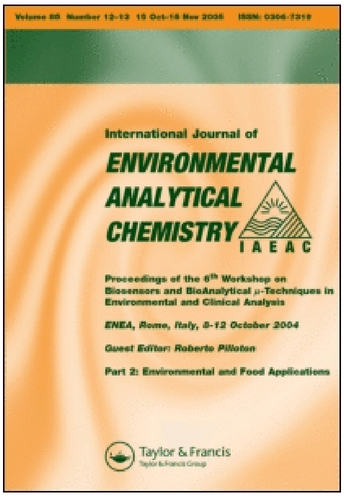

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Kotti, M. E. , Vlessidis, A. G. and Evmiridis, N. P.(2000) 'Determination of Phosphorous and Nitrogen in the Sediment of Lake 'pamvotis' (Greece)', International Journal of Environmental Analytical Chemistry, 78: 3, 455 — 467
To link to this Article: DOI: 10.1080/03067310008041360
URL: http://dx.doi.org/10.1080/03067310008041360

Intern. J. Environ. Anal. Chem., Vol. 78(3-4), pp. 455-467
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DETERMINATION OF PHOSPHOROUS AND NITROGEN IN THE SEDIMENT OF LAKE 'PAMVOTIS' (GREECE)

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(Received 15 October 1999; In final form 25 April 2000)

Phosphorous and nitrogen nutrients in the sediment of the lake Pamvotis were determined by standard methods of analysis. The pore water of the sediment was also analyzed for orthophosphate, ammonia and nitrate content. The results give evidence that nutrient phosphorus content of the sediment is increased at the summer periods and with nitrogen content being available during the whole year gives eutrophic behavior in the lake waters. However, the winter rains reduce the phosphorous content during the spring months. The phosphorus is introduced into the lake by agricultural runoffs and by trenches from urban areas. Several isolated events originating from activities of the inhabitants of the small island and the human activities around the lake give rise to temporary pollution of the lake waters.

Keywords: Phosphorus; nitrogen; lake sediments

INTRODUCTION

Lake Pamvotis is situated close to the city of Ioannina at a level of 600 m above sea level at the foots of nearby surrounding mountains. The lake is supplied with clean natural underground waters through shallow holes in the basin and from trenches that bring rain water from the nearby lands. It is populated by several kinds of living organisms such as fishes, eels, amphibia, and water plants; it is also known as a recreation area for the people of Ioannina city.

Through the years several water sources have ceased or have been cut off from the lake and the water volume and area have considerably decreased[1,2], while the lake has assumed eutrophic characteristics. In addition, recent developments in the area increased the population of Ioannina city and with the growth of

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industrial and agricultural activities the inflows of the lake became contaminated with nutrients and as a result increased the eutrophic regime of the lake despite the construction of the wastewater treatment plant of the city.

On the contrary the city of Ioannina with the surrounding mountains and the lake of Pamvotis with its small inhabited island in its center provides a picturesque view that attracts many tourists during the whole period of the year. Great concern was therefore given by the municipal authorities to the sanitation and maintenance of the quality of the lake waters

Among the measures taken by the municipal authorities was the construction of municipal wastewater treatment plant with underground tube network to drive the urban sewage and factory wastewaters to the treatment before being discarded to the nearby river through the Lapsista trench, and the funding of studies for the establishment of a data base with the variables that decide the seasonal changes of lake appearance at short-time and long-time period scale, as well as studies to remedy eutrophication[3].

The present study deals with the assessment of the nutrient content of the sediment and its pore water and contributes to provide information for a data basis, as well as to support the understanding for the processes that lead to eutrophication of the lake waters.

EXPERIMENTAL

Zone of study

Lake Pamvotis extends to an area of 22 km^2; the basin of the lake contains an aqueous volume of approx. 90×10^6 m^3; the height of the aqueous column is variable and its maximum reaches 7.0 m.; the volume and area have decreased from 1932 to 1982 at approximately a linear rate of 0.7×10^6 m^3/year and 0.1 m^2/year, respectively. The main basin also decreased from >10 m to 7.0 m depth over the same interval. During the present work the meteorological and the hydrological measurements varied as follows:

- Major wind events in excess of 4 m/s (hourly averages) occurred 2–3 times a month during the winter season.
- Air temperatures ranged from −10°C (minimum) in December 1998 and February 1999 to nearly seasonal maximum in excess of 35°C in August 1998. From May till September the temperature ranged from 5°C to 38°C at the island station. During the summer months of June, July and August the temperature difference was 15°C whereas during May and September it was 10°C and 5°C.

