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## A PRELIMINARY GEOCHEMICAL STUDY OF TWO CORES FROM MASSACIUCCOLI EUTROPHIC LAKE, NORTHERN TUSCANY, AND PALEOCLIMATIC IMPLICATIONS

**Abstract** - Elevated organic carbon concentration in present sediments commonly derives from human and industrial activities and reflects the eutrophic status of a system. Furthermore, amount and type of organic matter may be used to reconstruct marine, lacustrine and continental paleoenvironments and paleoclimates because they depend on production and preservation rates, direct consequences of environmental changes. In September 2003 five 50 cm long cores were sampled in Massaciuccoli Lake, northwestern Tuscany, and two of them were chosen to investigate the impact of organic pollution sources on the system. Total content of organic carbon (TOC) and nitrogen (TN) were examined to study the eutrophic status of the lake, while TOC/TN ratio was used to distinguish between terrestrial and aquatic origin of organic matter. Results evidenced the presence of high organic matter concentrations in sediments and, in particular, its terrestrial origin, thus confirming inputs from land reclamation to water and sediment. According to such results, it appears that immission of nutrients, with consequent algal blooms, have a smaller impact than immission of land-derived organic matter in sediments. Moreover, one core probably recorded a climatic cycle, three times reiterated in the stratigraphic sequence.

**Key words** - TOC, TN, TOC/TN ratio, Massaciuccoli, eutrophication, climatic cycle.

**Riassunto** - Studio preliminare di due carote del sistema lacustre eutrofizzato di Massaciuccoli, Toscana settentrionale, e ipotesi paleoclimatiche. Concentrazioni elevate di carbonio organico in sedimenti attuali derivano generalmente da attività umane e industriali e riflettono lo stato eutrofico di un sistema. Inoltre, quantità e tipo di materia organica possono essere utilizzati per ricostruire i paleoambienti lacustri, marini e continentali e le loro caratteristiche paleoclimatiche poiché la loro produzione e i relativi tassi di preservazione sono diretta conseguenza di variazioni ambientali. Nel settembre 2003, cinque carote, lunghe 50 cm, sono state campionate nel lago di Massaciuccoli (Toscana nord occidentale) e due di queste sono state scelte per studiare l'impatto delle sorgenti organiche inquinanti in questo sistema lacustre. Il contenuto di carbonio organico totale (TOC) e di azoto totale (TN) sono stati esaminati per studiare lo stato di eutrofizzazione del lago, mentre il loro rapporto (TOC/TN) è stato utilizzato per distinguere tra l'origine terrestre o acquatica della materia organica. I risultati evidenziano la presenza di un'alta concentrazione di materiale organico nei sedimenti e in particolare la sua origine terrestre, confermando apporti provenienti dalle aree della bonifica verso acque e sedimenti. Questi risultati suggeriscono che l'immissione di nutrienti, con un conseguente *bloom* algale, ha un minore impatto rispetto alla materia organica proveniente dalle bonifiche. Infine in una carota sembra essere registrato un ciclo climatico, ripetuto tre volte nella sequenza verticale.

**Parole chiave** - TOC, TN, TOC/TN, Massaciuccoli, eutrofizzazione, ciclo climatico.

### INTRODUCTION

Amount and type of organic matter in a sediment reflect production and preservation rates, that are consequences of environmental and climatic changes. These properties may be used to reconstruct marine, lacustrine, continental paleoenvironments and paleoclimates (Meyers, 1997). In particular, sedimentation rates in deep sea basin are on the order of few centimetres per 1000 year and in lakes they are about a meter per 1000 years (Meyers, 1997): marine records are therefore good indicators of long-term paleoenvironmental changes while lacustrine sediments are useful in reconstruction of local and/or high-resolution changes. Elevated organic carbon concentration in present sediments commonly derives from human and industrial activities, such as agricultural practise, industrial and animal wastes, reflecting the eutrophic status of a system (e.g. Ouyang, 2003; Jia & Peng, 2003; Neumann *et al.*, 2002; Turcq *et al.*, 2002; Emeis *et al.*, 2000). In September 2003 five 50 cm long cores were sampled in Massaciuccoli Lake (northern Tuscany) and total contents of organic carbon (TOC) and nitrogen (TN) were determined in two of them, to study the eutrophic status of the lake. In addition, the TOC/TN ratio allowed the distinction between terrestrial and aquatic origin of organic matter (e.g. Luniger & Schwark, 2002; Prartono & Wolff, 1998; Meyers, 1997; Tyson, 1995; Meyers & Ishiwatari, 1993). Although it must be considered that preferential degradation of nitrogen-contained organic matter often falsifies this ratio (Lew, 1981; Muzuka & Hillaie-Marcel, 1999): this diagenetic alterations may be compensated by comparing of multidisciplinary proxies.

