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Recent Environmental Changes in the Shallow Lake Pamvotis (NW Greece): Evidence from Sedimentary Organic Matter, Hydrocarbons, and Stable Isotopes

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Abstract Lake Pamvotis is a shallow Mediterranean lake located in northwestern Greece that has been recognized as an internationally important conservation site. Here, an unprecedented investigation was undertaken to obtain and evaluate data related to sedimentary organic matter, hydrocarbon content, and stable isotopes of Lake Pamvotis sediments, thus tracking the origin of organic inputs and providing a record of environmental status. The study revealed a distinct spatial distribution of polycyclic aromatic hydrocarbons (PAHs) with values between 34.7 and 1600 μg/kg and a rather uniform pattern for *n*-alkanes with concentrations falling below 41.4 μg/g. A significant contribution of an unresolved complex mixture indicated anthropogenic petroleum contamination. Further study of relevant indexes and geochemical biomarkers supported a mixed-source input of aliphatic hydrocarbons. With regard to PAHs, there was strong evidence that their dominant origin is pyrogenic. Finally, considerable excursion in $\delta^{13}C_{org}$ was attributed to changes in dissolved inorganic carbon accompanied by increased input of effluents and recycling of organic carbon within the lake, whereas the rise in isotopic composition of nitrogen was associated with agricultural runoff and sewage input from the town of Ioannina.

Introduction

The greatest concern in lacustrine systems has been the eutrophication caused by various anthropogenic activities. The rapid control of eutrophication by reducing the point sources for phosphorus input is one of the clearest cases, in which science has contributed to quickly solve a major environmental problem. However, nutrient loading and other chemicals from nonpoint diffusive sources like agriculture and atmospheric deposition, their accumulation in the sediment, and recycling between sediments (especially in anoxic sediments) and water remains a problem (Schindler 2006).

Knowledge of the composition of organic matter in lacustrine sediments is a powerful tool for assessing environmental variations. Within the complex mixture of organic compounds in sediments, aliphatic hydrocarbons are widely distributed and they commonly derive from anthropogenic and natural sources (Colombo et al. 2005; Latimer and Quin 1996; Wakeham and Carpenter 1976). The hydrocarbon fraction of organic matter in modern lake sediments is a combination of biologically synthesized components, compounds derived from diagenetic alteration of biological matter, and materials of anthropogenic origin, mainly petroleum residues. The main sources of anthropogenic hydrocarbons in the aqueous environment are industrial effluents, sewage, river drainage, and boat traffic. Petroleum

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hydrocarbons are complex mixtures in both composition and molecular structure. They might enter the environment through accidents, spills, or leaks from industrial releases or as byproducts from commercial or domestic usage.

Polycyclic aromatic hydrocarbons (PAHs) have, in general, high molecular weight and low volatility. Their molecular structure comprises several inlaid benzene rings. PAHs might arise from petroleum pollution, from incomplete high-temperature combustion of organic materials such as wood, coal, and oils and vehicle emissions, and from microbial modification of biogenic precursors (Harvey 1997; Howsam and Jones 1998). PAH contamination not only reduces the quantity and quality of natural resources but might also have detrimental impact on wildlife (IARC 1983; Kennish 1997; Neilson 1998). Once in the aquatic systems, most PAHs are associated to the particulate phase due to their hydrophobic properties, resulting in accumulation in the bottom sediments (Laflamme and Hites 1978).

Hydrocarbons introduced to lake sediments tend to have long residence times for two reasons: First, higher-molecular-weight hydrocarbons have relatively low water solubilities and vapor pressures and, consequently, associate with sediment particles. Second, hydrocarbons as a group are less susceptible to degradation than most forms of organic matter because they lack the functional groups that impart chemical reactivity. Because hydrocarbon molecules are relatively more resistant to diagenetic modifications than other forms of organic matter, they provide long-term indications of changes in organic matter sources (Bourbonniere and Meyers 1996). Potential long-term detrimental effects of hydrocarbon pollution to organisms and human health, through trophic transfer, has driven intensive research on hydrocarbon pollution in aquatic environments using specific biomarkers and biological indices (Volkman et al. 1992; Wang and Fingas 2003).

In order to distinguish between the different origins of sedimentary organic matter, atomic C/N ratios have often been used. It is well known that algae have C/N ratios between 5 and 8, whereas vascular plants have C/N ratios $\geq$20 (Meyers 1994). Variations in the isotope composition of C and N in sedimentary organic matter integrate the overall changes in the relative abundance of organic matter sources of particulate and dissolved C and N as well as biogeochemical processes, affecting these two nutrients in the water column. Sources of dissolved C and N taken up by aquatic plants include atmospheric CO_2 and N_2, dissolved inorganic C, and dissolved nitrates and ammonia derived from the catchment (Herczeg et al. 2001). Therefore, atomic C/N ratios and stable isotopes of organic C and N have often been used to distinguish between the different sources of sedimentary organic matter (Deines 1980; Herczeg et al. 2001; Meyers 1994).

Lake Pamvotis has been the subject of several limnological studies in the past 20 years because of its significance from the geological and ecological standpoint (Kagalou et al. 2008; Romero et al. 2002; Stalikas et al. 1994, 1999; Tzedakis et al. 2003). Although metal content in sediments has been determined, there is a dearth of investigations on the sedimentary organic matter, especially on the occurrence of molecular markers. Therefore, it would be of interest to focus on a chemical, isotopic, and biomarker approach in order to study the effect of anthopogenic inputs and the effects of biological processes on organic matter quality during summer and winter periods. This article deals with the study of the nonpolar organic fraction for aliphatic hydrocarbons and PAHs associated with the sedimentary organic matter to determine its sources and spatial and temporal variabilities. In addition, the organic carbon (C_{org}) and total nitrogen (N) concentrations as well as stable organic carbon ($\delta^{13}C_{org}$) and nitrogen isotopes (δ^{15} N) were determined in the sediments to distinguish the different sources of sedimentary organic matter in Lake Pamvotis.

