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Gases (CH_4, CO_2 and N_2) and pore water chemistry in the surface sediments of Lake Orta, Italy: acidification effects on C and N gas cycling

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ABSTRACT

Lake Orta, a subalpine, warm monomictic lake in northwestern Italy was heavily polluted from rayon factory discharges of ammonium and copper since 1926. In the 1950s accumulations of contaminants resulted in whole lake pHs of 3.8-4.0 from ammonium oxidation. Partial remediation started in the 1950s, but by 1985-89 the water remained acidified at pHs of 4.0. Artificial liming (14,500 t) in 1989-90 resulted in improved water quality and substantial recovery of the biological community. Sediment gases, sampled in 1989 before liming, from the lake's four basins showed severe inhibition of methanogenesis (CH_4 = 0.0-0.15 mM) in the surface sediments (0.5-5 cm) of the southern basin, location of the plant effluent, as compared to the deep central and northern basins (0.9-1.4 mM). Four years after liming, cores collected in 1994 near the 1989 southern basin sites showed a slight change in surface sediment methane (0.07-0.82 mM), yet suggested continual sediment toxicity, at least to carbon cycling through methanogenesis. Calculations of diffuse flux of CH_4 at the sediment-water interface (SWI) in 1989 were 6.6-7.4 mM m^{-2} day^{-1} for the central and northern basins and 0.13 for the southern basin. CH_4 fluxes increased 16x to 2 mM m^{-2} day^{-1} in 1994 in the southern basin, possibly from remediation of near surface sediments. The impact of pollution on denitrification (formation of sediment N_2 gas) was not so obvious since two processes could counteract each other (high NO_3^- stimulating denitrification versus possible negative effects from acidity and metals). The calculated flux of N_2 from the southern basin sediments increased 5x four years after liming compared to the period of acidification, suggesting possible toxicity towards denitrifiers during the earlier period. Core overlying water (0.68 mM) exhibited N_2 concentrations close to saturation, while most surface sediments were twice as much (1.5 mM). Surface (0-6 cm) sediment N_2 was similar at most sites, with the exception of 0.82 mM in the low porosity sediments of the Omegna basin at the lake's outlet. The calculated diffuse flux of N_2 at the SWI averaged 4 mM m^{-2} day^{-1} for the entire lake and varied between 1.3 at Omegna to 7.3 at the Central basin. It is suspected that surface sediment N_2 production from denitrification and subsequent flux from sediments to overlying waters should resolve much of the deficit in the mass budget for water column nitrogen during the acidification period where only 35 percent of the ammonium oxidation could be accounted for as nitrate.

Key words: lake sediment, gases, nitrogen, methane, carbon dioxide

1. INTRODUCTION

Lake Orta, a warm monomictic lake in the southwestern section of the Lake Maggiore drainage basin in northern Italy, is the sixth largest Italian lake by volume. In 1926 a rayon factory in the southern end of the lake started discharging an effluent of ammonium sulfate (1950-3350 t y^{-1} inorganic N) and copper (40-60 t y^{-1}). By 1929 fish were absent from the lake and nitrification of the ammonium effluent changed the lake water to about 4-4.2 pH. Copper discharge was reduced in 1956 by the installation of a recycling plant at the Bamberg rayon facility, however electroplating factories continued to be responsible for high levels of copper, chromium and zinc, which concentrated in the sediments until the present time (Baudo *et al*. 1989, 1997). In 1980 an ammonium sulfate treatment plant was installed, reducing the N loading to 30 t y^{-1}. From May 1989 to June 1990 the lake was artificially limed with 14,500 tons of $CaCO_3$. Since this time the water column pH increased to 6 and the plankton, littoral and fish fauna have quickly responded with reasonable recovery (Bonacina & Pasteris 2001).

In 1989, a research project was initiated to evaluate the effect of the lake's acidic condition and the high levels of sediment metals on the cycling of carbon (C) and nitrogen (N), mainly as microbiological end-product gases [pore water methane (CH_4), carbon dioxide (CO_2) and di-nitrogen (N_2)], in the near surface sediments of the lake's four basins (southern, central, northern and Omegna). The Omegna Basin is located at the lake's discharge (4.81 m^3 s^{-1} mean outflow; Baudo *et al.* 1997) to the Nigoglia River. As a complimentary program, the sediment pore water chemistry was evaluated at the lake's two shallow basins (southern and Omegna in Fig. 1). In addition, changes in the pore water gases, which might have occurred in the sediments four years after liming, were measured in the southern basin (location of rayon factory effluent) in 1994; only the highly impacted southern basin was sampled at this time (Fig. 1).

The main objectives of this research were to:

1) evaluate if the composition of sediment gases and pore water chemistry reflected the acidified environment of the overlying water column;

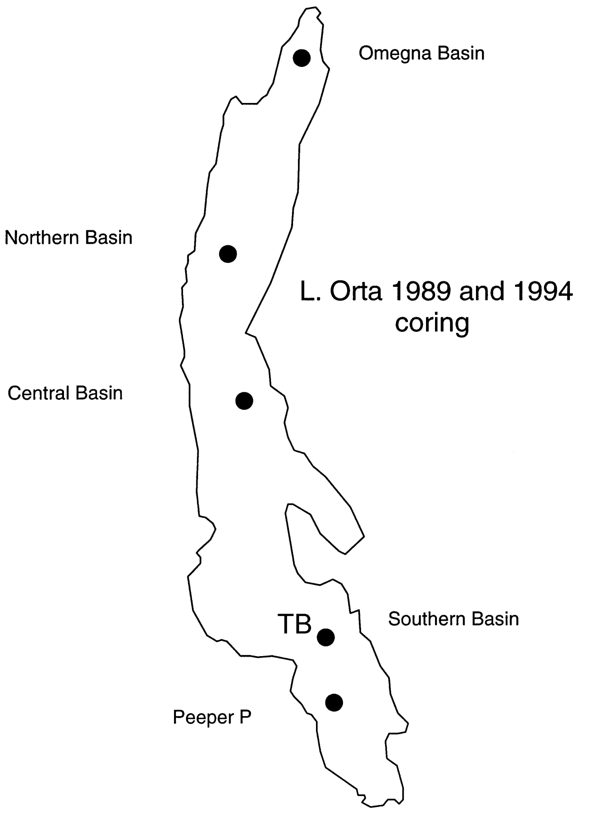

Fig. 1. Sediment sampling stations in Lake Orta, Italy, during 1989 in southern (P and TB sites), central, northern and Omegna basins and 1994 (southern basin near P and TB sites only).

