). San Vincenzo marble (SV1) and AR1 water, calibrated *vs* V-SMOW and SLAP reference standards, were used as external standards. The experimental errors were ±0.1 and ±1 ‰ for the $\delta^{18}O\text{-}H_2O$ and $\delta D\text{-}H_2O$ values, respectively.

The $^{13}C/^{12}C$ ratios of DIC (expressed as $\delta^{13}C_{DIC}$ ‰ V-PDB) were determined on CO_2 produced by reaction of 3 mL of water with 2 mL of anhydrous phosphoric acid in pre-evacuated tubes (Salata *et al.*, 2000) using a Finningan Delta Plus XL mass spectrometer. The recovered CO_2 was analyzed after a two-step extraction and purification procedures of the gas mixtures by using liquid N_2 and a solid-liquid mixture of liquid N_2 and trichloroethylene (Evans *et al.*, 1998; Vaselli *et al.*, 2006). The analytical error for $\delta^{13}C_{DIC}$ was ±0.05.

Dissolved gas composition was calculated from the composition of the gas phase stored in the headspace of the sampling glass flasks on the basis of i) gas pressure, ii) headspace volume and iii) the solubility coefficients of each gas compound (Whitfield, 1978). The inorganic compounds in the flask headspace (CO_2, N_2, O_2, Ar, Ne and H_2) were analyzed with a gas-chromatograph (Shimadzu 15A) equipped with a Thermal Conductivity Detector (TCD), while CH_4 was analyzed with a Shimadzu 14A gas-chromatograph equipped with a Flame Ionization Detector (FID) (Tassi *et al.*, 2004). The analytical error for dissolved gas analysis was ≤5%. The $\delta^{13}C\text{-}CO_{2STRIP}$ analyses (expressed as ‰ V-PDB) were carried out with a Finningan Delta S mass spectrometer after purification of the gas mixture by standard procedures (Evans *et al.*, 1998; Vaselli *et al.*, 2006). Internal (Carrara and San Vincenzo marbles) and international (NBS18 and NBS19) standards were used to estimate external precision. The analytical error and the reproducibility were ±0.05‰ and ±0.1‰, respectively.

The analysis of $\delta^{13}C\text{-}CH_4$ and $\delta D\text{-}CH_4$ (expressed as ‰ V-PDB and ‰ V-SMOW, respectively) were carried out by mass spectrometry (Varian MAT 250) according to the procedure described by Schoell (1980). The analytical error was ±0.15‰.

RESULTS

Lake morphology

Lake Paterno is located at an altitude of 430 m asl and has an ellipsoidal shape (190 m×150 m), a surface of about 22,300 m^2, a volume of 1.05×10^6 m^3 and a maximum depth of 54 m. An artificial channel discharges the lake water into the Velino river at a flow rate of 16 L sec^{-1}. This unequivocally indicates that the lake is fed by sub-lacustrine springs, although no direct evidences are reported. Lake bathymetry (Fig. 2) was obtained in February 2011 when the lake depth was measured at 50 different sites, evenly distributed, using a Humminbird Legend 1005 portable Eco-sonar. The ratio between the average depth and the maximum depth of lake Paterno is 0.87, *i.e.* the lake shape approximates a steep-sided frustum model corresponding to steep sides and flat bottom (Lehman, 1975), typical of lakes of recent formation and affected by elevated sedimentation rates. The relatively high value of this parameter, known as *depth-ratio* (Carpenter, 1983), indicates that the morphology of lake Paterno tends to favour water stratification (Hutchinson, 1957).

Temperature, EC, pH and dissolved O_2 vertical profiles

Temperature (in °C), EC, pH, and dissolved O_2 concentrations (in mg L^{-1}) along the vertical profiles of lake Paterno are shown in Fig. 3 a,d. In February 2011, water temperature (~6.5°C) did not display any significant variation with depth. In July 2011 the lake surface was relatively warm (up to 23.2°C) and two thermoclines occurred at depths of 4-6 m and, less pronounced, ~35 m, respectively. Water temperature at the lake bottom (7.4°C) slightly exceeded that measured in February (6.5°C) (Fig. 3a). The vertical pattern of EC in February (Fig. 3b) was constant (~0.64 mS cm^{-1}) up to the depth of -35 m, then it increased at -35 and -52.5 m depth, up to 0.66 and 0.73 mS cm^{-1}, respectively. In July, EC of the surface lake water was relatively low (0.53 mS cm^{-1}), and rapidly increased with depth reaching ~0.76 mS cm^{-1} at the depth of -13 m; a second significant EC increasing trend started at the depth of ~45 m and the maximum EC value was 0.89 mS cm^{-1} at the lake bottom (Fig. 3b). The pH vertical profiles had a *S* shape for both February and July (Fig. 3c). They indeed showed maximum pH at the lake surface (7.75 and 8.13 in February and July, respectively), a rapid decrease (down to 7.2 and 7.3 in February and July, respectively) between 0 and -10 m depth, and a flat pattern approaching the lake bottom where they showed a significant further decrease (down to 7.18 and 6.97 in February and July, respectively). Dissolved O_2 in February was relatively constant (~6 mg L^{-1}) down to the depth of 51 m, where it suddenly decreased reaching 2.1 mg/L at the lake bottom (Fig. 3d). On the contrary, in July the dissolved O_2 concentrations were relatively high in the shallow waters (up to 12.7 mg L^{-1} at the depth of 8.7 m) and then showed a rapid decrease at increasing depths (<0.1 mg L^{-1} at depths >12.5 m) (Fig. 3d). The occurrence of anoxic water below the shallower thermocline may explain the macro-invertebrate population dynamics observed during underwater visual census carried out in different seasons since 2009 (Palozzi *et al.*, 2010). In summer, fishes are only found in the epilimnion, *i.e.* the only portion of the lake where free-

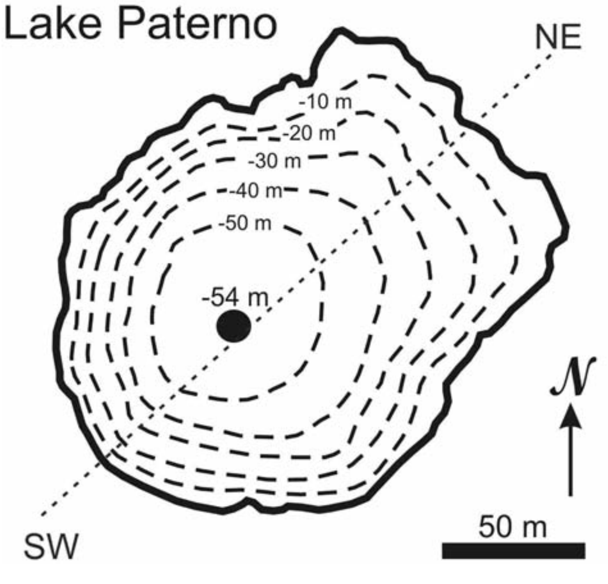

Fig. 2. Bathymetric map of lake Paterno.

O_2 is available; in winter, fishes populate the deep waters, since water vertical mixing transports oxygenated water down to the lake bottom.