- No rainfall occurred from mid-June to mid-August; periods of strong rainfall occurred in September, November, December and January.
- Water level at full supply reaches the value of 470.25 m above sea level from April to June 1998 and from December to February 1999. During the high lake levels, stream inflows and rainfall were large; on the contrary during the low lake levels, evaporation and irrigation water use was high.

Sampling sites

Sediment samples were grabbed with Van Veen type sediment sampler from five different stations which were located by a GPS unit. One sample was collected from each of the five stations. The sediment stations, the inflows and the outflows of the lake are shown in Figure 1. Station 1 (water depth=5.3 m) lies near the confluence of the smaller northwestern basin to the much larger southeastern basin; it is the closest station to the island. Station 2 (water depth=6.5 m) is considered to be the representative mid-lake station near the center of the lake. Station 3 (water depth=4.5 m) is considered to be representative of the open water of the shallow northwestern basin. Station 4 (water depth=5.5 m) is near the agricultural areas and one of the inflows. Station 5 (water depth=6.6 m) is in the eastern sector of the basin and near the other inflow.

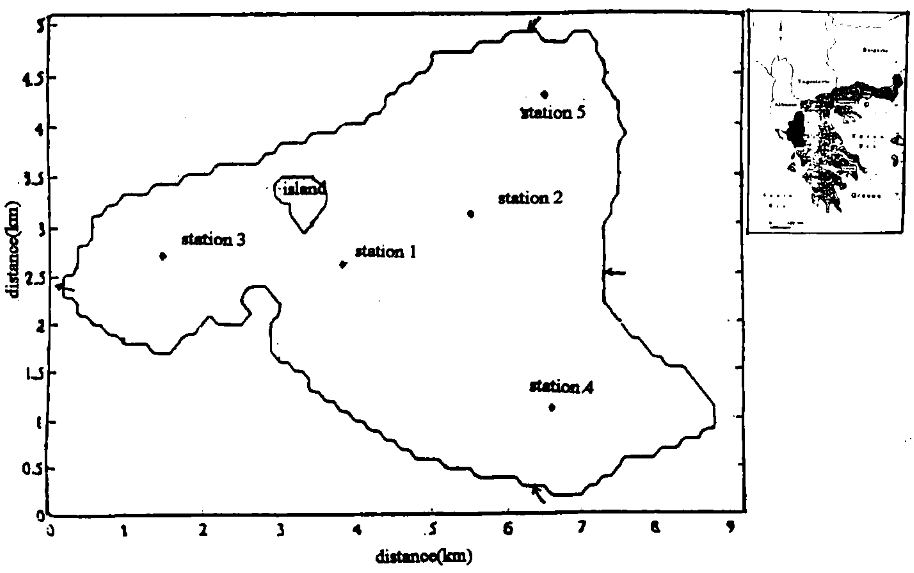

FIGURE 1 Location of the sediment sampling stations in lake Pamvotis used in this study

Methods of analysis

The determination of the nutrients of the pore water and the sediment was assessed by the standard methods[4,5] after filtering the pore water and drying for 2 hours the sediment at 110°C.

The nitrates were determined spectrophotometrically by reduction to nitrite and the method of diazotation and condensation with salicylate (RSD = 10%).

The orthophosphates were determined spectrophotometrically by the molybdenum blue method (RSD = 2%).

Ammonium content was determined spectrophotometrically by Nessler method (RSD = 10%).

The total nitrogen in the sediment (T-N) was determined titrimetrically after digestion and distillation by the Kjeldahl method (RSD = 15%).

The total phosphorous content (T-P) in the sediment was determined by converting to orthophosphates by Kjeldahl digestion method and determination of orthophosphates by the molybdenum blue method.

The nitrates determination in the sediment was obtained by reduction to nitrites and diazotation method as previously mentioned (RSD = 10%).

The RSD data were obtained by analyzing standard samples or materials whose content was determined by standard methods of analysis (elemental analysis). The standard deviation of the standard samples when compared with the standard deviation of the real samples was found to be statistically insignificant.

RESULTS

The total nitrogen and phosphorous content in the sediment is determined from samples taken from five sampling stations of the lake basin and the results are given in Figures 2 and 3, respectively. From Figure 2 it is realized that the overall average value of the total nitrogen content – calculated from all the measurements – is 2.5 mg/g with a scatter of 50% for the individual data points and few outliers restricted to sampling stations 1 and 2 at specific sampling dates.

Table I shows the values of T-N for each sampling station and date as well as the average of each sampling station within the sampling dates. From Table I it is seen that the average T-N content within sampling dates for each sampling station and its distribution of data points between the sampling dates is as follows:

- Sampling site 5 has an average of 3.0 mg/g; it is not changing with sampling date very much; a significant positive deviation in the period of September and October and a significant negative deviation in the samples of June and January are observed.