2) determine if there were differences in pore water gases between the four basins of the lake that might relate to the long-term effects of factory effluent (mainly in the southern basin) and the accumulation of pollutants in the sediments;
3) calculate theoretical diffusive fluxes of CH_4 and N_2 at the sediment-water interface and evaluate their importance to the lake's C and N cycles;
4) ascertain if the high concentrations of inorganic nitrogen in the water column could impact the sediment N gas cycle by altering the nitrification/denitrification pathways.

2. METHODS AND MATERIALS

2.1. Field techniques

Bottom sediments were collected by gravity coring with a small Phleger corer (Mudroch & MacKnight 1994), using 4.4-cm I.D. acrylic plastic liners without a metal barrel, or from cores collected with scuba divers. Sediments were sampled to a depth of 12 to 50 cm (the shallow 12-cm core penetration in the Omegna Basin sediments reflected their low porosity). Core catchers were not used, relying on a vacuum created with a rubber valve at the top of the Phleger corer. Sediment cores were collected for pore water gases from Lake Orta on two occasions: July-August 1989 (9 cores) and June 1994 (2 cores); only the Southern basin was cored during the second period. Cores were processed by removing sediments into special gas syringes at a nearby boat marina within a few hours after coring (Adams 1994). To avoid disturbance of the gases, cores were never transported overland.

The 1989 sampling occurred a few months before liming commenced. All four basins of the lake (southern, central, northern and Omegna near the outflow) were sampled and peepers (Adams 1994) were deployed at various shallow water sites in the southern and Omegna basins. These *in situ* equilibration systems (van Eck & Smits 1986), called peepers (Hesslein 1976), were used to collect pore water for pH, dissolved nutrients and metals, but not for gases. pH was also measured on other intact cores. In earlier studies Adams & van Eck (1988) and Adams (1992) observed differences in gas concentrations between peepers and low-porosity sediments collected by gravity coring at the same sites; this suggested the lack of *in situ* gas equilibration with the peeper cells. Cores were also taken in the Omegna Basin by scuba divers to compare collection techniques (gravity coring *vs* scuba) for sediment gases. However, the sediments in this basin were more difficult to penetrate, even with scuba divers, likely because of the lower sediment water content (i.e., low porosity) and the lack of organic matter accumulation resulting from the higher current velocities near the lake's exit.

During the 1994 expedition, four years after liming, two sediment cores were obtained from the southern basin. Core processing also took place at the shore of the lake. However, sediment gas syringes, cooled and stored in helium-filled bags, were transported to Kastanienbaum (EAWAG/ETH's Lake Research Center), Switzerland, for gas analyses. After gas analyses, within 2-3 days after coring, sediments from the 1994 cores were submitted to long-term incubation to evaluate the potential for methanogenesis (Adams *et al.* in prep.).

In all cases, sediment cores were processed inside a helium-filled glove bag within a few hours after collection. Cores showing substantial bubbling, or where bubbles were lost during sediment processing, were discarded. Sediments were transferred at 1-2 cm depth intervals, using a core adapter syringe sampling system (called CASS; Adams 1994), directly from the core liners to 25-ml Sarstedt (Sarstedt, Numbrecht-Rommelsdorf, Germany) monovette plastic syringes and glass scintillation vials while the glove bag was flushed with helium. Using a YSI oxygen meter, the internal air of the glove bag was kept at about 0.2-0.5 ppm O_2 during sediment processing to avoid air contamination (Fendinger & Adams 1986), especially since sediments were analyzed for pore water O_2, if present, and Ar and N_2. Core processing for *ca* 20 gas syringes usually took one hour. All sediment gas syringes were immediately stored on ice in helium-filled, heavy-duty (4 mil) freezer bags for transport - 1989 to Pallanza, Italy (2 hours), and in 1994 to Kastanienbaum, Switzerland (1 day) - for laboratory gas chromatographic measurements.

Peepers were deployed and recovered with scuba divers in the southern and Omegna Basins to measure a variety of chemicals in the sediment pore water (see Adams 1994 and van Eck & Smits 1986 for peeper design). The peepers were equilibrated with N_2-purged water prior to deployment and they were left in the sediments for at least two weeks (Angelidis 1990). A solid cover plate was slid over a non-degradable, dialysis membrane, which covered the peeper cells, prior to deployment and again before removal from the sediments. All joints between the cover plate and peeper body were covered with mud. This plate was kept in place to inhibit O_2 penetration during sampling of the peeper equilibration cells through side ports, containing septa, which were flushed with N_2 during pore water removal (van Eck & Smits 1986).

2.2. Sediment gas measurements

Analysis of sediment gases normally took place 24 hours (except during the 1994 campaign) after coring and immediate glove bag operations. At this time sediment gas syringes were submerged in a water bath at constant temperature (20 °C) and 5.0 ml of helium added to each syringe; manipulations took place under water to avoid possible atmospheric contamination. Extraction of sediment gases into the helium headspace of each syringe was facilitated by vibration for 3.5-4 minutes (in a helium-filled bag) followed by removal of 0.8-ml helium headspace with a gas-tight syringe. A Carle model 310M gas chromatograph was used to measure the following gases: headspace extractable argon (Ar), oxygen (O_2), di-nitrogen (N_2), methane (CH_4) and carbon dioxide (CO_2). A flame ionization detector (FID) was used to measure CH_4 at low concentrations (usually in the water column) while a thermal conductivity detector (TCD) was employed to measure Ar, O_2, N_2, CH_4 and CO_2 in sediment headspace samples. An in-line methanizer removed oxygen from a duplicate gas sample to determine argon. Because of problems with the analyses, there were few measurements of pore water CO_2. Since O_2 should not appear in the sediment pore water, its presence indicated atmospheric contamination of the sample during core processing and the gas data were usually discarded. N_2/Ar ratios were used for assessing *in situ* N_2 production from denitrification (Noshio *et al.* 1981). Gases were separated by a variety of gas chromatographic solid supports contained in 3.175 mm (1/8 inch) I.D. columns; these were molecular sieve 5A (activated at *ca* 350 °C) and Porapak Q or S, with a helium gas flow rate of 60 ml min^{-1}. Most solid supports were 60/80 mesh sizes. The detectors were standardized with air (78.084% N_2, 20.984% O_2 and 0.934% Ar) and pure gases (CH_4 and CO_2); certified Swiss standards were used in the 1994 gas analyses.