Eutrophication results as a consequence of over-bio-production: lakes generally represent closed systems, where outer inputs exceed outputs. This repeated process (Hamilton-Taylor & Davison, 1995) makes such environments, in particular sediment/water interface, accumulation areas: lacustrine waters and sediments become storing up nutrients, like nitrogen (N), phosphorus (P) and carbon (C). Carbon is abundant in aquatic environments, while nitrogen and phosphorus are limited and highly depend on runoff of land areas: lakes, being surrounded by land, receive great amounts of nutrients and smaller lakes are more productive than larger one (Meyers, 1997). This process is on the increase or on the decrease according to the local precipitation and to the natural and human per-

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turbations – e.g. deforestation, agricultural tilling, fires –, increasing erosion of soils (Meyers, 1997). In the upper part of the water body (*epilimnion*) nutrients are assimilated by planktonic synthesis and in the lower part (*hypolimnion*) they are released by bacterial degradation (Manahan, 1994), while sediments may release elements by resuspending (Frignani & Turci, 1981) or by interstitial water liberation through brackish water infiltration (Smetacek *et al.*, 1976) or under specific physico-chemical condition. This phenomenon's size depends on: i) depth of the water column, that affects oxygen distribution; ii) sediment accumulation rate and sediment characteristics, that influence both nutrient adsorption and release processes; iii) concentration of introduced nutrients, straight depending on inputs/outputs ratio. In conclusion, eutrophication results from the combination of outer nutrients contribution and inner nutrients recycling. Then understanding an eutrophic system needs to investigate on nutrients distribution and their availability in water body and in bottom sediments.

#### STUDY SITE

##### Geological setting

Massaciuccoli Lake (northwestern Tuscany, Italy) is located in the central portion of the coastal plain of Versilia and Pisa (Fig. 1). This plain was built up by the filling of tectonic extensional depression systems (NW-SE direction) developed along the Tyrrhenian margin of the Apennine mountain chain. Such sedimentation began in Late-Tortonian, related to the Tyrrhenian rifting and the counter-clockwise migration of the chain-foredeep-foreland-system (Elter *et al.*, 1975; Malinverno & Ryan, 1986; Sartori, 1989; Patacca *et al.*, 1990).

Multidisciplinary proxies derived from late Quaternary sediments – ENEA well (Antonioli *et al.*, 2000; Grassi *et al.*, 2000; Menozzi *et al.*, 2003), perfored near the lake – evidence two continental-marine cycles in the last 125,000 yr B.P.

The first marine cycle, located between -90 and -70 m depth in sandy deposits, was assigned to 5e isotopic stage (MIS 5e; Jansen, 1989) on the basis of some radiometric dating ( $^{230}\text{Th}/^{234}\text{U}$ ) carried out on samples of *Cladocora caespitosa*, resulting  $129,200 \pm 15,000$  ka and  $132,800 \pm 15,000$  ka respectively (Antonioli *et al.*, 2000).

Successively, a continental cycle developed until -34 m, where an erosive surface constitutes the basis of the Holocene cycle. This is supported by  $^{14}\text{C}$  AMS dating, that shows a retrogradational phase, corresponding to the Versilian transgression and the sequent progradational phase, which is the cause of the present coastal plain morphology.