Experimental

Description of the Study Area

Lake Pamvotis is a shallow Mediterranean lake situated at 470 m above sea level (a.s.l.) in northwestern Greece. It occupies an area of 22.8 km^2, with a mean depth of 4.5 m and a maximum depth of 8 m. The lake is located in the vicinity of the town of Ioannina with ~150,000 inhabitants and is classified as eutrophic (Kagalou et al. 2008; Lawson et al. 2004). Lake Pamvotis has been recognized as an internationally important conservation site and is listed in the Natural Special Conservation areas under the European Community Council Directive on the conservation of natural habitats and of wild fauna and flora (Habitats Directive, EC, 92/43).

The catchment of Lake Pamvotis, which has undergone substantial agricultural and urban development over the past 30 years, consists of limestones, cherts, and flysch and the fine (silty to silty-clay) surface sediment consists of carbonates, quartz, feldspars, and clay minerals. The size of the lake was dramatically reduced by agricultural drainage schemes, which began around 1600 and culminated in the drilling of a tunnel to the west in 1944 (Higgs et al. 1967). There are no major fluvial inputs and outputs, but only ephemeral streams on the surrounding hills with most precipitation percolating directly into the bedrock (Lawson et al. 2004). The area receives, on average, 1200 mm of precipitation per year due to orographic uplift of moist warm air from the Adriatic See (Lawson et al. 2004).

Eutrophication of Lake Pamvotis has been a major problem for decades, as anthropogenic activity, such as irrigation and domestic sewage discharge, has altered its trophic status (Romero et al. 2002). This alteration involves a change from a macrophyte-dominated clear water state to a phytoplankton-dominated turbid state, with deleterious effects to the ecosystem (Kagalou and Leonardos 2006a; Kagalou et al. 2006b). Moreover, lake sediments contain degraded organic matter of both terrestrial and lacustrine origin, due to direct inputs, sedimentation of organic matter, and organic material redeposition after resuspension events. Since 1995, sewage was diverted to a treatment plant.

Sampling

Sediment samples were obtained by sediment coring, using a Box corer from seven sampling sites spread over the entire area of the lake (Fig. 1), in December 2005 and July 2006. Undisturbed surface sediments were obtained from the top 2 cm. In this way, a total of 14 (2 × 7) surfacial sediment samples were taken from the respective sampling points during the two sampling episodes. To obtain an insight on the depth profile of hydrocarbons, core sediments were obtained by coring from the two central points of the lake corresponding to the general outflow and inflow parts of the lake (i.e., locations S2 and S3). The cores were subsequently sectioned into 2-cm segments. For elemental and stable isotopic analyses, a sediment core collected from S2 sampling station in December 2005 was sliced into 1-cm slices.

Samples were stored in sterilized bags and frozen for subsequent analysis. All sediment samples were freeze-dried before further treatment.

Total Organic Matter

The readily oxidizable organic matter was determined in freeze-dried sediments by heating and oxidation with potassium dichromate and concentrated H_2SO_4, followed by the titration of excess dichromate (Walkey-Black 1947).

Sediment Extraction and Fractionation

Freeze-dried portions of the sediments were weighed and transferred into cellulose thimbles. Organic matter was Soxhlet extracted with a 2:1 mixture of dichloromethane/methanol for 12 h. Extracts were spiked with analyte surrogates and fractionated into aliphatic and aromatic hydrocarbons on deactivated silica column using hexane and hexane/dichloromethane (80:20) as eluants. Activated copper powder was used to remove sulfur. The extracts were evaporated under vacuum to ~2 mL in a rotary evaporator, at 30°C and used subsequently for analysis.

Fractions containing aliphatic alcohols, sterols, and fatty acids were obtained with successive elutions and retained for future use.

Gas Chromatography

The gas chromatography–mass spectrometry (GC-MS) analysis of the target compounds was performed on a Shimadzu GC-17A gas chromatograph interfaced with a Shimadzu QP 5000 mass spectrometer. Separation was conducted on a Supelco 30-m × 0.25-mm inner diameter fused-silica capillary column (SPB-5, film thickness 0.25 μm). The GC oven temperature was programmed as follows: 60°C for 1 min, to 250°C at 7°C/min, to 290°C at 10°C/min, held for 10 min. The injector and interface

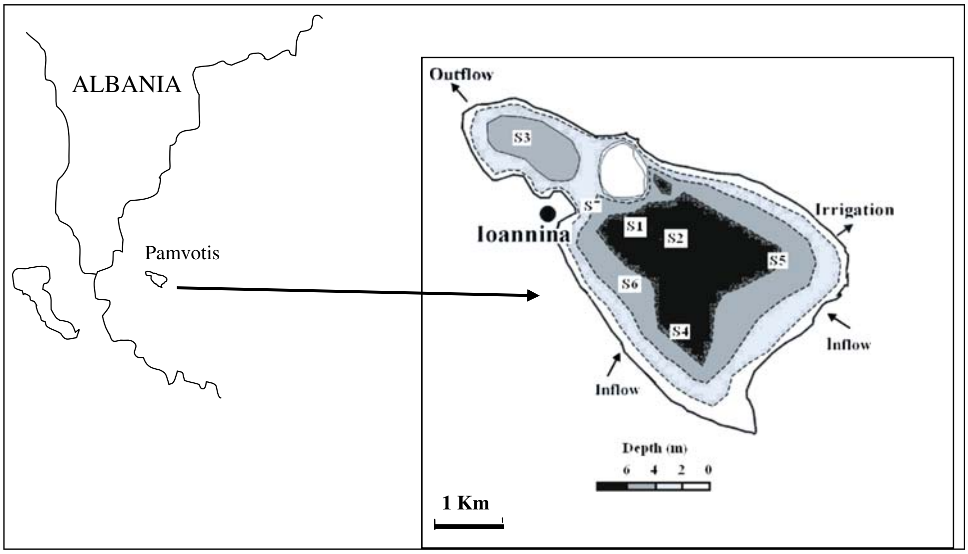

Fig. 1 Bathymetric map of Lake Pamvotis along with the locations of sediment sampling

temperatures were set at 250°C and 290°C, respectively. The mass fragments of the derivatives were obtained in the full-scan mode in the scan range from *m/z* 50 to 550 in the electron impact mode. A solvent delay time of 5.0 min was used to protect the ion multiplier of the MS instrument from saturation.