2.3. Pore water chemistry

Most of the peeper data are listed in Angelidis (1990). During pore water sampling care was taken to avoid oxygen contamination (Adams 1994) by employing techniques developed by van Eck & Smits (1986). Pore water was removed from equilibration chambers, under an N_2 atmosphere, within two hours after removing the peeper from the sediments. Ions (Cl^-, SO_4^{2-}, NH_4^+ and NO_3^-) were measured with a Dionex ion chromatograph within 24 hours and iron (Fe^{2+}) was analyzed by flame atomic absorption of acidified pore water (Angelidis 1990). Sediment pH was determined on both cored sediments (by extrusion; this research) and from peeper-collected pore water samples (from Angelidis, pers. comm.).

2.4. Sediment measurements

Sediments in tared glass scintillation vials, collected during the processing of cores for sediment gases, were dried to constant weight at ca. 60 °C for sediment water content. Loss on ignition (LOI) for selected sediments, taken from the gas syringes after analyses, were dried and then combusted at 540 °C for 2 hours. Sediment LOI data were also provided by Angelidis (pers. comm.) for comparison purposes.

3. RESULTS

Statistical information for sediment gases (CH_4, CO_2 and N_2) and sediment water content (%H_2O) and loss on ignition (LOI) from the four basins of Lake Orta is listed in table 1 (gas concentrations in mM). Pore water gases from collected cores and sediment water content and loss on ignition for southern basin sites during July-August 1989 are shown in figure 2 [depth designated as above and below the sediment-water interface (SWI); in this case gas concentrations are shown in ml l^{-1} pore water = mM × 22.414]. Note that depths below the SWI in all figures (and in the text) are listed as negative values. Pore water gases were not measured in peepers deployed near some of the coring sites. LOI and sediment water contents for November 1990, 15-16 months later (Agelidis, per. comm.) are included for comparison purposes. The southern basin cored sites are noted as P, taken near various peeper locations, "P1, etc.", close to the Bemberg factory outfall, and at a more distant southern basin site near the buoy TB (Fig. 1). The 1989 collection dates are listed in the figures (dup = duplicate core at the same site). Southern basin methane concentrations were almost zero (avg. + std. dev. = 0.05 + 0.06 mM, n=10 in table 1; mM × 22.414 = ml l^{-1} in Fig. 2A) in the 0 to -5 cm section below the sediment-water interface. These values were much less than observed in the other two major basins (central and northern) for the

Tab. 1. Statistical information for three pore water gases and two sediment variables (water content, % H_2O, and loss on ignition, LOI) measured in cores collected from the four basins of Lake Orta during 1989 and 1994. Only the southern basin was sampled in 1994. Values are divided into either the surface sediments or the entire core length. Data are listed as average ± std. dev. (one sigma), with concentration ranges and number of analyses. Pore water gas concentrations are provided in mM and sediments values are given in percent (%).

Basin	CH_4	N_2	CO_2	% H_2O	LOI
			SURFACE (0.5 cm to approximately –6 cm) SEDIMENTS		
Southern	0.05 ± 0.06*	1.55 ± 0.40	Only one	86.9 ± 4.8	22.1 ± 4.7
1989	0.001–0.15 (10)	0.40–2.4 (8)	(0.13 at –5)	75–92 (15)	11–28 (11)
Southern	0.38 ± 0.25	1.46 ± 0.13	No data	86.1 ± 6.0	No data
1994	0.07–0.82 (8)	1.25–1.62 (8)		78–94 (8)	
Central	1.06 ± 0.2**	1.59 ± 0.41**	No data	88.1 ± 3.6**	21.7 ± 6.62**
	0.93–1.4 (4)	0.99–1.92 (4)		85–93 (4)	16–25 (4)
Northern combined with Central basin			0.89 ± 0.08 0.81–0.97 (3)		
Omegna	0.05 ± 0.04***	0.82 ± 0.10	0.17 ± 0.06	82.4 ± 4.7	18.2 ± 3.8
	0.001–0.09 (7)	0.68–0.90 (4)	0.13–0.27 (4)	76–89 (8)	11-24 (8)
			ENTIRE CORE LENGTHS		
Southern	0.50 ± 0.32	1.46 ± 0.40	0.27 ± 0.08	78.9 ± 6.3	15.9 ± 4.9
1989	0.02–1.11 (33)	0.40–2.41 (34)	0.14–0.39 (6)	66–92 (59)	9.5–28 (40)
Southern	0.63 ± 0.32	1.14 ± 0.32	No data	78.4 ± 7.1	No data
1994	0.07–1.33 (24)	0.46–1.62 (24)		66–94 (24)	
Central	2.73 ± 1.19	1.27 ± 0.26	No data	81.5 ± 6.1	15.8 ± 6.7
	0.93–4.02 (10)	0.99–1.67 (10)		71–93 (10)	10–29 (7)
Northern	3.07 ± 1.50	1.39 ± 0.41	1.30 ± 0.42	76.5 ± 10.4	13.5 ± 5.3
	1.04–6.55 (12)	0.81–2.19 (12)	0.81–2.08 (9)	59–89 (12)	8–25 (11)
Omegna	0.17 ± 0.10	0.93 ± 0.19	0.20 ± 0.05	71.0 ± 11.1	12.8 ± 4.3
	0.03–0.34 (8)	0.68–1.34 (8)	0.13–0.29 (8)	54–89 (34)	8–24 (33)

* Four “0” values assigned 0.001 mM; without this assignment avg. ± std. dev. = 0.08 + 0.05 mM (n = 6).

** Combined the sediment surface (0.5-4.5 cm) data for the central and northern basins.

***Two “0” values assigned 0.001 mM; without this assignment avg. ± std. dev. = 0.07 + 0.02 mM (n = 5).

same depth interval. However, both water content (86.9 + 4.8%) and LOI (22.1 + 4.7%) were similar for the same depth intervals in the southern and two other major basins (central and northern), suggesting similarities in organic matter content (as precursor materials for gas generation). CO_2 was measured in the sediments of only one core (Fig. 2B). Low sediment concentrations were not observed for pore water N_2, where values ranged from saturation to as high as 3 times saturation (Fig. 2C). For saturation calculations it was assumed that N_2 above the sediment-water interface was 16.6 ml l^{-1} or 0.74 mM, which would be maximum solubility at the coldest time of year (4 °C). Core liner overlying water, siphoned off into glass bottles, were capped for gas analysis. N_2 in these samples averaged 0.68 mM (n=4, range 0.52-0.79 mM), which was close to the assumed saturation values of 0.74 mM. It was also assumed that the surface water equilibrated with the atmosphere before sinking and remained in contact with the sediments.