Chemical and isotope (δ^{18}O-H_2O, δD-H_2O and $\delta^{13}C_{DIC}$) compositions of waters

Chemical composition (in mg/L) and δ^{18}O-H_2O, δD-H_2O and $\delta^{13}C_{DIC}$ ratios of lake Paterno water, as well as those of San Vittorino (SV) and Terme Cotilia (TC) mineral spring waters, are listed in Tab. 1. Trace element concentrations are reported in Tab. 2.

Lake Paterno had a Ca^{2+}-HCO_3^- composition and TDS values <850 mg L^{-1}, typical of worldwide superficial waters and shallow aquifers, and similar to that recorded for the SV and TC springs. Nevertheless, the latter are characterized by significantly higher TDS concentrations (2730 and 3100 mg L^{-1}, respectively) with respect to those of lake Paterno. These geochemical features are consistent with the analytical data reported by Annunziatellis *et al.* (2004). The concentrations of Cl^- (from 5.2 to 8.2 mg L^{-1}), Mg^{2+} (from 22 to 27 mg L^{-1}), Na^+ (from 4.7 to 5.9 mg L^{-1}) and K^+ (from 1.6 to 3.2 mg L^{-1}) of the lake waters did not show significant variations with depth neither with time. Sulfate concentrations were relatively constant from the surface to the depth of 50 m (from 32 to 34 and from 35 to 39 mg L^{-1} in February and July, respectively), whereas they significantly decreased at the lake bottom, clustering around 25 mg L^{-1} for both surveys. An opposite behavior was shown by Ca^{2+} concentrations, which ranged from 137 to 143 mg L^{-1} from the surface to -50 m depth (with the exception of the shallow water samples collected in July: ≤120 mg L^{-1}), whereas at the lake bottom Ca^{2+} contents increased up to 156 (February) and 148 (July) mg L^{-1}. In February, the HCO_3^- vertical profile had two peaks (up to 519 and 525 mg L^{-1}) at the depth of 35 and 54 m, respec-

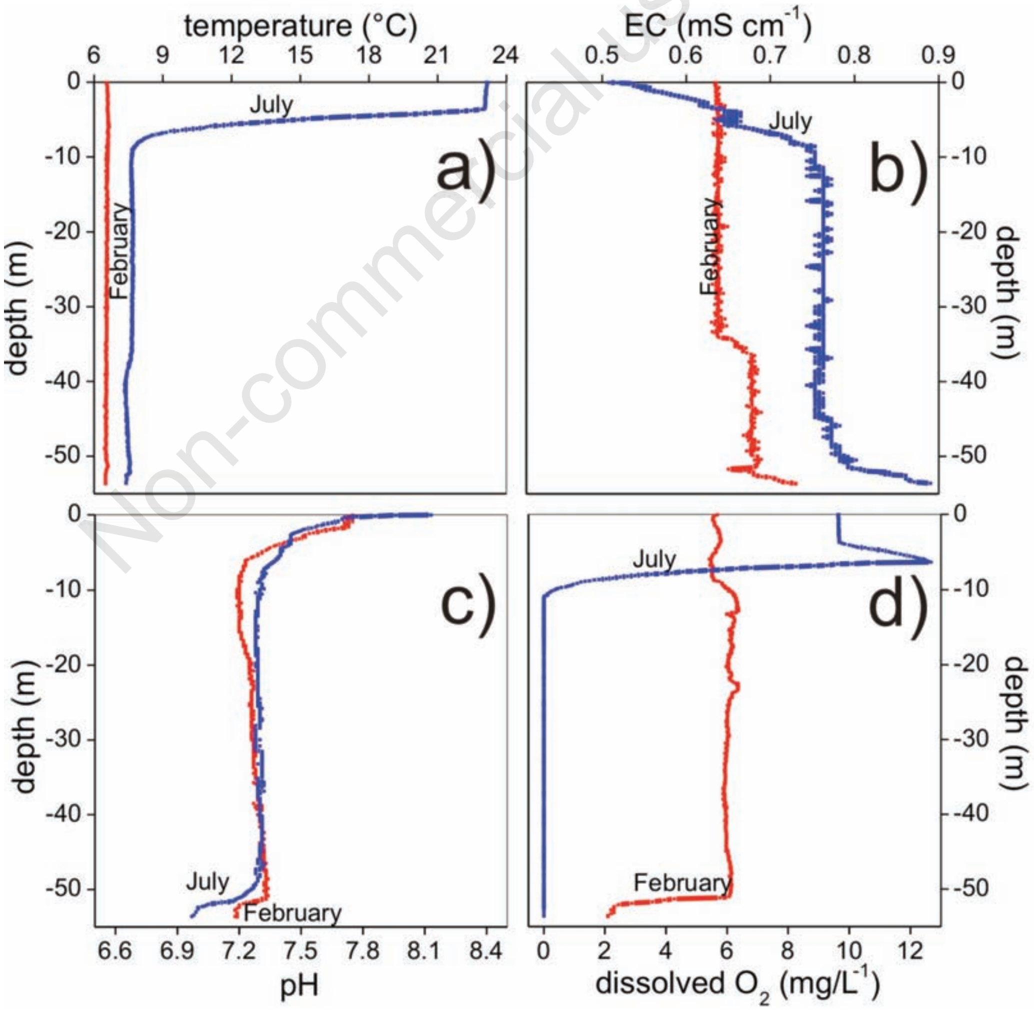

Fig. 3. Vertical profiles of a) water temperature; b) electrical conductivity (EC); c) pH; and d) dissolved O_2 concentrations of lake Paterno measured from the surface to the bottom in February and June 2011.

Tab. 1. Temperatures (°C), pH, chemical composition, $\delta^{13}C_{DIC}$ and $\delta^{13}C_{DICcalc}$ (expressed as ‰ V-PDB), and $\delta^{18}O\text{-}H_2O$ and $\delta D\text{-}H_2O$ ratios (expressed as ‰ V-SMOW) of water samples collected from lake Paterno, from the surface to the bottom (each 5 m), in February and July 2011, and of San Vittorino and Terme Cotilia mineral springs. Ion contents are in mg L^{-1}.