For aliphatic hydrocarbons determination, *m/z* 57 was used, and then based on peak areas of individual alkanes, the respective concentrations of them in samples were calculated. Quantification was performed by external standards of hydrocarbons mixtures of n-C_8 to n-C_{34}. Sixteen typical PAHs were used as external standards for the identification of each PAH peak in the samples. The individual *m/z* for each PAH was used for data collection. Identification of the analytes was based on the comparison of their retention times with those of authentic standards and by interpretation of mass spectra.

Chromatograms were characterized by a hump representing an unresolved complex mixture (UCM) of hydrocarbons, which belongs mainly to the branched cyclic naphthene series. The UCM was quantified by calculating the mean response factor of n-C_{23} and n-C_{24} in a GC-FID (flame ionization detector) chromatogram and correlating it with the sum of chromatographic peaks appearing from n-C_{17} to n-C_{31}.

Well-defined quality assurance and quality control procedures were undertaken to support the quality of data and the entire investigation. Quality control of the GC analyses relied on regular injection of the two standard kits composed of mixtures of *n*-alkanes each (from n-C_8 to n-C_{20} and from n-C_{21} to n-C_{34}, respectively). In addition, routine control measures, such as instrument calibration, procedural blanks, and replicate analyses, method detection limits for each target analyte and matrix spike surrogate recoveries, and cleanup of cellulose thimbles, sodium sulfate, and silica gel were undertaken. Recoveries for the overall procedures based on surrogate data were typically as follows: tetradecylchloride 88 ± 6%, 5α-cholestane 91 ± 8%, *m*-terphenyl 98 ± 6%, chrysene-d_{10} 85 ± 8%. Reported values were not corrected by surrogate recoveries. The relative standard deviations were less than 7% and 8% for aliphatic and aromatic hydrocarbons, respectively.

Elemental (C_{org} and N) and Stable Isotopic Analyses

Both C_{org} and total N concentrations were measured after removal of inorganic C (carbonate) with HCl (Hedges and Stern 1984) using a CHN elemental analyzer (Carlo Erba EA 1008). Prior to the determination of isotopic composition of C_{org}, carbonates were removed with diluted HCl and dried. The stable isotopic composition of C_{org} was determined on a continuous-flow Europa Scientific 20–20 ANCA-SL isotope ratio mass spectrometer. For the determination of the isotopic composition of nitrogen, homogenized bulk sample material was placed into tin capsules and measured on a Finnigan DELTA^{plus} XP continuous-flow stable isotope mass spectrometer with Eurovektor CHNS Elemental Analyser (Vreča et al. 2008). Isotopic ratios are expressed in standard delta notation ($\delta^{13}C_{org}$ and δ^{15} N), which is the per mil (‰) deviation from the V-PDB ($\delta^{13}C_{org}$) and air (δ^{15} N) standard.

Statistical Analysis

Spearman's rank correlation was used to evaluate the relationships between the physicochemical parameters in each period and core sediment.

Results and Discussion

Organic Matter

Total organic matter provides a first overview of the sedimentary organic content in Lake Pamvotis. The organic matter records reflect fluctuations indicating differences in composition, deposition, and organic matter preservation. The lake sediments are organic-rich with organic mater content ranging from 4.8% to 15.3% in surface sediments as well as in the lower portions of both cores. This is in concurrence with the high productivity in Lake Pamvotis during summer and external input of organic burden due to anthropogenic processes (sampling sites S2 and S7).

As expected, organic matter content in the silt-clay rich sediments (S2, S3, S5, and S7) are higher. In contrast, lower organic matter content is observed at sampling sites S4 and S6 (6.6% and 4.8%, respectively) along the southwestern shoreline, where coarser sandy sediments prevail (Romero et al. 2002). Finally, the sediment cores contain a high, but a decreasing trend of organic matter content with depth (between 15.3% and 7.8%), at sampling sites S2 and S3.

Elemental and Stable Isotopic Composition of S2 Sediment Core

Detailed C and N elemental and isotopic compositions were determined for the sediment core S2 and results are summarized in Table 1 and presented in Fig. 2. C_{org} content in the core decreased with depth and varied between 37 and 94 mg/g. N content followed the changes in C_{org} content and ranged between 3 and 7 mg/g. An increase in the content of both is observed in the upper 7 cm of the core and is the evidence of changes in organic matter delivery and preservation as a consequence of the progressive enrichment in nutrients, eutrophication, and

Table 1 Carbon and nitrogen elemental and isotopic compositions in core sediment S2 (December 2005)

Depth (cm)	C_{org} (mg/g)	N (mg/g)	C/N atomic	$\delta^{13}C_{org}$ (‰)	δ^{15} N (‰)
1	66	6.3	12.2	−27.2	4.3
2	68	6.1	12.9	−27.3	4.3
3	64	5.6	13.3	−26.9	4.5
4	94	6.8	16.0	−26.3	4.7
5	52	4.7	12.9	−25.7	4.7
6	43	3.7	13.8	−25.2	4.9
7	37	3.3	13.0	−24.8	4.6
8	48	4.8	11.6	−24.2	2.6
9	42	4.1	11.8	−23.8	1.8
10	44	4.7	11.0	−23.9	1.8
11	49	4.2	13.6	−23.7	1.6
12	45	4.2	12.5	−23.2	1.5
13	46	5.3	10.2	−22.7	1.5

human-induced changes that were intense, especially in the surroundings of the lake (Lawson et al. 2004; Kagalou et al. 2001; Kagalou et al. 2003; Romero et al. 2002).