Pore water chemical data from peeper collections for the southern basin (from Angelidis 1990) are given in figure 3 (values are listed in mg l^{-1}); note that five high NO_3^- data points (7-30 mg l^{-1}) from peeper 8 (Fig. 3D) were removed to show the variability for other collection dates.

Because of the water depth at the sampling sites in the central and northern basins (125-140 m; see Fig. 1) and the high gas concentrations, which resulted in sporadic bubbling during retrieval, few cores were collected for sediment gases; peepers were not deployed by scuba diver because of the depth. Data for these two basins showed similarities in pore water CH_4, N_2, sediment water content and LOI (Fig. 4). Unlike the southern and Omegna basins, 0 to -5 cm surface CH_4 concentrations

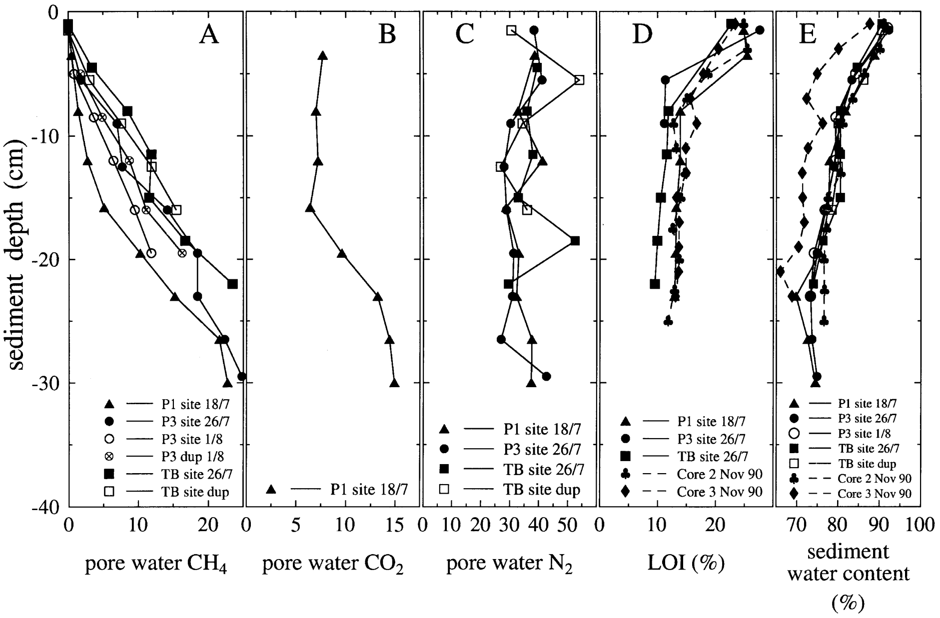

Fig. 2. Pore water gases (concentrations in ml l^{-1}) and sediment loss on ignition (LOI) and water content (%) at the southern basin sites during July and August 1989. Dup = duplicate cores at the same site; P1, etc. refers to different peeper deployment sites. Data for November 1990 are courtesy of Thomas Angelidis, ISPRA.

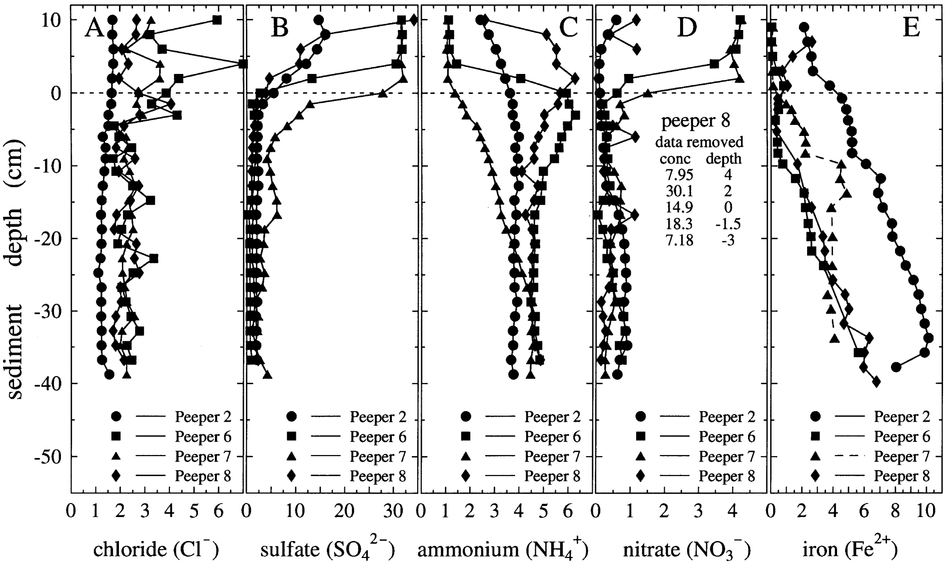

Fig. 3. Overlying water and sediment pore water chemical variables from the southern basin collected from different peeper sites. Five nitrate (box D) values from peeper 8 were removed, see inserted depths above and below the SWI and concentrations. All peeper data are courtesy of Thomas Angelidis, ISPRA.

were much higher (1.06 + 0.20 mM; Tab. 1). However, like the southern basin, water content (88.1 + 3.6%) and LOI (21.7 + 6.6%) were the same for similar surface (0 to –5 cm) depth intervals; this was not the case for water content and LOI in the Omegna basin. CO_2 was measured in one core from the northern basin (Fig. 4B). Pore water N_2 concentrations were similar to the southern basin, i.e., supersaturated at most depths in the cores (Fig. 4C). However, the water column depth would control any *in situ* bubble formation because of the pressure.