Sample depth	Date	T	pH	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	F^-	NO_3^-	NH_4^-	Li^+	$\delta^{18}O$	δD	$\delta^{13}C_{DIC}$	$\delta^{13}C_{DICcalc}$
0 m	Feb. 12, 2011	6.5	7.75	484	5.4	33	142	25	5.4	2.1	0.19	0.20	0.090	0.007	na	na	na	nc
5 m	Feb. 12, 2011	6.6	7.31	477	5.7	32	142	25	5.5	1.8	0.18	0.26	0.077	0.007	-7.1	-52.3	na	nc
10 m	Feb. 12, 2011	6.6	7.13	478	5.8	33	139	24	5.9	1.7	0.28	0.21	0.077	0.007	na	na	na	nc
15 m	Feb. 12, 2011	6.6	7.19	476	5.3	33	140	25	5.7	1.6	0.19	0.18	0.077	0.007	-7.5	-52.1	na	nc
20 m	Feb. 12, 2011	6.6	7.26	486	5.2	32	140	25	5.7	2.6	0.21	0.48	0.065	0.007	na	na	na	nc
25 m	Feb. 12, 2011	6.6	7.35	481	5.5	33	142	24	5.6	1.5	0.26	0.74	0.10	0.007	na	na	na	nc
30 m	Feb. 12, 2011	6.6	7.33	478	5.9	32	142	25	5.3	1.7	0.36	0.71	0.077	0.007	-8	-55.9	na	nc
35 m	Feb. 12, 2011	6.5	7.36	519	6.6	32	137	27	5.1	2.6	0.44	0.73	0.065	0.007	na	na	na	nc
40 m	Feb. 12, 2011	6.5	7.37	500	5.4	34	141	26	5.2	2.2	0.22	0.65	0.077	0.007	na	na	na	nc
45 m	Feb. 12, 2011	6.5	7.36	494	6.1	35	143	25	5.6	2.9	0.35	0.55	0.077	0.007	-8.2	-57.1	na	nc
50 m	Feb. 12, 2011	6.5	7.41	500	5.9	32	141	25	5.4	1.9	0.47	0.55	0.077	0.007	-8.5	-58.3	na	nc
54 m (bottom)	Feb. 12, 2011	6.5	7.19	525	5.3	25	156	26	5.6	2.1	0.23	0.12	0.86	0.007	-8.5	-58.4	na	-1.1
0 m	July 23, 2011	23.2	8.13	328	7.5	36	74	22	5.3	2.7	0.19	0.03	0.18	0.007	-6.7	-51.2	-9.1	nc
5 m	July 23, 2011	14.9	7.40	472	8.2	38	120	24	5.6	2.2	0.20	0.04	0.26	0.007	-7.2	-52.3	-9.2	-1.1
10 m	July 23, 2011	10.0	7.30	540	7.6	39	142	24	5.4	2.0	0.23	0.10	0.24	0.007	-7.4	-52.5	-9.2	-0.7
15 m	July 23, 2011	7.7	7.28	540	7.5	39	141	24	5.1	2.3	0.23	0.28	0.22	0.007	-7.4	-52.4	-9.3	-0.5
20 m	July 23, 2011	7.7	7.29	542	7.8	39	142	24	5.9	2.8	0.33	0.31	0.23	0.007	-7.4	-52.8	-11.2	-0.7
25 m	July 23, 2011	7.7	7.29	543	7.6	39	140	24	4.7	1.6	0.22	0.35	0.24	0.007	-7.9	-56.8	-11.3	-1.0
30 m	July 23, 2011	7.7	7.30	540	7.5	39	138	24	5.0	2.4	0.22	0.27	0.25	0.007	-8.0	-56.7	-11.2	-0.8
35 m	July 23, 2011	7.6	7.31	538	7.7	39	139	24	5.1	3.0	0.30	0.42	0.32	0.007	-8.3	-56.6	-11.2	-0.7
40 m	July 23, 2011	7.6	7.29	536	7.5	39	140	24	4.9	2.5	0.21	0.38	0.30	0.007	-8.3	-58.6	-11.3	-0.6
45 m	July 23, 2011	7.4	7.31	545	7.5	37	140	24	4.9	1.8	0.23	0.06	0.51	0.007	-8.5	-58.5	-11.4	-0.5
50 m	July 23, 2011	7.5	7.31	561	7.8	35	143	24	5.9	3.2	0.37	0.04	0.98	0.007	-8.5	-59.4	-11.7	-0.5
54 m (bottom)	July 23, 2011	7.4	6.97	618	7.7	24	148	25	6.1	2.0	0.42	0.02	3.46	0.007	-8.5	-59.3	-11.8	-0.3
SV	Feb. 11, 2011	13.0	6.03	1730	28	274	567	92	29	5.5	0.38	0.39	0.97	0.15	-6.8	-44.4	na	nc
TC	Feb. 11, 2011	15.0	6.17	2060	1.9	256	643	99	29	5.8	0.03	0.05	2.1	0.17	-7.2	-46.3	na	nc

SV, San Vittorino; TC, Terme Cotilia; na, not analyzed; nc, not calculated.

Tab. 2. Chemical composition of trace elements (Al, As, B, Ba, Cd, Cs, Cu, Fe, Mn, Mo, Ni, P, Pb, Rb, Sb, Sc, Si, Sr, U, V, and Zn) of water samples collected from lake Paterno from the surface to the bottom (each 10 m), in February and July 2011. Element concentrations are in μg L^{-1}.

Sample depth	Date	Al	As	B	Ba	Cd	Cs	Cu	Fe	Mn	Mo	Ni	P	Pb	Rb	Sb	Sc	Si	Sr	U	V	Zn
0 m	Feb. 12, 2011	2	2.1	73	52	0.6	0.6	0.8	<10	1.0	0.6	<0.2	22	<0.1	3.7	0.07	<1	2560	851	0.7	0.4	0.6
10 m	Feb. 12, 2011	2	12	72	50	0.7	0.5	1.6	<10	4.4	0.8	<0.2	30	0.1	3.7	0.07	<1	2560	804	0.7	0.4	4.7
20 m	Feb. 12, 2011	5	2.4	73	55	0.9	0.6	1.3	<10	4.3	0.5	0.3	31	0.4	4.0	0.08	<1	2740	884	0.7	0.4	8.4
30 m	Feb. 12, 2011	5	2.4	74	58	0.7	0.7	1.6	<10	2.7	0.2	<0.2	32	0.4	4.1	0.07	<1	2840	947	0.7	0.5	14
40 m	Feb. 12, 2011	8	1.9	83	53	1.0	0.6	1.4	<10	2.9	0.7	0.4	40	0.4	3.6	0.07	<1	2610	840	0.7	0.4	19
50 m	Feb. 12, 2011	3	1.8	68	50	0.8	0.5	1.3	<10	3.3	0.8	0.4	31	0.2	3.6	0.08	<1	2610	811	0.7	0.4	10
54 m	Feb. 12, 2011	3	2.9	77	79	0.7	0.7	0.8	250	1170	0.4	<0.2	342	0.1	4.2	0.10	2	4640	991	0.5	0.4	12

Sample depth	Date	Al	As	B	Ba	Cd	Cs	Cu	Fe	Mn	Mo	Ni	P	Pb	Rb	Sb	Sc	Si	Sr	U	V	Zn
0 m	July 23, 2011	4	1.2	74	35	<0.05	0	0.8	<10	0.7	0.6	1	17	0.2	3	0.5	<1	387	558	0.5	0.7	1.4
10 m	July 23, 2011	1	1.3	67	38	0.09	0	0.5	<10	1.4	0.6	0.6	20	<0.1	3	0.1	<1	2467	619	0.5	0.3	3.3
20 m	July 23, 2011	2	1.3	65	40	0.05	1	0.5	<10	2.7	0.6	<0.2	19	0.3	3	0.1	<1	2592	659	0.5	0.4	1.9
30 m	July 23, 2011	4	1.3	68	39	<0.05	1	0.7	<10	2.4	0.7	<0.2	19	<0.1	3	0.1	<1	2605	634	0.5	0.4	3.6
40 m	July 23, 2011	3	1.4	69	39	<0.05	0	0.6	<10	6.6	0.6	0.5	37	0.2	3	0.1	<1	2717	648	0.5	0.3	3.3
50 m	July 23, 2011	2	2.4	69	52	<0.05	0	0.4	100	870	0.5	2.5	125	<0.1	3	0.1	<1	3252	673	0.5	0.5	0.9
54 m	July 23, 2011	2	2.4	69	100	<0.05	0	0.4	290	1040	0.1	<0.2	560	0.1	3	0.5	<1	4950	692	0.3	0.7	1.2

tively; in July, the HCO_3^- concentrations strongly increased from the lake surface (328 mg L^{-1}) to -10 m (540 mg L^{-1}) and from -45 to -54 m depth (up to 618 mg L^{-1}) (Fig. 4a). The two vertical patterns of the NO_3^- concentrations (from 0.12 to 0.74 and from 0.03 to 0.42 mg L^{-1} in February and July, respectively) consistently showed a significant increase of this compound at depth between 15 and 40 m, followed by a sharp decrease as approaching the lake bottom (Fig. 4b). Conversely, both trends of NH_4^+ had significant increases close to the lake bottom, where NH_4^+ concentrations were 0.86 and 3.46 mg L^{-1} in February and July, respectively (Fig. 4c). The water samples collected at the lake bottom during the two sampling campaigns showed anomalously high concentrations of several trace elements with respect to those of the shallower waters, *e.g.* Ba (up to 100 μg L^{-1}), Fe (up to 290 μg L^{-1}), Mn (up to 1170 μg L^{-1}), P (up to 560 μg L^{-1}), and Si (up to 4950 μg L^{-1}).