##### Present characteristics

Massaciuccoli Lake is a coastal shallow lake with an average depth of 2 m, a surface area of water of 6.8 km<sup>2</sup> and a whole basin area of 90 km<sup>2</sup>. The plain making up the lake's basin is formed by a sandy coast strip and by marshes and reclaimed marshes, internally. Before the

present anthropization, plain of Versilia was constituted by alluvial cones passing seaward to sandy beach ridge systems separated each other by low-energy water bodies («*lame*» auctorum, Federici, 1993). During the Late Quaternary, the interplay among subsidence, sedimentary supply (mainly derived by the Arno-Serchio rivers system), and eustatic changes, provided the formation of the present plain of Versilia. A closely-planted network of natural and artificial canals developed in the northern part of the basin, where various sand quarries are present. The main canal is Burlamacca (10 km long), which represents the only connection between the lake and the sea, even if a not properly working bulkhead system would prevent the water getting in from the sea (Meriggi & Spandre, 1996).

At the first half of 20<sup>th</sup> century, Massaciuccoli Lake was described as oligotrophic (Brunelli & Cannicci, 1942). Few decades later, great amount of nutrients – P, N, K, C – and contemporaneous limited water turnover drove the whole lacustrine system to eutrophication (Cenni, 1997). Nowadays it would appear to be on the eutrophic/hypertrophic border (Mason, 1997). Sewage treatment works from the surrounding villages –Massarosa, Vecchiano, Migliarino, Torre del Lago, Viareggio –, three irrigation pumps – Vecchiano, Massaciuccoli, Pioppogatto –, reflux waters of reclamation districts and reflux waters of a cattle-breeding and of a food-industry are the main polluting sources. The pumps of Vecchiano and Massaciuccoli together provide 72% of total known loads to the lake (Mason, 1997). Furthermore, a lot of terrigenous materials removed from reclamation districts increases the load of sediments in the lake; while, in the summer time, when the lake level is below the sea one, marine waters gets in through the Burlamacca canal, taking part in altering the equilibrium of the lake (Amos *et al.*, 2004; Baneschi, 2003; Gulia, 2003).

#### MATERIALS AND METHODS

##### Sediment sampling

To investigate the impact of pollutant sources on the system, the following coring sites were chosen: i) IBA core, collected in the proximity of the Barra Canal mouth and ii) BUR core, sampled in the Burlamacca Canal, close to its mouth in lake, where sediments are mainly subject to fall-out depositional mechanism. The former was collected to evaluate the consequences of sediment immission by Vecchiano and Massaciuccoli irrigation pumps; the latter to evaluate the impact of brackish water both in the canal and in the lake. The sediment cores were manually raised with an Osterberg-type thin wall core barrel, that has the property of sampling undisturbed sediments. After collection, the samples were settled vertically to prevent cross-pollution, and then were gradually frozen, from 0°C to -10°C, in a week-interval.

##### Sediment treatment and analysis

Frozen cores were vertically divided in equal parts with a small metal manual saw, at room temperature.