The Omegna Basin showed low surface CH_4 (0.05 + 0.04 mM, n=7; Tab. 1) for the 0 to –5 cm depth interval, which was similar to the southern basin. However, Omegna sediments exhibited much lower water content

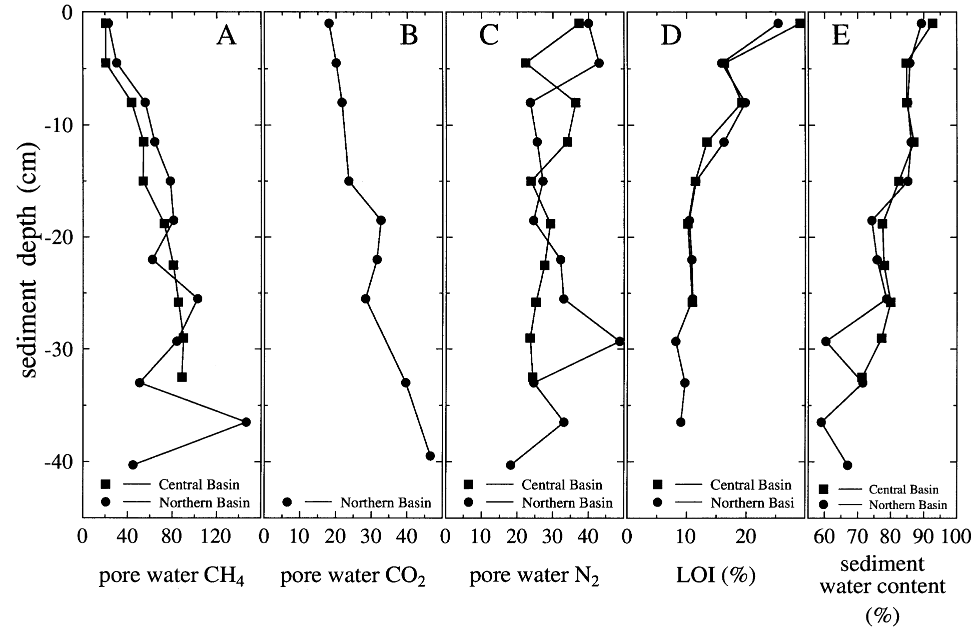

Fig. 4. Pore water gases (concentrations in ml l^{-1}) and sediment loss on ignition (LOI) and water content (%) at the central and northern basin sites during July and August 1989.

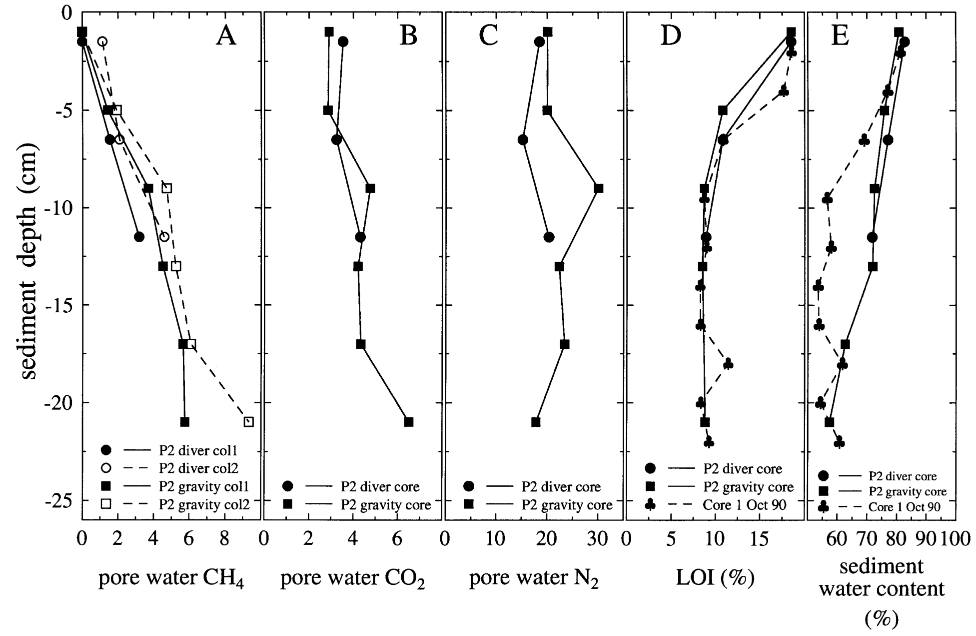

Fig. 5. Pore water gases (concentrations in ml l^{-1}) and sediment loss on ignition (LOI) and water content (%) at the Omegna Basin during July and August 1989. Data are from gravity and scuba-collected (= diver) cores. Data for October 1990 are courtesy of Thomas Angelidis, ISPRA.

(82.4 + 4.7%) and LOI (8.2 + 3.8%) than any of the other coring sites in the lake (Fig. 5D, E). The lowest of all methane values at depth (Fig. 5A) were observed in the Omegna Basin sediments (maximum depth of -22 cm for gravity coring and -12 cm for cores collected by scuba divers) compared to the southern basin (Fig. 2A). While pore water CH_4 in the southern basin averaged 0.68 + 0.17 mM for the -16 to -23 cm depth interval, the Omegna Basin was less than half (0.30 + 0.08 mM) and the central and northern basins were 5-10 times greater (3.31 + 0.40 mM) for the same depth interval. Like methane, N2 gas was also much lower throughout the Omegna basin cores (0.93 + 0.19 mM, n = 8) as compared to the southern basin (1.46 + 0.39 mM, n = 34;

Tab. 1). Sediment pore water CO_2, also very low, was measured in the sediments from two cores (scuba-collected and gravity; Fig. 5B). This suggested a lack of microbial activity (organic matter decomposition, methanogenesis and denitrification), likely because of the high current velocities and lower sediment water and organic matter content (LOI, Tab. 1). Core penetration was also limited, perhaps by the greater amount of clays at this site (diver W. Mingolla, pers. comm.). Both scuba diver collected and gravity core data are given in figure 5 to illustrate comparisons between collection techniques. Data for LOI and water content from one core obtained in Oct. 90 were provided by Agelidis (pers. comm.).

For comparison with the southern basin (Fig. 3), the Omegna Basin pore water chemical variables for peepers are given in figure 6 (data from Angelidis 1990). With the exception of Fe^{2+}, which showed a general increasing trend with depth in the southern basin (but not in the Omegna Basin below -10 cm), the pore water chemical data were similar between these two shallow basins. In both basins, the zone of nitrate reduction was located in the surface 0 to -2 cm sediment depth and likely extending to +2 cm above the sediment-water interface in the southern basin. The zone of sulfate reduction was located in the surface 0 to -5 cm depth interval in the sediments of both basins (compare Figs 3B and 6B).

Because of analytical problems, helium-extractable pore water CO_2 was measured in only one core each from the southern and northern basins and two (gravity and scuba-collected cores) from the Omegna Basin. In the shallow basins there was twice as much CO_2 as CH_4 in the surface sediments; however, CH_4 increased more rapidly with depth. In the 140 m deep northern basin surface sediment CH_4 and CO_2 were about equal (Fig. 4A, B). The concentration of CO_2 averaged 0.20 + 0.05 mM (n = 8) in two Omegna cores, 0.27 + 0.08 mM (n = 6) for one core from the southern basin and 1.3 + 0.4 (n = 9) for one core from the northern basin (Tab. 1).