The $\delta^{18}O$-H_2O and δD-H_2O values of the two samplings were consistent and ranged from -8.5 to -6.7 and from -59.3 to -51.2‰ V-SMOW, respectively. The $\delta^{13}C_{DIC}$ ratios, which were analyzed in summer, ranged from -11.8 to -9.1‰ V-PDB, and regularly decreased from the lake surface to the bottom.

Chemical and isotope ($\delta^{13}C$-CO_2, $\delta^{13}C$-CH_4 and δD-CH_4) compositions of dissolved gases

The chemical composition of the dissolved gases (in μmol L^{-1}) is shown in Tab. 3, while the $\delta^{13}C$-CO_2, $\delta^{13}C$-CH_4 and δD-CH_4 ratios are reported in Tab. 4.

In February, the concentrations of most of the main dissolved gases, *i.e.* N_2, Ar, and Ne (up to 781, 16 and 0.08 μmol L^{-1}, respectively) did not show significant variations along the vertical profile, O_2 ranged between 148 and 164 μmol L^{-1} from the lake surface to the depth of 45 m and then decreased to μmol L^{-1} at 54 m. The concentrations of H_2 were <1 μmol L^{-1} and CO_2 and CH_4 (up to 155 and 15 μmol L^{-1}, respectively) were only detected at depth >45 m. In July, N_2, Ar and Ne (up to 679, 17 and 0.01 μmol L^{-1}, respectively) showed patterns similar to those of the February campaign. On the contrary, O_2 rapidly decreased with depth and was <1 μmol L^{-1} (detection limit) below -15 m depth, in agreement with the data measured using the Idrolab multiprobe (Fig. 3d). Methane, CO_2 and H_2 strongly increased with depth up to 426, 493 and 334 μmol L^{-1}, respectively, at the lake bottom.

To calculate the $\delta^{13}C$ ratios of dissolved CO_2 ($\delta^{13}C$-CO_2) from the measured $\delta^{13}C$-CO_{2STRIP} ratios, the ^{13}C equilibrium fractionation between dissolved and gaseous CO_2 due to liquid-to-gas transfer of CO_2 during sampling was quantified by using the ε_1 factor suggested by Zhang *et al.* (1995) on the basis of empirical measurements, as follows:

$$\varepsilon_1=\delta^{13}C\text{-}CO_2-\delta^{13}C\text{-}CO_{2STRIP}=0.0049\times T(°C)-1.31 \quad \text{(eq. 1)}$$

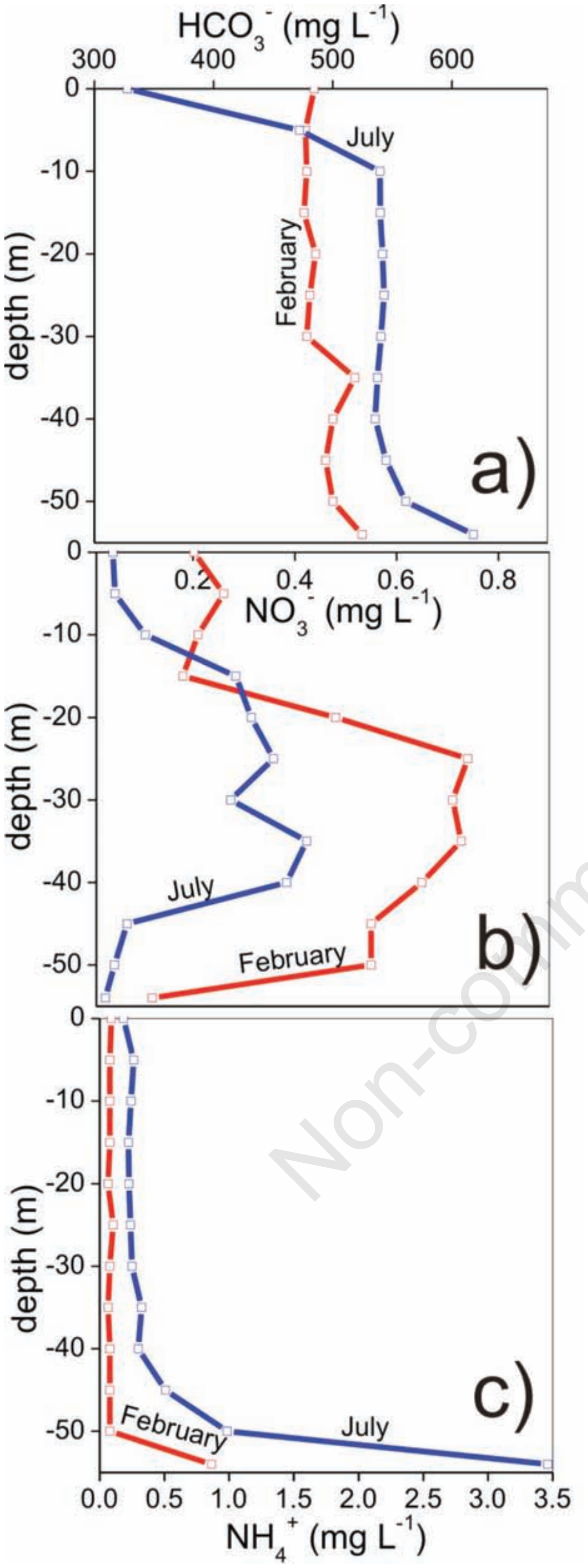

Fig. 4. Vertical profile of a) HCO$_3^-$; b) NO$_3^-$; and c) NH$_4^+$ concentrations of lake Paterno water in February and June 2011. Water samples were collected each 5 m from the surface to the bottom.

At 20°C (laboratory temperature) ε_1 is equal to -1.21. The calculated δ^{13}C-CO$_2$ value of the sample collected in February from the maximum depth was -10.92‰ V-PDB, whereas those of samples collected in July slightly decreased from -10.10 to -10.52‰ V-PDB passing from the -5 to -25 m depth, whilst at depths >25 m they regularly increased up to the lake bottom (-9.82‰ V-PDB).