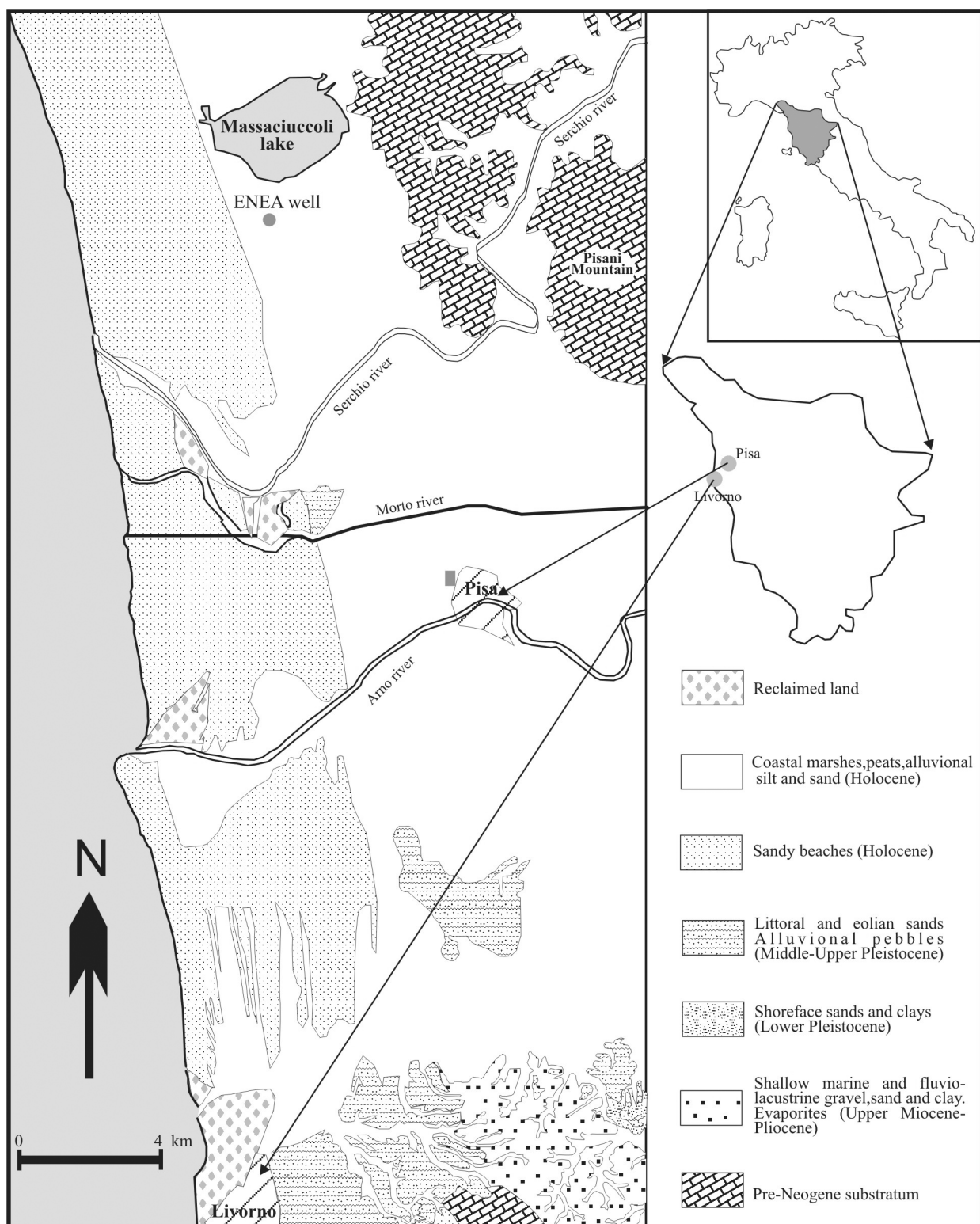


Fig. 1 - Geological map with location of the study area.

After 48 h, the time needed to a complete defrosting, samples were dried in a stove at 105°C for 24 h; then macroscopic and microscopic shell remains and vegetable fragments were removed by hand.

The total organic carbon (TOC) and total nitrogen (TN) contents were analyzed with a Carlo Erba Elemental Analyzer.

## RESULTS

### IBA core

The sediments (Fig. 2 and Tab. 1) are relatively homogeneous and consist of peat and silt, with fragments of not-classifiable molluscs.

TOC and TN profiles (Fig. 2 and Tab. 1) show a symmetrical increasing-decreasing trend, three times reiterated in the stratigraphic sequence. Assuming high accumulation rates in this area owing to outer inputs – similar to those observed in Aredsee Lake (Neumann *et al.*, 2002) – it could reflect cyclic inputs of nutrients from water-scooping machines of Massaciuccoli and Vecchiano. On the contrary, if accumulation rates were roughly stationary in the whole system, really very unlikely, according to estimated rate for ENEA well (Antonoli *et al.*, 2000), the IBA sequence might reflect a climatic cycle of the last 800 yr and, according to S1 well (Bianciardi *et al.*, 1999), of the last 600-650 yr. Obviously, the presence of the outer inputs in lake reduce that temporal interval. In particular, high TOC values may indicate humid conditions (*e.g.* Ortega *et al.*, 2002; Thevenon *et al.*, 2002; Turcq *et al.*, 2002; Xiao *et al.*, 2002), indeed water discharge and consequent nutrient input are important factors for carbon accumulation (Turcq *et al.*, 2002) and this input increases with increasing rainfall.