Even though the sediment pH was monotonously the same at about 6.6 throughout the -5 to -35 cm zone, there was, in most cases, a slight increase in pH within the surface sediments. The southern basin exhibited a slight increase to 6.4 in the water above the SWI (compared to 5.7 in most overlying water); there was a rapid decrease across the SWI, followed by an increase within the surface 0 to -5 cm zone (Fig. 7); these abrupt changes were not readily observed in the two deep basins. Even though measurements were not frequent, sediments from the Omegna Basin were anomalous with pHs averaging 6.9 at depth. Because of low values, some overlying water data for the Omegna peeper sites were excluded; however, these values are listed in figure 7 (with date and water height above the SWI). Peeper pH data from the southern and Omegna basins are included for comparison purposes; core pH measurements could not be taken from the Omegna Basin sediments because of their stiffness and the possibilities of breaking the electrode. Overlying water pH (0 to +100 cm) for all the basins ranged between 4.2 to 5.7 in 1989 (see excluded data in Fig. 7).

4. DISCUSSION

Microbiological pathways involving gas formation and consumption in the sediments have been detailed in numerous publications (Bowden 1987; Seitzinger 1988; Zehnder & Stumm 1988; Boone 1991; Adams 1996; Fenchel *et al.* 1998). These pathways are somewhat different for the gaseous carbon components versus the nitrogen gases. Organic matter decomposition (and carbonate dissolution) evolves CO_2 as an end product gas, while both methanogenesis and methane oxidation result in reactions involving both carbon gases - CH_4 and CO_2. The formation of N_2 as part of the N-pathway of denitrification, requires inorganic nitrogen (NO_3^-, and indirectly NH_4^+ through nitrification) as well as organic substrates (Seitzinger 1994); losses of molecular nitrogen are a result of N_2-fixation.

4.1. Carbon gases (methane and carbon dioxide)

Even though there are few sediment gas measurements from acidified environments (Adams *et al.* 1987; Naguib & Adams 1996) there is more information from other freshwater sediments, as reviewed by Adams (1996). Gas data from Tonteich, a clay pond in northern Germany containing sediments with neutral pH underlying acid waters, suggests little accumulation of pore water CH_4 yet higher amounts of sediment CO_2 (Naguib & Adams 1996). This would be expected under conditions of active sulfate reduction in this pond. In Lake Orta, sediment CO_2 was analyzed for cores collected at the two shallow and one deep (northern) basin; many more cores were collected for other gas analyses, but few were processed for CO_2 because of the analytical difficulties. In spite of the low levels of both C gases in the surface sediments, there was a greater amount of CO_2 than CH_4 (see Figs 2, 4, and 5). Even though low values of both C gases were observed in the two shallow basins (southern and Omegna), Lake Orta's deep central and northern basin sediments contained CH_4 concentrations similar to other freshwater sedimentary environments, for example the lakes of northern Germany (Casper 1996; Adams & Naguib 1999) and New Zealand (Adams 1992). Normally, breakdown of organic matter results in the accumulation of carbon gas end products with a ratio of about 1:1 for CH_4:CO_2 during anaerobic decomposition. However, this ratio can vary considerably (Adams & Naguib 1999) and was about 2.1 + 0.9 (n = 9) for the northern basin sediments (varying from 1.8 in the surface to 2.5 at depth). In the two shallow basins this ratio also changed from 0.5 in the surface sediment interstitial water to 1.6 at greater depth. Sulfate reduction in the surface 0 to -5 cm sedi-

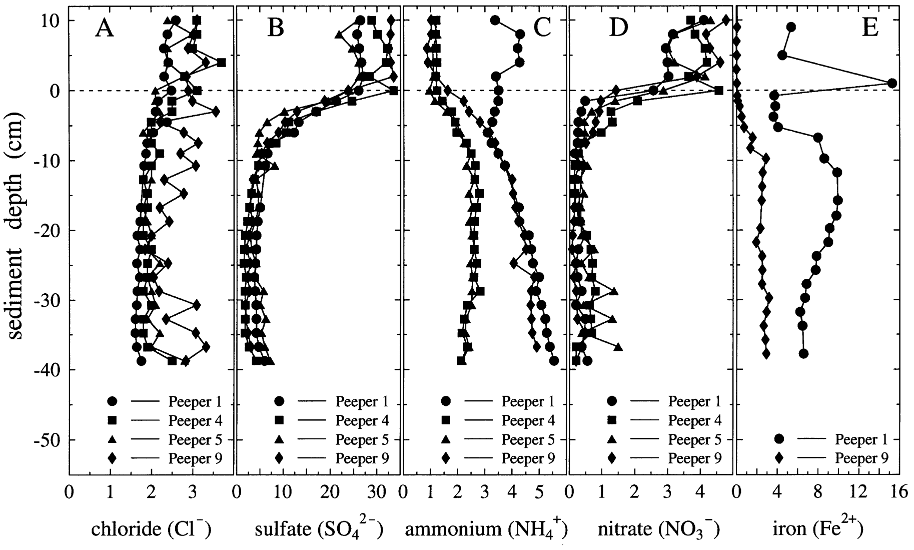

Fig. 6. Overlying water and sediment pore water chemical variables from the Omegna Basin collected from different peeper sites. All peeper data are courtesy of Thomas Angelidis, ISPRA.