The δ^{13}C-CH$_4$ and δD-CH$_4$ values of the sample collected at the maximum depth in February were -60.9‰ V-PDB and -259‰ V-SMOW, respectively. In July, the δ^{13}C-CH$_4$ values significantly decreased with depth, from -56.1 (at -20 m depth) to -66.7‰ V-PDB (at -54 m depth), whereas the δD-CH$_4$ ratios ranged between -258 and -266‰ V-SMOW with no specific trends along the vertical profile.

DISCUSSION

Origin of water and dissolved gases

The δ^{18}O-H$_2$O and δD-H$_2$O ratios of water collected from the lake bottom (Fig. 5) plot in correspondence to the local meteoric water line (LMWL) inferred by Giggenbach (1988) for precipitations in the Alban Hills, a volcanic system located about 70 km SW of the study area. This indicates that the sub-lacustrine springs feeding lake Paterno have a meteoric origin. The isotopic compositions at different depths define a linear trend having a slope of about 5 with respect to the LMWL. Such slope is typically produced by evaporation in lakes at ambient temperature (Matsubaya and Sakai, 1978; Rowe, 1994). Therefore, the progressive increases of the δ^{18}O-H$_2$O and δD-H$_2$O ratios at decreasing depth (Fig. 5) were likely due to downward circulation of water from the lake surface, where isotope fractionation caused by evaporation occurs. The water isotopic compositions of the SV and TC springs suggest that the thermal aquifer sourcing the mineral springs of the area through the main fault systems (Fiamignano-Micciani and the Velino faults) has a meteoric recharge. The high solute contents and relatively low pH (~6) characterizing this deep aquifer (Tab. 1) are caused by addition of deep-originated gases, such as CO$_2$ and H$_2$S (Annunziatellis *et al.*, 2004). This hypothesis is corroborated by the hydrogeochemical conceptual model proposed by Petitta *et al.* (2011) suggesting that, on the basis of hydrochemical and isotopic data, the chemistry of the mineralized springs of the area is controlled by mixing between shallow Ca^{2+}-HCO$_3^-$ groundwater from carbonate aquifers and a highly saline thermal Ca^{2+}-HCO$_3^-$-SO$_4^{2-}$ end-member. The relatively low salinity of the lake (Tab. 1) suggests that water contribution from the deep thermal system, if present, is negligible. Nevertheless, non-atmospheric gases (CO$_2$, CH$_4$ and H$_2$) were detected at significant concentrations in the deep lake waters (Tab. 3). The strongly negative isotope signature of CH$_4$ (Tab. 4) supports the idea that this gas is produced by methanogenic processes related to anaerobic activity of archeabacteria (Schoell, 1980; 1988; Barker and Fritz, 1981), occurring in the lake as well as within the lake bottom sediments, as described by the following reactions:

$$CO_2+8H^++8e^-\rightarrow CH_4+2H_2O \qquad \text{(eq. 2)}$$

and

$$^*CH_3COOH \rightarrow {}^*CH_4 + CO_2 \qquad \text{(eq. 3)}$$

where * indicates the intact transfer of the methyl position to CH_4. Reactions (2) and (3) describe carbonate-reduction and acetate fermentation pathways, respectively (Whiticar, 1999). The former process is the dominant methanogenic pathway in sulfate-free marine sediments, whereas in freshwater environments the two processes are competitive (Takai, 1970; Belyaev *et al.*, 1975; Winfrey *et al.*, 1977). As shown in the $\delta^{13}C$-CH_4 *vs* δD-CH_4 diagram (Fig. 6), where the isotopic compositional fields for the two different methanogenic pathways are reported (Whiticar *et al.,* 1986), both carbonate reduction and acetate fermentation likely contribute to CH_4 production in lake Paterno. Hydrogen, which in July was detected in dissolved gas samples from depths ≥25 m (Tab. 3), is an important intermediate in mineralization processes of organic matter under anaerobic conditions, *e.g.* it functions as electron donor by methanogenic and sulfate-reducing

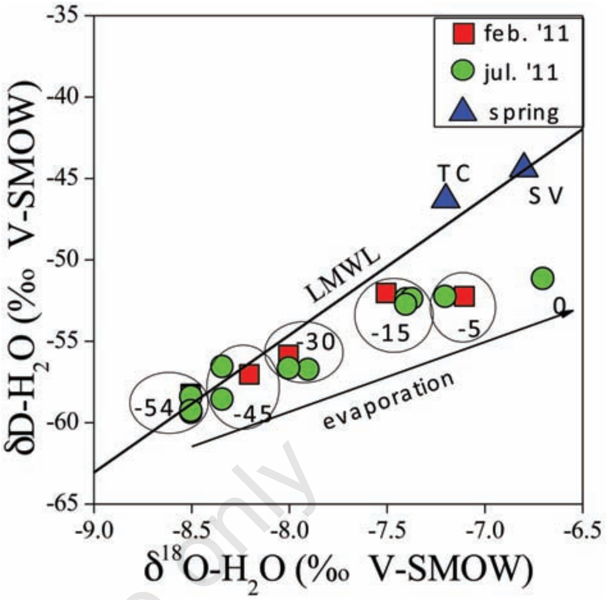

Fig. 5. δD-H_2O *vs* $\delta^{18}O$-H_2O plot of lake Paterno water in February and June 2011. Water samples were collected each 5 m from the surface to the bottom. The local meteoric water line (LMWL) (Giggenbach, 1988) was also reported. Square, February 2011; circle, July 2011; triangle, spring.

Tab. 3. Chemical composition of dissolved gases (CO_2, N_2, CH_4, Ar, O_2, Ne and H_2) collected in February and July 2011 from the surface to the bottom (each 5 m) at lake Paterno. Theoretical CO_2 concentrations (CO_{2eq}) were also reported. Concentrations of dissolved gases are in μmol/L.

Sample depth	Date	CO_2	N_2	CH_4	Ar	O_2	Ne	H_2	TOT	CO_{2eq}
0 m	Feb. 11, 2011	nd	769	nd	16	161	0.008	nd	946	466
5 m	Feb. 11, 2011	nd	776	nd	16	148	0.008	nd	940	1270
10 m	Feb. 11, 2011	nd	774	nd	15	164	0.008	nd	953	1940
15 m	Feb. 11, 2011	nd	778	nd	16	158	0.008	nd	951	1680
20 m	Feb. 11, 2011	nd	781	nd	16	148	0.008	nd	945	1460
25 m	Feb. 11, 2011	nd	771	nd	16	160	0.008	nd	948	1170
30 m	Feb. 11, 2011	nd	780	nd	16	146	0.008	nd	943	1220
35 m	Feb. 11, 2011	nd	775	nd	16	144	0.008	nd	935	1240
40 m	Feb. 11, 2011	nd	769	nd	15	155	0.008	nd	939	1160
45 m	Feb. 11, 2011	33	769	1.5	16	158	0.008	nd	977	1180
50 m	Feb. 11, 2011	94	774	5.0	16	73	0.008	nd	961	1060
54 m (bottom)	Feb. 11, 2011	155	766	15	16	54	0.008	nd	1106	1840
0 m	July 23, 2011	nd	558	nd	13	175	0.006	nd	746	95
5 m	July 23, 2011	3.6	677	nd	17	199	0.008	nd	896	854
10 m	July 23, 2011	13	673	nd	17	11	0.010	nd	714	1360
15 m	July 23, 2011	78	664	nd	16	nd	0.008	nd	757	1500
20 m	July 23, 2011	191	635	6.2	16	nd	0.008	nd	847	1470
25 m	July 23, 2011	322	644	32	16	nd	0.008	25	1014	1480
30 m	July 23, 2011	306	634	94	16	nd	0.008	38	1049	1430
35 m	July 23, 2011	325	649	145	16	nd	0.008	29	1135	1400
40 m	July 23, 2011	319	662	162	17	nd	0.010	140	1160	1460
45 m	July 23, 2011	373	667	329	17	nd	0.010	253	1386	1420
50 m	July 23, 2011	385	677	439	17	nd	0.010	234	1518	1460
54 m (bottom)	July 23, 2011	426	679	493	17	nd	0.010	334	1615	3530

nd, not detected.