At low inorganic nitrogen concentration, the TOC/TN ratio is a frequently used index for recognize the organic matter origin: marine algae, due to richness in protein and absence of cellulose, have C/N ratio between 4 and 10 while vascular plants, rich in cellulose, have C/N ratio of 20 and greater (Meyers, 1994).

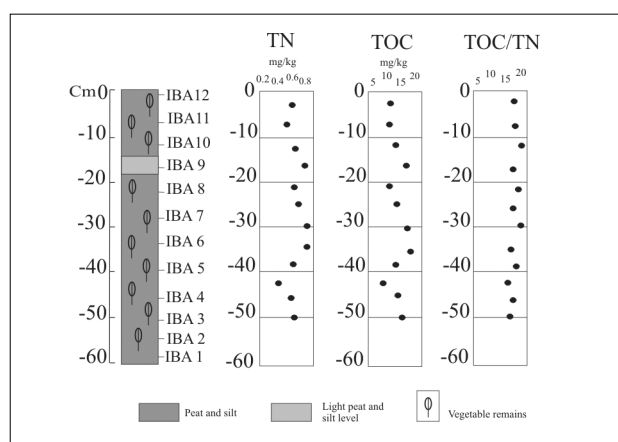


Fig. 2 - IBA core and relative values total nitrogen (TN), total organic carbon (TOC) and their ratio (TOC/TN).

TOC/TN ratio (Tab. 1) for the IBA core is steady and ranges between 15 and 19, suggesting a mixture of autochthonous and allochthonous materials. However, terrestrial organic matter getting in water and sediments from land reclamation prevails over algal organic matter.

### BUR core

BUR core (Fig. 3 and Tab. 2) is made up by dark clayey- silt, rich in organic matter, fragments and shells of molluscs. The most abundant types of molluscs abundant between -15 and -25 cm depth are *Gyalus laevis*, *Theodoxus fluviatilis*, *Bithynia tentaculata*, *Acroloxus salinis* (Gulia, 2003). These are typical species of weak-running water with a salinity ranging between 3 and 16‰. It is then confirmed the ingression of brackish water in the lacustrine system. Low-Mg calcite encrustations on roots (Fouch & Dean, 1983) have been also collected in the core.

TOC (Tab. 2) has a quite omogeneous trend, the highest values of which correspond to remains-rich-levels; by contrast, TN concentrations (Tab. 2) are variable. Different trends of TOC and TN in the core and, primarily, between the two cores may indicate a current unbalance in the system (Jia & Peng, 2003).

TOC/TN ratios (Tab. 2) reach values between 14 and 21, according to IBA readings, suggesting prominent inputs of terrestrial organic matter to water and sediment.

## DISCUSSION AND CONCLUSION

In the last decades, developments of agriculture and industry, with consequent increasing in the use of fertilizers and continuous sewage input, have resulted in eutrophication of Massaciuccoli lacustrine system (*e.g.* Baneschi, 2003; Gulia, 2003; Cenni, 1997; Mason, 1997). The TOC/TN ratio values indicate, in both cores, a terrestrial origin of organic matter. In particular, the BUR core is characterized by the highest values of both TOC and TN ratio. The TOC/TN ratio may be affected by different-sized fractions of sediments (*e.g.* Keil *et al.*, 1994): in general, the TOC/TN ratios of organic matter in fine-sized sediments are lower than those of coarse sediments. Indeed, coarse sediments contain a larger

Tab. 1 - Values of total nitrogen (TN), total organic carbon (TOC) and their ratio (TOC/TN) in IBA core.