The surface sediment C/N (atomic) ratio amounts to 12.2, indicating that allochthonous and autochthonous sources contribute to organic matter depositing in the lake. However, allochthonous sources (i.e., terrestrial vegetation) tends to have C/N ratios >20 and autochthonous sources (i.e., algae) are generally higher in N content (Herczeg et al. 2001; Meyers 1994). Therefore, the total range of C/N ratios indicates that terrestrial litter makes up a minor part of organic matter preserved in the sediment. In the deeper sediments, a subsurface maximum is observed, where C/N ratio amounts to 16.0. In this section, the sediment contains a relatively higher proportion of allochthonous organic matter. At the same depth, the highest C_{org} and N values are also observed. In the rest of the core, C/N ratios vary slightly ranging from 10.2 to 13.8. Although N is preferentially degraded in sediments, these low C/N ratios indicate that autochthonous sources are more important organic matter sources.

The isotopic composition of sedimentary organic carbon ($\delta^{13}C_{org}$) was found to increase progressively with depth (from −27.3‰ to −22.7‰). The isotopic composition of N varies between +1.2‰ and +1.8‰ in sediments below 8 cm, whereas in the upper sediments, a distinctive increase of δ^{15} N (up to +4.9‰) is observed. Considerable changes in C and N cycles recorded in the sediments that were deposited in the upper 7 cm compared to deeper sediment layers, are presented in Fig. 2. Changes in both isotopic records indicate alterations in aquatic C and N cycles, rather than changes in the amount of allochthonous versus autochthonous organic matter reflected in slight changes in C/N ratio.

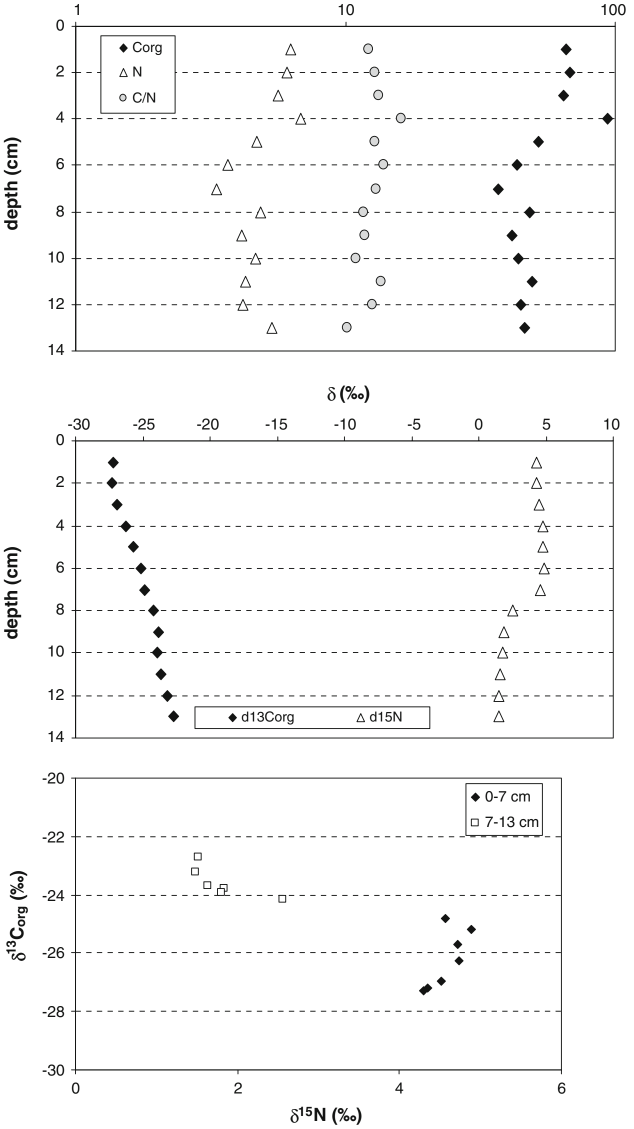

Fig. 2 Changes in C_{org}, N, C/N ratio (upper), isotopic composition of $\delta^{13}C_{org}$ and δ^{15} N (middle) and $\delta^{13}C_{org}$ versus δ^{15} N (lower) at sampling point S2. C_{org} and N concentrations are reported in milligrams per gram on a logarithmic scale

An explanation of the observed $\delta^{13}C_{org}$ and δ^{15} N changes is difficult because of the lack of isotope data. However, the progressive enrichment in ^{13}C with the sediment depth (Fig. 2) could be explained by the degradation of sinking and sedimentary organic matter during early diagenesis when isotopic composition of sedimentary organic matter tends to increase (Vreča 2003). Considerable influence of this process should be reflected also in the increasing C/N ratio that was not observed in our case. Therefore, we might assume that changes in $\delta^{13}C_{org}$ have to be related to changes in (1) the isotopic composition of dissolved inorganic C (DIC) sources and (2) the isotopic composition of atmospheric CO_2. DIC markedly influences the C cycle in carbonate environments. In recharge areas below the tree line, the lighter isotopic composition of DIC is consistent with the production of DIC by carbonate weathering with CO_2 derived from the oxidation of soil organic matter (Vreča and Muri 2006). It is also possible to attribute the negative shift in isotopic composition of C in recent sediments to the increased input of sewage effluents from the town of Ioannina and to recycling of C_{org} within the lake during moderate to severe eutrophication (Hollander and Smith 2001; Vreča and Muri 2006). In addition, annual stocking of lake with fish (Romero et al. 2002) could also contribute to the decrease in isotopic composition of organic matter (Vreča and Muri 2006, and references therein). The historic depletion of $\delta^{13}C$ in atmospheric CO_2 due to fossil fuel burning is usually corrected for this effect, in dated sediments, by using the model proposed by Schelske and Hodell (1995). However, an estimate of contribution of historic $\delta^{13}C$ depletion for Lake Pamvotis could not be possible because the sediments were not dated.