bacteria (Mah *et al.*, 1977; Zehnder, 1978; Thauer and Badziong, 1980). As also observed in other meromictic lakes (Schweizer and Aragno, 1975; Conrad *et al.*, 1983; Bianchi *et al.*, 2010), during the stratified period (July), H_2 likely diffused from the lake sediment toward the surface and progressively consumed by hydrogen-oxidizing bacteria during its migration (Aragno and Schlegel, 1981; Bowien and Schlegel, 1981).

The carbon isotope signature of dissolved CO_2 ($\delta^{13}C$-CO_2 >-11‰ V-PDB) is heavier than that produced by a biogenic source ($\delta^{13}C$-CO_2 ≤-20‰ V-PDB) (O'Leary, 1988; Hoefs, 2008), but lighter than the bubbling CO_2 of the SV spring ($\delta^{13}C$-CO_2 ≤-3.08‰ V-PDB). This implies, at least, two possible sources for the dissolved CO_2 of lake Paterno: i) bacterial-driven reactions, such as denitrification, methanogenesis, and Fe^{3+}, Mn^{3+} and SO_4^{2-} reduction (Wetzel, 2001; Schlesinger, 2005), occurring within the lake; ii) deep fluid circulation system related to the Tuscan Roman Degassing Structure (TRDS; Chiodini *et al.*, 2004), characterized by CO_2 produced by a combination of different processes, such as i) mantle degassing and ii) thermo-metamorphic reactions within the Mesozoic limestone and/or the metamorphic basement (*e.g.* Minissale, 2004; Chiodini *et al.*, 2011). The possible occurrence of CO_2 addition from a sublacustrine source supports the idea that ground collapses, related to deep piping processes caused by underground circulation of highly mineralized $CO_2(H_2S)$-rich fluids, is the main genetic mechanism for the sinkholes of the S. Vittorino plain, as also suggested by Caramanna *et al.* (2008).

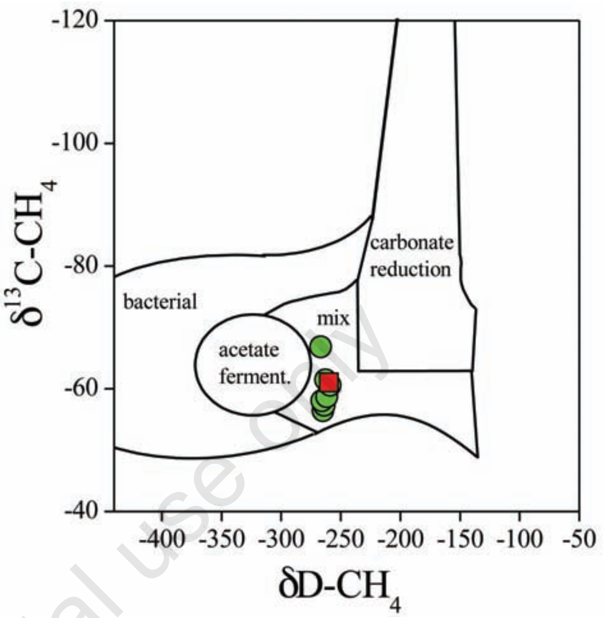

Fig. 6. $\delta^{13}C$-CH_4 *vs* δD-CH_4 plot of lake Paterno water in February and June 2011. Isotopic compositional fields for gases produced by carbonate-reduction and acetate fermentation (Schoell 1980; 1988; Whiticar 1999) were also reported. Square, February 2011; circle, July 2011.

Tab. 4. $\delta^{13}C$-CO_2 (expressed as ‰ V-PDB), $\delta^{13}C$-CH_4 (expressed as ‰ V-PDB) and δD-CH_4 (expressed as ‰ V-SMOW) ratios of gas samples collected from lake Paterno at selected depths in February and July 2011.

Sample depth	Date	$\delta^{13}C$-CO_{2STRIP}	$\delta^{13}C$-CO_2	$\delta^{13}C$-CH_4	δD-CH_4
50 m	Feb. 11, 2011	na		-58.1	na
54 m (bottom)	Feb. 11, 2011	-9.71	-10.92	-60.9	-259
San Vittorino	Feb. 11, 2011	-3.08		na	na
Sample depth	Date	$\delta^{13}C$-CO_{2STRIP}	$\delta^{13}C$-CO_2	$\delta^{13}C$-CH_4	δD-CH_4
5 m	July 23, 2011	-8.89	-10.10	na	na
10 m	July 23, 2011	-9.04	-10.25	na	na
15 m	July 23, 2011	-9.02	-10.23	na	na
20 m	July 23, 2011	-9.16	-10.37	-56.1	na
25 m	July 23, 2011	-9.31	-10.52	-56.3	-264
30 m	July 23, 2011	-9.15	-10.36	-57.1	-263
35 m	July 23, 2011	-9.02	-10.23	-57.9	-265
40 m	July 23, 2011	-8.94	-10.15	-58.5	-261
45 m	July 23, 2011	-8.82	-10.03	-60.4	-258
50 m	July 23, 2011	-8.76	-9.97	-61.3	-262
54 m (bottom)	July 23, 2011	-8.61	-9.82	-66.7	-266

na, not analyzed.

The $\delta^{13}C_{DIC}$ values, which are produced by combining the $\delta^{13}C$ values of the main inorganic carbon species (HCO_3^- and CO_2), are in the same range of the $\delta^{13}C$-CO_2 ones (Tab. 1). Isotopic fractionation caused by reaction between dissolved CO_2 and HCO_3^- is quantified by the enrichment factor (ε_2), as follows (Mook *et al.*, 1974):

$$\varepsilon_2=\delta^{13}C\text{-}HCO_3^- - \delta^{13}C\text{-}CO_2=9483/T(K) - 23.9 \qquad \text{(eq. 4)}$$

Theoretical $\delta^{13}C_{DIC}$ values ($\delta^{13}C_{DICcalc}$) can be computed by:

$$\delta^{13}C_{DICcalc}=\delta^{13}C\text{-}CO_2+\varepsilon_2\times(HCO_3^-)/[(HCO_3^-)+(CO_2)] \qquad \text{(eq. 5)}$$

The $\delta^{13}C_{DICcalc}$ range from -1.1 and -0.3 ‰ V-PDB, *i.e.* they are significantly less negative than the measured $\delta^{13}C_{DIC}$ values (Tab. 1). The large difference between measured and calculated $\delta^{13}C_{DIC}$ values suggests that CO_2 produced by both biogenic processes and added to the lake from the deep abiogenic sources has not achieved an isotopic equilibrium with HCO_3^-.