Code	Depth cm	TN mg kg <sup>-1</sup>	TOC mg kg <sup>-1</sup>	TOC/TN
IBA 1	-4.5	1.37	20	14.62
IBA 2	-9.0	1.44	25	17.4
IBA 3	-13.5	1.38	26.74	19.34
IBA 4	-18.0	1.58	26.38	16.74
IBA 5	-22.5	1.54	32.72	21.23
IBA 6	-27.0	1.52	31.4	20.62
IBA 7	-31.5	1.59	28.99	18.18
IBA 8	-36.0	1.42	26.84	18.85
IBA 9	-40.5	1.52	28	18.39
IBA 10	-45.0	1.49	29.31	19.64
IBA 11	-49.5	1.63	29.43	18.01

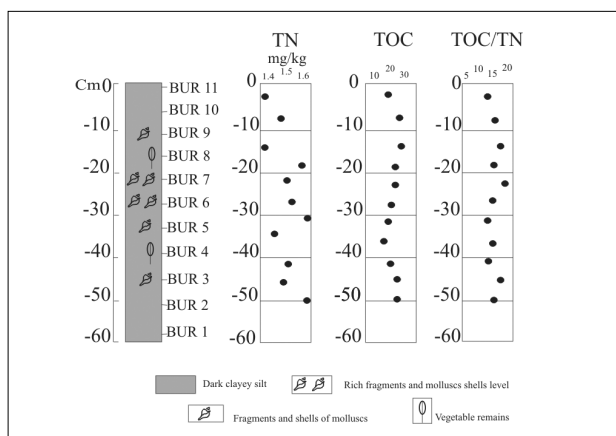


Fig. 3 - BUR core and relative values total nitrogen (TN), total organic carbon (TOC) and their ratio (TOC/TN).

proportion of intact land-plant debris than fine fractions. In addition, fine sediment fractions contain larger proportion of clay minerals, that have both large surface area and negative surface charges. They adsorb ammonia, lowering the TOC/TN ratio (Meyers, 1997). BUR and IBA sediments do not show noticeable differences in their grain-size, thus the TOC/TN ratio variations observed between them have to be ascribed to the origin of organic matter. It may be affirmed that immission of nutrients, with consequent algal blooms, have a small impact with respect to immission of land-derived organic matter in Massaciuccoli Lake's sediments.

TOC values in both cores are variable along the stratigraphic sequence. The increase in TOC preservation may be accounted for some non-exclusive possibilities (Zimmerman & Canuel, 2000): i) a sudden increase in water column productivity and subsequent organic matter delivery to the sediment; ii) a sudden seasonal oxygen depletion resulting in a minor degradation of particulate organic matter in the water column or superficial sediment; iii) an increase in terrestrial organic matter input. Other probable causes may be both climatological and anthropogenical; furthermore, suspended organic matter, under specific conditions, may adsorb large amount of nutrients.

An estimate of sedimentation rates could allow to evaluate the time interval represented in the 50 cm long core sample and then to detect if IBA core recorded a climatic cycle in the last 800-600 yr or the cyclic inputs of nutrients from water-scooping machines of Massaciuccoli and Vecchiano in the last decades.

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Tab. 2 - Values of total nitrogen (TN), total organic carbon (TOC) and their ratio (TOC/TN) in BUR core.

Code	Depth cm	TN mg kg <sup>-1</sup>	TOC mg kg <sup>-1</sup>	TOC/TN
BUR 1	-4.0	0.56	9.06	16.07
BUR 2	-8.0	0.53	9.33	17.53
BUR 3	-12.0	0.6	10.8	17.89
BUR 4	-16.0	0.81	13.61	16.74
BUR 5	-20.0	0.63	11.34	18.11
BUR 6	-24.0	0.67	12.02	17.91
BUR 7	-28.0	0.8	14.53	18.21
BUR 8	-32.0	0.81	13.72	16.96
BUR 9	-36.0	0.67	11.89	17.72
BUR 10	-40.0	0.48	7.26	15.02
BUR 11	-44.0	0.58	9.65	16.71
BUR 12	-48.0	0.61	9.1	14.96

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