In addition to $\delta^{13}C$ values, the δ^{15} N values also indicate organic matter sources and algal productivity in lakes (Herczeg et al. 2001). The changes in δ^{15} N values (Fig. 2) indicate that sources of dissolved inorganic nitrogen (DIN) changed. A pronounced increase in isotopic composition of N in the lake could be attributed to agricultural runoff and sewage effluents that increased the nutrient loading (Herczeg et al. 2001; Romero et al. 2002). The sewage is relatively enriched in ^{15} N and has isotopic composition between 5‰ and 20‰ (Talbot 2001, and references therein). Variations in N isotopic composition also reflect changes in the dominant phytoplankton species from N-fixing to non-N-fixing species. The former are able to fix atmospheric N when the DIN concentrations are low, resulting in δ^{15} N composition close to 0‰. Non-N-fixing phytoplankton has δ^{15} N composition greater than 0‰ due to the ^{15} N-enriched nature of the assimilated N (Herczeg et al. 2001). Additionally, introduction of exotic planktivorous species (i.e., grass carp; Kagalou et al. 2003) could contribute to the shift in N isotopic composition.

Composition of Aliphatic Hydrocarbons in Surface Sediments

The composition of aliphatic hydrocarbons found in sediments reflects the relative contributions from different sources. *n*-Alkanes can derive from epicuticular waxes of higher plants and phytoplankton and zooplankton, characterizing natural input, or from petrogenic products such as fuel, lubricating oils, or road asphalt (Kaplan et al. 2001). Several studies have also shown that microbial and planktonic successions can greatly affect the lipid distribution and composition of particles through biological reworking as they sink to the sediment. *n*-Alkanes with an odd number of C atoms up to C_{23} are attributed to phytoplankton, typically dominated by the *n*-alkane series from *n*-C_{15} to *n*-C_{20}, with an almost universal dominance of *n*-C_{17} for algae and *n*-C_{19} for some cyanobacteria (Cranwell et al. 1987). *n*-Alkanes found in epicuticular waxes of higher plants are typically in the range of *n*-C_{23} to *n*-C_{35}, with clear dominance of odd-C chain lengths (Rieley et al. 1991) and a characteristic chain length profile that exhibits a maximum concentration typically around *n*-C_{27} or *n*-C_{29}. The *n*-alkanes from many submerged and floating aquatic macrophytes are characterized by maxima at the positions of lower chain lengths *n*-C_{21}, *n*-C_{23}, or *n*-C_{25} *n*-alkanes (Ficken et al. 2000). Even-C number alkanes in the same range (i.e., up to 23) are due to the photosynthetic and nonphotosynthetic bacterial action (Grimalt and Albaiges 1987), where the dominant chain lengths have been noted between *n*-C_{16} and *n*-C_{21}.

Samples from Pamvotis were analyzed to determine whether *n*-alkanes are effective organic geochemical proxies for the sediments. *n*-Alkanes from *n*-C_{10} to *n*-C_{30} were present in all the samples analyzed. Figure 3a shows a representative chromatographic trace of an aliphatic hydrocarbon fraction in sediment. From a cursory inspection, it is clear that there is no predominance of odd over even *n*-alkanes ranging from *n*-C_{10} to *n*-C_{30}. Elevated *n*-alkane concentrations were noted during the summer sampling as compared to the winter sampling. Spearman's rank correlation analysis revealed a strong positive relationship ($R = 0.7857$, $p = 0.05$) between *n*-alkanes and organic matter for the sampling of July 2006. Evaluation of spatial distribution of these hydrocarbons did not show significant variation. Although the lake is eutrophic due to high nutrient levels and high phytoplanktonic productivity, short-chained *n*-alkanes derived from phytoplankton (i.e., *n*-C_{17} and *n*-C_{19}) are present in moderate amounts in lake sediments.

The composition of oil released into the aquatic environment changes as a result of evaporation, dispersion, dilution, and degradation. The lighter *n*-alkanes are lost first and eventually almost all of the *n*-alkanes are degraded, leaving behind a "hump" to be observed in the GC chromatogram. This hump or so-called UCM (Gough and Rowland 1990) is due to more recalcitrant components in oil, mainly alkylated and cyclic compounds. UCM is a commonly observed feature in anthropogenically impacted sediments (Blummer and Sass 1972; Frysinger et al. 2003). The UCMs are visible not only in the traces of surface sediments of Pamvotis (Fig. 3b) but also in the underlying sediments from greater depth, as detailed in the following subsection. The relevant data are provided in Table 2. Only a small variation of the concentrations of UCM is apparent in the upper layers of the lake, except sampling sites S1 and S7 for the samplings of June 2006 and December 2005,