Moreover, theoretical CO_2 concentrations (CO_{2eq}) calculated on the basis of water chemistry are significantly higher than those measured (Tab. 3), indicating that both HCO_3^- concentrations and pH values are not (or not only) controlled by this gas. It is worthy of noting that the $\delta^{13}C_{DICcalc}$ values are similar to those measured in water samples from springs of the San Vittorino plain, which range from -0.1 to 1.7‰ V-PDB (Petitta *et al.,* 2011).

Processes controlling chemical and isotope compositions of water and dissolved gases along the vertical profiles

The temperature vertical profiles (Fig. 3a) indicated that during the summer period (July) a well-defined thermal stratification established at lake Paterno, whereas in winter (February) the lake water was (almost) completely homogenized. The occurrence of annual meromixis is called monomixis, a typical feature of non-freezing lakes in temperate climates (Boehrer and Schultze, 2008). Seasonal meromixis at lake Paterno is likely created and sustained by both i) biogenic processes, *i.e.* decomposition of organic material and dissolution of its end products (Walker and Likens, 1975), and ii) lake morphology (Lemmin, 1995). In February, relatively high concentrations of HCO_3^-, Ca^{2+}, NH_4^+, Si, Fe, Mn, P, Ba, CO_2 and CH_4 (Tabs. 1, 2 and 3) were only measured in the bottom waters, suggesting that such enrichment processes, mainly occurring within the bottom sediments, cannot completely be masked by water circulation in the mixolimnion. In July, the stable hypolimnion allows a pronounced increase of the non-atmospheric dissolved gases starting from depth >5-8 m (Tab. 3), whereas the vertical profiles of solute major solutes and trace species (Tabs. 1 and 2) are similar to those measured in February. During this period, the thin epilimnion of lake Paterno is episodically re-circulated due to wind and/or diurnal-nocturnal temperature fluctuations, causing the release of CO_2 and CH_4 migrated up to the thermocline from the anoxic deep waters. Such a frequent degassing process, coupled with photosynthesis, contributed to the abrupt decrease of the non-atmospheric dissolved gases approaching the lake surface (Tab. 3). The relatively low Ca^{2+} and HCO_3^- concentrations measured in the shallow water layer (0-5 m depth) in July is likely related to calcite precipitation caused by the relatively high temperature up to 23.2°C at the lake surface. To validate this hypothesis, we calculated the Saturation Index (SI) with respect to the main salts (calcite, dolomite, fluoride and halite) of water samples from lake Paterno with the PHREEQC-2 computer program using the WATEQ4F thermodynamic database (Parkhurst and Appelo, 1999). Our results (Tab. 5) show that the two Ca^{2+}-bearing carbonate minerals (calcite and dolomite) are slightly oversaturated, thus mineral precipitation efficiently controls the distribution of Ca^{2+} and HCO_3^- along the lake vertical profile.

The CO_2 vertical profile in the hypolimnion developed in July (Fig. 7) highlighted the occurrence of two different layers: in the shallower one (layer I; depth <25 m), CO_2 had a strong decrease toward the surface; in the deeper one (layer II; depth >25 m), the CO_2 concentrations diminished at relatively low rate as depth was decreasing. The separation between layers I and II was also marked by the inversion in the behavior of the $\delta^{13}C$-CO_2 values. The carbon isotopic ratio indeed decreased from the lake bottom to the depth of 25 m, whereas it increased from 25 to 5 m. This suggests that photosynthesis plays an important role also in layer I, leading to a significant CO_2 consumption and, consequently, to a ^{13}C-enrichment of the residual CO_2. In layer II, where the presence of abundant suspended matter (Palozzi *et al.*, 2010) prevents the solar radiation to infiltrate, the vertical patterns of CO_2 concentration and $\delta^{13}C$-CO_2 are controlled by both contribution of isotopically heavy abiogenic CO_2 from the bottom and biogenic CO_2 production. The progressive decrease of CH_4 concentrations and the simultaneous increase of the $\delta^{13}C$-CH_4 values at decreasing depth (Fig. 8) is likely due to anaerobic oxidation, which seems to be more efficient at depths >40 m, probably because at shallower depth the relatively low CH_4 concentrations are not attractive to methanotrophs (Whiticar, 1999). Nitrate and sulfate can function as electron acceptors for microbial oxidation of organic material. Therefore, denitrification favors the decrease of NO_3^- in the deepest portion of layer II (Fig. 4b), where significant sulfate reduction also occurred (Tab. 1). Ammonia increase with depth may partly be dependent on NO_3^- reduction (Buresh and Patrick, 1981). However, in eutrophic lakes the activity of this latter process is an order of magnitude lower than denitrification (Stewart *et al.*, 1982). This suggests that NH_4^+ was mainly generated primarily in the lake sediments by the deamination of proteins and amino acids (Molongoski and Klug, 1980), as also supported by the dramatic NH_4^+ increase at the lake bottom (Fig. 4c).

The concentration patterns of Fe and Mn drastically increased toward the maximum depth. This may reflect a sediment source for both Fe^{2+} and Mn^{2+} (Davison *et al.*, 1980), which are relatively high in waters at the measured pH values. Furthermore, Fe and Mn reduction, as well as CO_2 dissolution, contributed to lower the pH values. Oxidation processes, with formation of insoluble Fe- and Mn-hydroxides, is the main factor limiting the concentrations of these two elements in the lake. The redox cycles of Fe and Mn control the distribution and speciation of other elements, such as phosphorus (Mortimer, 1942; Balistrieri *et al.*, 1992; Hongve, 1997). Phosphorus accumulation in anoxic deep lake waters is related to its rapid endogenous cycle (Schwedt, 1996): phosphate is assimilated during the photosynthesis of living organism and is released again within a few days; phosphorus is then scavenged from the epilimnion due to sorption to Fe and Mn precipitates and eventually, it is released by microbial degradation of detritus during sedimentation and during sediment diagenesis (Gächter and Bloesch, 1985; Gächter and Mares, 1985; Veronesi *et al.*, 2002). Therefore, during the summer period the vertical distribution of P, as well as that of Fe and Mn, was regulated by: i) limited upward diffusion of these elements from the bottom sediments up to the of ~45-50 m; and ii) co-precipitation of insoluble Fe-, Mn- and P-bearing compound at relatively shallow depth, where oxygen from different sources was available. In winter, the lake had a unique aerobic mixolimnion, thus significant concentrations of these three elements only occurred in lake water just above the bottom sediments.

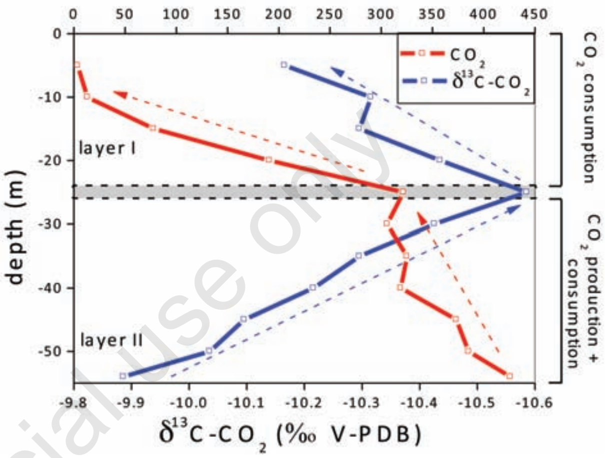

Fig. 7. Vertical profile of CO_2 concentrations (in μmol L^{-1}) and $\delta^{13}C$-CO_2 values (in ‰ V-PDB) of lake Paterno in June 2011, from the depth of 5 m to the lake bottom.