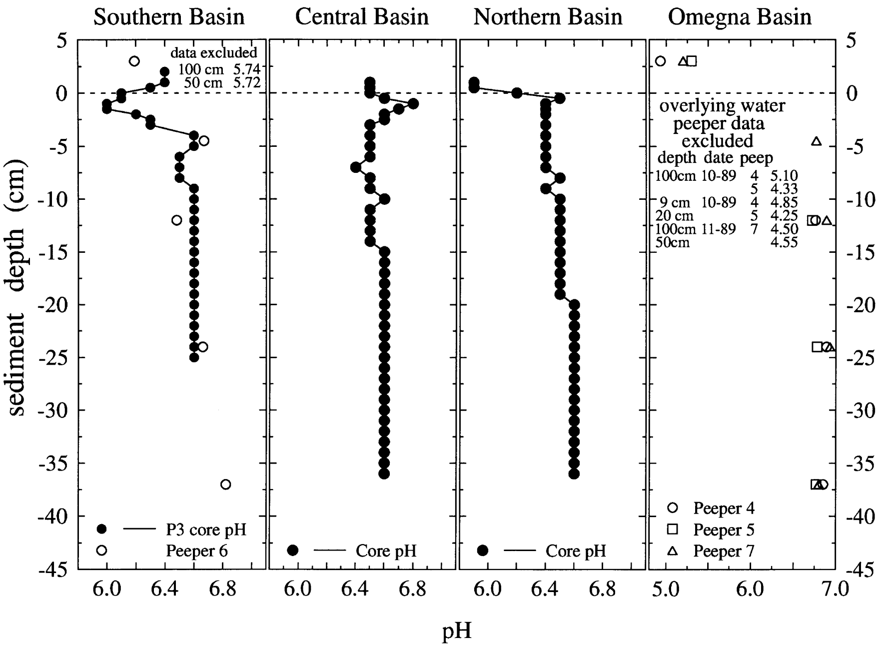

Fig. 7. Overlying water and sediment pH from cores collected from all four basins of Lake Orta, Italy. Peeper pH values are courtesy of Thomas Angelidis, ISPRA.

ments (see Figs 3B and 6B) would result in the formation of CO_2, and not CH_4, as a decomposition end-product, while CO_2 reduction and fermentation reactions in deeper sedimentary layers could result in greater amounts of CH_4 accumulation. Brandl *et al.* (1990) also reported inhibition of sediment methane production during bacterial sulfate reduction.

A slight increase in sediment gas concentrations in the southern basin was observed four years after liming (Fig. 8). This resulted in a higher calculated rate of CH_4 diffuse flux at the sediment-water interface, as described below. The major changes in CH_4 concentrations were observed at the southern basin site further removed from the Bamberg plant discharge (Buoy TB in Figs 1 and 8). Increases in CH_4 concentrations were not as noticeable for the one core collected on 20 June 1994, near the Bamberg factory effluent, when compared to the other nearby sites collected earlier (peepers 1 and 3 in 1989;

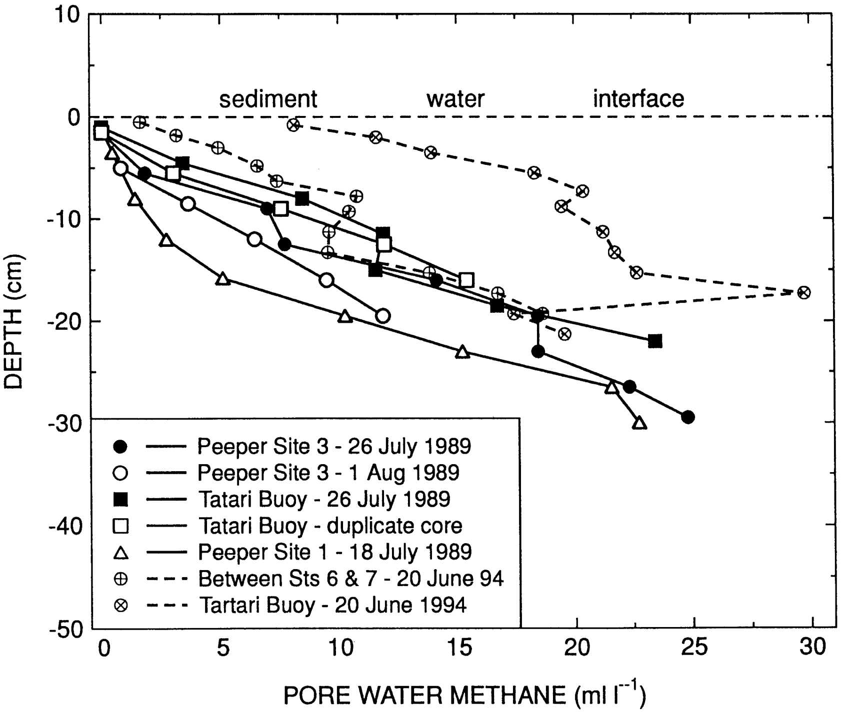

Fig. 8. Sediment pore water methane (ml l^{-1}) at the southern basin of Lake Orta during two different sampling periods – summer of 1989, before liming, and June 1994, four years after liming. Two locations (see Fig. 1) were cored each time – near the Bemberg plant effluent (peeper sites 1, 3 in 1989 and one core in 1994 between sts 6 and 7) and near the TB buoy at a further distance from the source of pollution.

Fig. 8). From tangential observations, it is suspected that considerable inhibition of methanogenesis is still exhibited in these sediments (Adams *et al.*, in prep.).

4.2. Nitrogen gas

Nitrogen gas in water overlying the sediments was near saturation (0.74 mM at 4 °C; Weiss 1970) while similar values were observed in the Omegna station sediments of low porosity (Fig. 5C) where little organic matter decomposition was observed (very low CH_4, CO_2 and lower LOI). For other locations in the lake, sediment N_2 averaged 2 times, and was as high as three times, supersaturation in the surface sediments (Tab. 1, surface). These values are similar to N_2 concentrations reported for Lake Erie in North America (2.2-3.5 times saturation; Fendinger & Adams 1987) and Lake Taupo, New Zealand (Adams 1992). Average N_2 gas for the entire cores were 1.3 to 2 times calculated saturation (Tab. 1). It is suspected that water column nitrification and high inorganic nitrogen in the water overlying the sediments stimulated nitrification and denitrification near the SWI, as reported by others (Seitzinger 1994; Mengis *et al.* 1997; Nowicki *et al.* 1997; Kana *et al.* 1998).

Ammonium discharges from the Bamberg plant were high from 1958 to 1979 at 1950-3350 ton N y^{-1} but decreased to 30 ton N y^{-1} after construction of a sewage treatment plant. During the earlier period very high ammonium (0.3-0.4 mM) and nitrate (0.3-0.5 mM) concentrations were measured in the water column (Mosello *et al.* 1986). During the period of water column acidification Mosello *et al.* (1986) calculated that lake ammonium oxidation (100 Mmol = 100 × 10^6 moles) did not balance the increase in total nitrate in the lake (35 Mmol). They suggested that the difference could possibly be attributed to their inability to include (from lack of precise information in the 1980s) the following losses of nitrogen in their mass budget: organic N fraction, loss of N from sedimentation and molecular nitrogen (N_2) export. It is likely that surface sediment N_2 production, observed in this study, would help in quantifying the large (*ca* 65%) deficit; diffuse losses of N_2 from the sediments to overlying waters from each of the basins are listed in table 2. N_2 flux was shown to be an important N-sink for U.S. estuarine and shelf waters (Nowicki *et al.* 1997); for example, 43-54% of total nitrogen input was calculated as denitrified-N lost from Delaware Bay (Nixon *et al.* 1996).