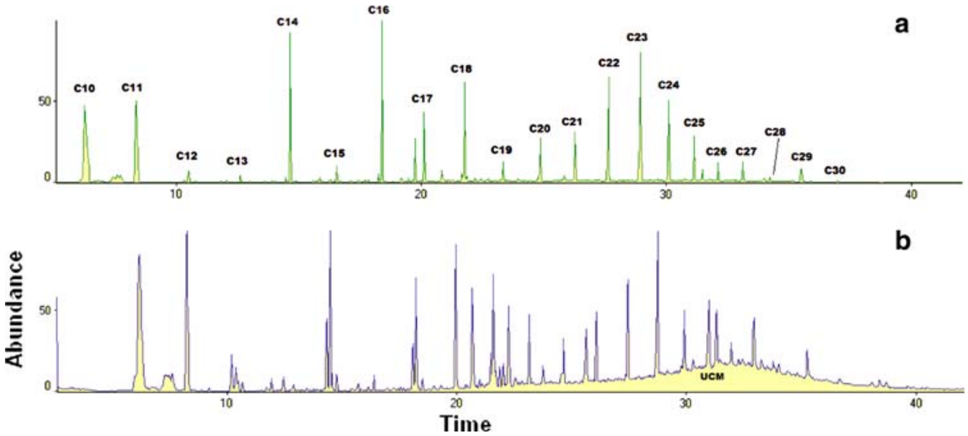

Fig. 3 GC traces of aliphatic hydrocarbons detected in Lake Pamvotis at sampling site S7 (July 2006). **a** Extracted ion chromatogram (*m/z* 57). Main *n*-alkanes with carbon number are indicated. **b** Total ion chromatogram. The loading of petroleum-derived hydrocarbons is indicated by the UCM

Table 2 Concentrations of PAHs, aliphatic hydrocarbons and their indexes in surface sediments of Lake Pamvotis for two sampling periods

Parameter	S1		S2		S3		S4		S5		S6		S7	
	Dec.	July	Dec.	July	Dec.	July	Dec.	July	Dec.	July	Dec.	July	Dec.	July
ΣAHC (μg/g)	18.9	17.1	7.7	29.3	12.8	28.0	9.8	23.7	10.3	31.6	16.3	10.9	13.9	41.4
UCM (μg/g)	128	47.1	55.6	66.0	78.4	72.1	45.1	59.4	49.1	77.1	39.4	29.7	52.8	100
$\Sigma C_{n+1}/\Sigma C_n$	0.94	0.89	1.14	0.71	1.06	0.66	0.84	0.98	0.83	0.78	0.78	0.88	0.83	0.73
CPI_{17-30}	1.73	1.86	1.83	1.64	2.12	1.22	1.64	2.14	0.95	1.83	1.31	1.59	1.83	1.51
UCM/Σ*n*-alkanes	8.15	2.61	7.18	2.25	6.13	2.58	4.59	2.51	4.76	2.44	2.44	2.71	3.08	2.42
ΣPAHs(μg/kg)	746	715	681	488	258	375	144	603	313	176	52.3	34.7	1600	1300

AHC: aliphatic hydrocarbons *n*-C_8 to *n*-C_{34}; PAHs: 16 EPA polycyclic aromatic hydrocarbons; UCM: unresolved complex mixture; C_{n+1}, C_n: aliphatic hydrocarbons with odd and even number of carbons; CPI: carbon preference index,

$$CPI_{17-30} = 1/2\left(\sum_{17}^{30}\frac{2n+1}{2n} + \sum_{17}^{30}\frac{2n+1}{2n+2}\right);$$

UCM/*n*-alkanes: ratio of the UCM to the resolved *n*-alkanes

respectively. The above sites are adjacent to the shoreline closest to the town of Ioannina and, hence, are more influenced in different ways (e.g., street runoff, boat traffic, domestic combustion, etc.) during the two sampling seasons. Invariably low is the UCM concentration at S6 due to the sandy texture of that sediment sample.

The carbon preference index (CPI) is also used for source apportionment of *n*-alkanes in sediments (Farrington and Tripp 1977). It is a measure of the relative abundance of odd- versus even-C numbered *n*-alkanes and can be used to assess whether the input source is predominately biogenic or petrogenic. The *n*-alkanes in the range *n*-C_{17} to *n*-C_{30} exhibit low CPI values ($\sim$1) in surface sediments, indicative of petrogenic input (Wang and Fingas 2003). In addition, the CPI values in the top samples might reflect the important living microbial biomass at the sediment–water interface. Although the CPI of high-molecular-weight homologs is commonly used to assess the presence of fossil fuel hydrocarbons, their values are not inversely proportional to the UCM. This might be due to the fact that the samples contain, in addition to the anthropogenic hydrocarbons, an amount of biomass- and bacterial-derived *n*-alkanes. Finally, the UCM-to-total *n*-alkanes ratio vary from 2.25 to 8.15, which is also an indicator of anthropogenic (usually $\geq$3) or mixed-source contamination (Ou et al. 2004).

Vertical Profiles of Aliphatic Hydrocarbons

The concentrations of aliphatic hydrocarbons fluctuate depending on the sedimentological history and human activities in the lake's catchment. The uppermost sediments in both cores have higher hydrocarbon content than the underlying sediments due to degradation processes. High values were present in recent sediments, especially at sampling site S3. The sediment cores contain decreasing hydrocarbon concentrations with depth: from 4.35 to 24.2 μg/g and from 8.0 to 31.5 μg/g aliphatic hydrocarbons and UCM, respectively (Table 3). Weak positive relationships (Spearman rank correlations) were found between *n*-alkanes and organic matter in both cores. Because lipids usually constitute only a few percent of the total organic matter, a correlation between both parameters is expected to be weak. The historical deposition and accumulation of

Table 3 Quantification of aliphatic hydrocarbons and their indexes for core sediment S2 of Lake Pamvotis

Core depth	0–2	2–4	4–6	6–8	8–10	10–12	12–14
Parameter							
ΣAHC (μg/g)	13.3	7.8	9.2	3.1	5.8	12.9	5.4
UCM (μg/g)	54.6	21.0	14.1	8.6	21.4	34.3	7.2
$\Sigma C_{n+1}/\Sigma C_n$	0.72	0.85	0.91	1.03	0.96	0.90	0.94
$CPI_{17–30}$	2.01	1.82	1.45	1.80	1.63	1.74	2.77
UCM/Σ*n*-alkanes	4.11	2.69	1.54	2.78	3.74	2.66	1.33

Note: For abbreviations, see Table 2

petroleum products is reflected by the UCM concentration profiles in sediments. In the recent sediments of Lake Pamvotis, the bioaccumulation of hydrocarbons rises markedly. UCM occurs in the underlying sediments, although concentrations decrease downcore (irregularly in sediment S2) and is greater in surface sediments. Reduction in contribution of UCM in the deeper layers (after 12 cm and 8 cm for S2 and S3, respectively) reflect a progressive proportional increase in petroleum hydrocarbon contributions to the biological accumulations in the modern sediments, making, also, allowance for the fact that diagenetic degradation of petroleum residues in older sediments is unlikely to proceed easily. Finally, CPI values in the carbon number from 17 to 30 vary between 1.45 and 2.77, confirming an origin from both bacterial inputs and contamination by petroleum products. Relevant values are provided in Tables 3 and 4.