Tab. 5. Saturation index with respect to calcite, dolomite, fluoride and halite of water samples collected from lake Paterno.

Sample depth	Date	Calcite	Dolomite	Fluoride	Halite
0 m	Feb. 11, 2011	0.86	1.01	-1.97	-9.09
5 m	Feb. 11, 2011	0.42	0.14	-2.01	-9.06
10 m	Feb. 11, 2011	0.23	-0.24	-1.63	-9.02
15 m	Feb. 11, 2011	0.29	-0.11	-1.97	-9.07
20 m	Feb. 11, 2011	0.37	0.05	-1.88	-9.08
25 m	Feb. 11, 2011	0.46	0.21	-1.69	-9.06
30 m	Feb. 11, 2011	0.44	0.18	-1.41	-9.06
35 m	Feb. 11, 2011	0.48	0.31	-1.25	-9.03
40 m	Feb. 11, 2011	0.49	0.30	-1.84	-9.10
45 m	Feb. 11, 2011	0.48	0.26	-1.43	-9.02
50 m	Feb. 11, 2011	0.53	0.36	-1.18	-9.05
54 m (bottom)	Feb. 11, 2011	0.37	0.02	-1.77	-9.08
0 m	July 23, 2011	1.06	1.92	-2.45	-8.98
5 m	July 23, 2011	0.56	0.63	-2.12	-8.91
10 m	July 23, 2011	0.51	0.36	-1.86	-8.95
15 m	July 23, 2011	0.45	0.20	-1.83	-8.97
20 m	July 23, 2011	0.46	0.23	-1.51	-8.89
25 m	July 23, 2011	0.46	0.23	-1.87	-9.00
30 m	July 23, 2011	0.46	0.24	-1.87	-8.98
35 m	July 23, 2011	0.47	0.25	-1.60	-8.96
40 m	July 23, 2011	0.45	0.21	-1.91	-8.99
45 m	July 23, 2011	0.48	0.25	-1.82	-8.99
50 m	July 23, 2011	0.50	0.29	-1.41	-8.89
54 m (bottom)	July 23, 2011	0.21	-0.29	-1.29	-8.89

Whatever the thickness of the water layer, we may refer the lake bottom as the layer III of Lake Paterno.

CONCLUSIONS

Bacteria-driven processes occurring in the hypolimnion of lake Paterno during summer, when thermal stratification favored by climate conditions produced the isolation of deep waters from the lake surface, are the main responsible for the distribution of biogenic (CO_2, CH_4, H_2, NH_4^+ and P) and minerogenic (Fe^{2+}, Mn^{2+}, Si and Ba) products along the vertical lake profile. Based on the chemical and isotopic characteristics of water and dissolved gases, different layers are distinguished: i) layer I, *i.e.* the epilimnion (from the surface to -8 m depth), where photosynthesis and frequent water mixing occur preventing accumulation of both biogenic elements and dissolved gases, and the relatively high temperature causes significant calcite precipitation; ii) layer II, the anoxic hypolimnion (depth >10 m), whose chemistry is controlled by the activity of different bacteria populations; iii) layer III, the lake bottom (-54 m depth), where the highest concentrations are recorded for those elements likely released at the sediment-water interface (Fig. 9a). During winter, the decrease of lake temperature, likely coupled with the effect of winter winds, allows the mixing of layers I and II, whereas continuous biogenic and minerogenic production maintains significant ion and dissolved gas enrichments in a thin water layer at the contact with the bottom sediments (Fig. 9b). The seasonal stratification of lake Paterno sheds light on the behavior of living macro-organisms, which during summer are forced to populate only the epilimnion. Occasional lake water mixing, caused for example by anomalous weather conditions, during the stratified period cannot be excluded. However, the low temperature of the deep waters (~7°C) suggests that such events can be forecasted to be rare, and lake Paterno can be considered monomictic. The carbon isotopic signature of CO_2 indicates that this gas partly originated from the hydrothermal system feeding the mineralized springs of the San Vittorino valley. This external input of CO_2 may play a significant role for the development of the seasonal stratification of lake Paterno. Moreover, the presence of deep-originated CO_2 within the lake supports the hypothesis that lake Paterno is a deep piping sinkhole (DPS), *i.e.* it originated from ground collapses caused by deep piping processes triggered by uprising acidic fluids from depth.

However, to exhaustively define the mechanisms regulating the temporal evolution of the water and dissolved gas chemistry of this lake, a comprehensive investigation of the distribution of bacteria and archaebacteria populations along the vertical water column is strongly recommended.

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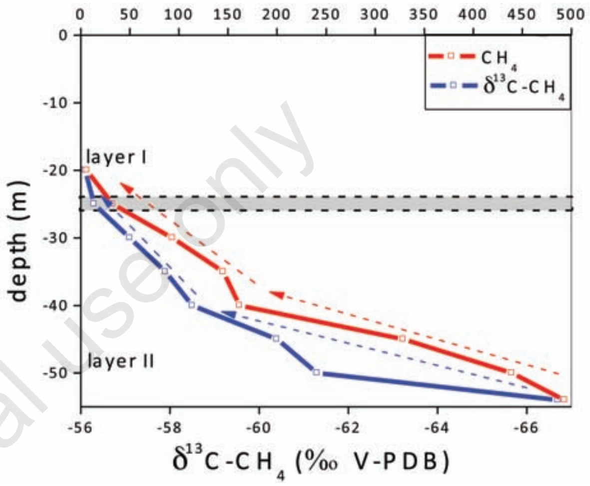

Fig. 8. Vertical profile of CH_4 concentrations (in μmol L^{-1}) and δ^{13}C-CH_4 values (in ‰ V-PDB) of lake Paterno in June 2011, from the depth of 20 m to the lake bottom.

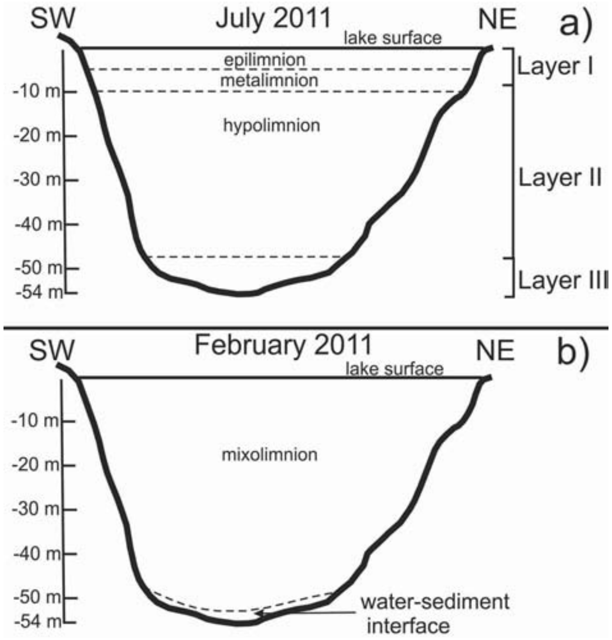

Fig. 9. Schematic section of lake Paterno along the vertical profile in a) July 2011 and b) February 2011.

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