4.3. Diffusive flux of gases from sediments to overlying water

The diffusive fluxes of pore water gases into and out of the sediments were calculated using Fick's first law of diffusion:

$$J = -\phi D_s (dc/dz),$$

Tab. 2. Theoretical diffusion of gases across the sediment-water interface of Lake Orta, Italy, before (1989) and after (Southern Basin 1994 only) liming. Other lakes are given for comparison. Units are in mM m^{-2} day^{-1}.

Site	Nitrogen (N_2)	Methane (CH_4)	Reference
LAKE ORTA, ITALY			
All Stations	4.0 ± 3.7 (n = 16)	1.7 ± 2.4 (n = 13)	This study
Southern Basin	2.6 ± 1.8 (n = 7)	0.13 ± 0.07 (n = 5)	
Southern Basin (1994)	12.4 ± 2.7 (n = 4)	2.12 ± 1.1 (n = 3)	
Central Basin	7.31	6.62	
Northern Basin	3.34	7.37	
Omegna Basin (clayey sed at lake outlet) 1989 – acidic lake water 1994 – four years after liming)	1.34 ± 0.4 (n = 3)	0.17 ± 0.07 (n = 3)	
OLIGOTROPHIC LAKE TAUPO, NEW ZEALAND			
Central Basin (155 m)	8.7 - 12.9	0.2 - 1.3	Adams 1992
Taupo Bay (90 m)	3.7	0.4	
OTHER LAKES			
Lake Sempach (artificially aerated eutrophic Swiss)		profundal 3.1 littoral 1.4	Urban *et al.* 1997
Lake Baldegg (66 m) (artificially aerated eutrophic Swiss)	4.3		Mengis *et al.* 1997 (isotope pairing)
Lake Søbygaard (hypertrophic Danish)	1.3 (May) 3.6 (Sept)		Risgaard-Petersen *et al.* 1999 (isotope pairing)

where: J = the diffusive flux, ϕ = porosity at the sediment-water interface, D_s = sediment diffusion coefficient for each individual gas, and dc/dz = the concentration change of each gas with depth. Ds was calculated from the molecular diffusion coefficient in pure water (D_o) at 5 °C for each of the gases using the empirical formula $D_s = D_o \phi^2$ Lerman (1979). Porosity (ϕ) at the sediment-water interface was approximated by fitting the interface and two subsequent deeper porosity values to a linear least squares regression and calculating the porosity at z = 0. A correction was also applied to D_o for the tortuosity of the sediments using $D_s = D_o / \Theta^2$ where Θ = sediment tortuosity (Berner 1980). Sediment Θ was estimated using the empirical relationship developed by Sweerts *et al.* (1991),

$$\Theta^2 = -0.73\phi + 2.17$$

for numerous fresh water environments. Changes in pore water gas concentrations with depth, dc/dz, for CH_4, CO_2 and N_2 were calculated between the core overlying water and the first gas measurement in the surface sediment. The surface depth averaged 2.4 + 1.8 cm and ranged between –0.5 cm to –5.5 cm below the SWI. N_2 concentrations at the sediment-water interface (SWI) were assigned values measured in the core overlying water (siphoned from about +3 cm). Water overlying the SWI measured 0.68 + 0.10 mM (n = 7) with a range of 0.52 to 0.79 mM N_2; these values were close to saturation at 4 °C (0.74 mM). The overlying water was always aerobic, therefore CH_4 was considered 0 mM at z = 0 cm for the purpose of diffuse flux calculations.

Diffusive loss of CH_4 from the sediments of Lake Orta to overlying waters ranged from 0.13 mM m^{-2} day^{-1} in the southern basin to 7.4 mM m^{-2} day^{-1} in the deep northern basin. The average was 1.7 + 2.4 (n = 13) mM m^{-2} day^{-1} for all stations (Tab. 2). In the case of N_2 calculations of diffuse loss from the sediments, values ranged from 1.3 mM m^{-2} day^{-1} in the Omegna Basin to 7.3 mM m^{-2} day^{-1} at the deep central basin, and averaged 4.0 + 3.7 (n = 16) mM m^{-2} day^{-1} for all sites. After liming in 1990, the diffusive losses of both gases at the SWI in the southern basin increased considerably in the four years between the two coring periods - 1989 (acid waters) and 1994 (neutral pH conditions). Diffuse flux at the SWI changed from 0.13 (1989) to 2.1 (1994) mM m^{-2} day^{-1} for CH_4 and from 2.6 (1989) to 12.4 (1994) mM m^{-2} day^{-1} for N_2 (see Tab. 2). These data were calculated for the southern basin where cores were collected during both periods. Caution must be attached to the 1994 flux values since they are representative of only two coring sites; in 1989 there were five coring sites. If these few measurements are representative, then it would seem that the flux of both gases has increased considerably from the period of pollution in the southern basin to the period of water column neutralization after liming. This suggests a much more active bacterial community in the near surface sediments after liming – both methanogen and denitrifier populations. It also indicates that both methanogenic and denitrification activities were suppressed during the earlier period of acidification.

5. CONCLUSIONS

With the exception of the two shallow basins (southern and Omegna), concentrations of CH_4 and N_2 in the sediments and their losses at the SWI are comparable to other lakes. Sediment methane concentrations in the southern basin were very low, suggesting inhibition of methanogenesis. However, slight changes in CH_4 concentrations and a 16× increase in calculated fluxes were observed four years after liming in the southern basin. The sediment concentrations and diffuse losses of CH_4 from the central and northern basins are similar to values from eutrophic lakes. If a comparison could be made between Lake Orta and other aquatic environments, normally exhibiting lower water column inorganic nitrogen, it would seem that denitrification activity in the sediments was relatively normal. However, Lake Orta experienced both high inorganic nitrogen and acidity, which could have opposing effects on denitrification. The only direct evidence of these impacts to N-cycling was the 5× increase in southern basin denitrification four years after liming compared to the period of acid conditions. Caution should be employed, however, since only two cores involving four flux calculations could be used for the 1994 period. The large change in calculated N_2 fluxes (from 2.6 to 12.4 mM m^{-2} day^{-1}) from Lake Orta southern basin surface sediments to overlying waters could indicate earlier inhibition in denitrifiers. These large N_2 losses would certainly contribute to balancing the N mass budget deficit for this lake during the period of acidification.

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