The lake is shallow and, as a consequence, surficial sediments are resuspended frequently as a result of wind-driven turbulence. Labile organic material is most probably degraded in the water column and sediments throughout the year. A compositional shift of hydrocarbons along the cores indicates that the downward reduction in aliphatic content is associated with microbial alteration rather than with reduction in input in the past. The downcore occurrence of *n*-C_{15}, *n*-C_{17}, and *n*-C_{19} is scarce and dissimilar to that of *n*-C_{14}, *n*-C_{16}, and *n*-C_{18}, advocating the absence of petroleum impact. In addition, as the short-chain algal *n*-alkanes are more vulnerable to microbial mineralization than their long-chain counterparts, their abundance in Lake Pamvotis sediments is controlled by both input-related changes and biodegradation.

Table 4 Quantification of aliphatic hydrocarbons and their indexes for core sediment S3 of Lake Pamvotis

Core depth	0–2	2–4	4–6	6–8	8–10	10–12	12–14
Parameter							
ΣAHC(μg/g)	24.2	7.8	6.8	7.1	6.3	6.2	4.3
UCM (μg/g)	31.5	23.9	14.2	11.9	9.9	8.6	8.0
$\Sigma C_{n+1}/\Sigma C_n$	0.72	0.71	0.68	0.70	0.66	0.74	0.61
$CPI_{17–30}$	1.45	1.46	1.45	1.48	1.66	1.91	1.48
UCM/Σ *n*-alkanes	1.31	3.08	2.08	1.68	1.56	1.38	1.85

Note: For abbreviations, see Table 2

Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons are generated by two main processes: combustion of organic matter (pyrolytic) and release of petroleum (petrogenic). It is well established that pyrolysis and combustion of fossil fuel yield PAHs, which are introduced in the aquatic environment by runoff and direct dry or wet deposition from the atmosphere (Fernández et al. 1999). Sixteen PAHs (listed by the US Environmental Protection Agency) were quantified and indexes were calculated for source apportionment. Surface sediments in Lake Pamvotis are dominated by anthracene and naphthalene up to the four-ring pyrene. Nonetheless, the concentrations of PAHs in the lake sediments are relatively low. These values, in the sampling site in the vicinity of the town of Ioannina (S7), are at least twice as high as those in the rest of the sampling points due, apparently, to anthropogenic inputs (Table 2). Based on literature reports, such PAH concentration levels are below or well below the low effect range (ERL), threshold effect level (TEL), and probable effect level (PEL) reported by Long et al. (1995) and MacDonald et al. (1996).

The three-ring PAHs constitute one of the dominant PAH groups in fossil fuels but might also occur in combustion-derived material. Therefore, it is difficult to distinguish PAHs of petroleum origin from PAHs of pyrolytic origin because they often occur concurrently in the environment. The discrimination of organic inputs in the lake is allowed by calculating certain ratios of (parent) PAHs. The pyrogenic process is a fast reaction that forms the less stable, kinetic product. Diagenesis favors the most stable, the thermodynamic product, at a longer reaction time. However, analysis of PAH ratios can be used to distinguish between pyrolytic and petrogenic sources. By examining several ratios simultaneously, it can be possible to distinguish between pyrolytic and petrogenic sources; for example, the anthracene-to-(anthracene plus phenanthrene) ratio can distinguish such inputs. For petrogenic input, this ratio shows a value lower than 0.10, whereas pyrogenic input exhibit higher values. The values obtained for this ratio range from 0.4 to 1.0. Likewise, the phenanthrene-to-anthracene ratio implies petrogenic contribution when its value is greater than 4. The values of this ratio converge to the range of 0.1–1.0. The evidence from both of these ratios points to predominantly pyrogenic sources of the PAHs. The fluoranthene-to-(fluoranthene plus pyrene) ratio of 0.50 is defined as the petroleum/combustion transition point, although, in practice, this boundary appears to be less definitive than the criterion of the anthracene-to-(anthracene plus phenanthrene) ratio, already mentioned (Yunker et al. 2002). In our case, the fluoranthene-to-(fluoranthene plus pyrene) ratio varies between 0.15 and 0.51 and shows the influence of fossil fuel combustion on the distribution of PAHs. It is worth noting that after their incorporation into sediments, three-ring PAHs could be preserved from removal processes. This is attributed to their specific associations with particles (inclusion), which render them unavailable for biodegradation (Gschwend and Hites 1981; Jones et al. 1986).

Geochemical Biomarkers

It can sometimes be difficult to identify petrogenic sources of PAHs using PAH concentration ratios alone. Due to the chronic input of pyrolytic PAHs into the environment, the PAH profiles are normally dominated by the pyrolytic PAHs and any petrogenic input might be masked. On the other hand, the geochemical biomarkers, such as the pentacyclic triterpanes (hopanes), are resistant to weathering degradation and their profiles remain relatively unaltered with time. Contrary to other petroleum fingerprints like pristane and phytane, hopanes exhibit greater resistance to biodegradation processes (Venosa et al. 1997) although the biodegradation pattern of hopane homologs has been a controversial issue concerning the lower- versus higher-molecular-weight susceptibility against microbial attack (Peters and Moldowan 1993). Fragmentograms of *m/z* 177 and *m/z* 191 in the Lake Pamvotis sediments reveal the presence of hopanes with 27–35 carbon atoms. This pattern holds true for all sampling points throughout lake surface and is commensurate with the potential sources of hydrocarbons used or introduced in the lake with the boat traffic, runoff, and so forth. Additionally, although they are not used to fingerprint unequivocally petroleum hydrocarbons in sediments, methyl hopanes have been the subject of scrutiny as indicators providing a considerable amount of information about petroleum-derived products (Volkman et al. 1992). In the sediments of Lake Pamvotis, chromatographic peaks were identified bearing characteristic main fragments at *m/z* 195 and 205. Such peaks, assigning methyl hopanes, are traced in the second fraction (hexane/dichloromethane: 80/20) throughout the surface sediments. Even though the presence of hopanes and methyl hopanes is more pronounced at sampling sites S1 and S3 during the winter, there were no spatial and temporal trends clearly evident and, all in all, these indications were deemed to be of rather moderate contamination from petroleum products.

Siloxanes in the Nonpolar Fractions of Lake Sediments

Silicones are synthetic polymers useful for their unique physical properties and chemical stability. Their special attributes has encouraged their use in a myriad of consumer products. Silicones appear to collect preferentially on sedimentary particles, probably as a manifestation of their surface-active properties. Because siloxanes have come into widespread use only since the early 1950 s, sediments deposited prior to 1945 showed no siloxanes (Pellenbarg et al. 1997). Siloxanes were dominant throughout sediments of Lake Pamvotis, as evidenced by the occurrence of relevant peaks in chromatographic traces, albeit to different extent in terms of peak abundance and intensity. The sediments record a trend of increasing sedimentary poly(organo)siloxanes (silicones) in contemporary sediments (sampling sites S2 and S3), as a reflection of the increasing use of silicones. Additionally, there is clear

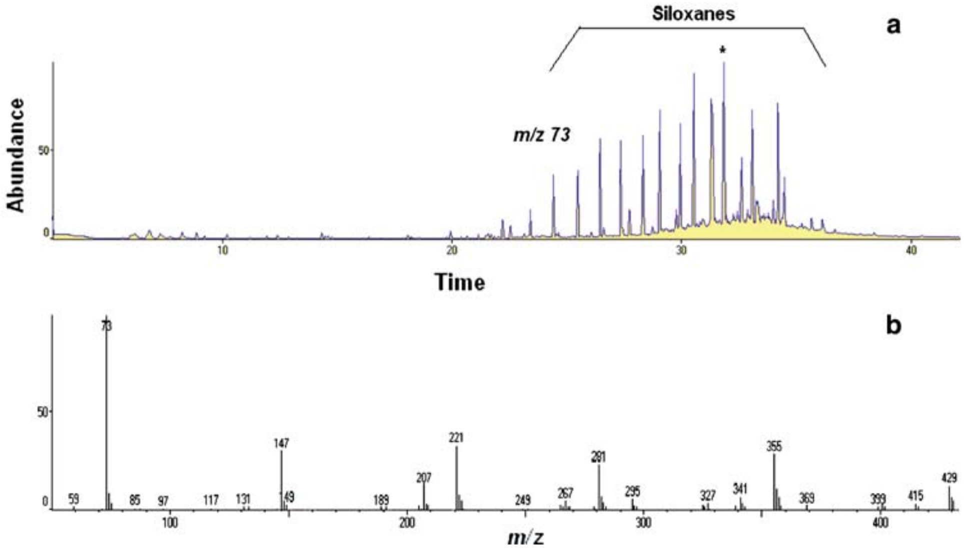

Fig. 4 **a** Extracted ion chromatogram (*m/z* 73) of surface sediment (S4). **b** Mass spectrum of chromatographic peak marked with asterisk. Tentative assignment based on NIST 107 library: 1,1,1,5,7,7,7-heptamethyl-3,3-bis [trimethylsiloxy]tetrasiloxane

evidence of higher accumulation in S4 surface sediment that appears to be associated with major inputs from the adjacent ditch, street runoff, and the discarded consumer products. A relevant chromatogram along with a representative mass spectrum is given in Fig. 4.

Conclusion

Although lipids make up only a small part of organic matter, they can provide useful information about the source, diagenetic alteration, preservation and changes of organic matter, and trophic status of lakes. Results presented in this study point to the utility of using hydrocarbon content and stable isotope data to characterize organic matter in sediments from Lake Pamvotis. The study revealed a spatial variation of PAHs with concentrations between 34.7 and 1600 µg/kg and a rather uniform pattern for *n*-alkanes with concentrations falling below 41.4 µg/g. A significant contribution of UCM indicates anthropogenic petroleum contamination and further study of relevant indexes and geochemical biomarkers supported a mixed-source input of aliphatic hydrocarbons. With regard to PAHs, there is strong evidence that their dominant origin is pyrogenic. The sediments also record a trend of increasing sedimentary poly(organo)siloxanes in contemporary sediments as a reflection of the increasing use of silicones. Furthermore, considerable excursion in $\delta^{13}C_{org}$ is attributed to the contribution of DIC sources accompanied by increased input of effluents, recycling of organic carbon within the lake, and historic depletion of $\delta^{13}C$ in atmospheric CO_2. The rise in isotopic composition of nitrogen is associated with agricultural runoff and sewage input from the town of Ioannina.

As to the levels of the studied chemical groups in comparison with other European lakes, it seems that Lake Pamvotis sediments have an acceptable quality level. However, more detailed sampling and analysis of the rest of lipid fractions together with other micropollutants might be useful for defining changes in a more rational way as well as for discriminating the contribution of sources and designing future strategies for the protection and management of Lake Pamvotis.

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