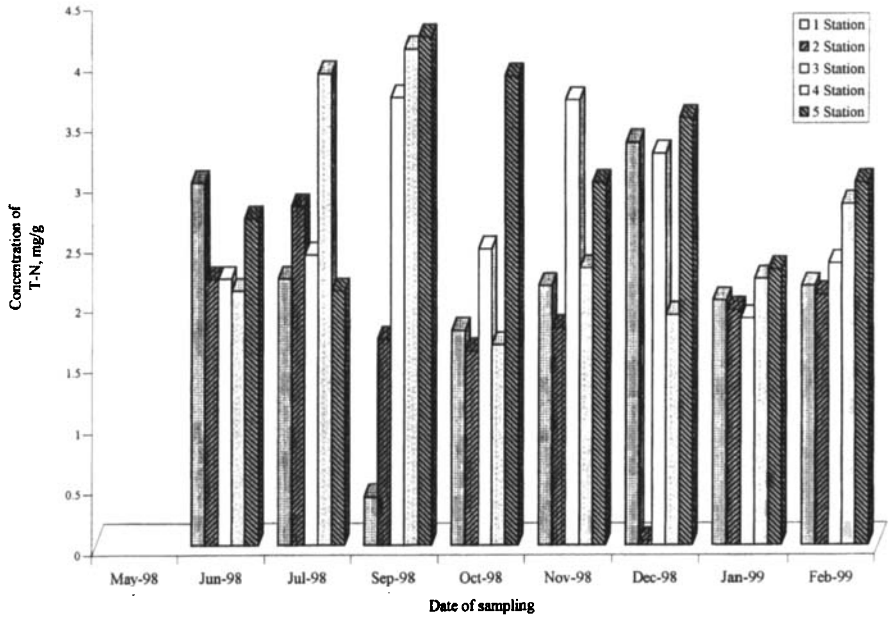

FIGURE 2 Temporal variation of the total nitrogen (T-N) content in the dry sediment

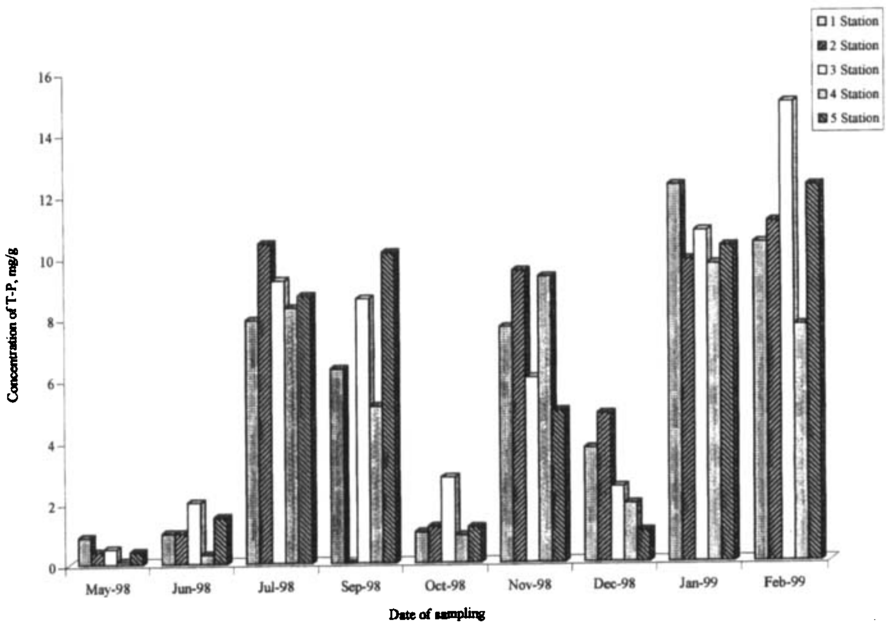

FIGURE 3 Temporal variation of the total phosphorous (T-P) content in the dry sediment

- Sampling station 4 (with inflow from agricultural sources) has an average of 2.65 mg/g; it is significantly higher in the sampling dates of July up to September and later in November.
- Sampling station 3 (shallow water) has an average of 2.8 mg/g; it is significantly higher in the sampling dates of September, November and December while it is far lower in sampling date of June.
- Sampling station 2 (deep water) has an average of 1.8 mg/g; it is less than 3.0 mg/g in all sampling dates with the exceptionally low value of 0.1 mg/g in December.
- Sampling station 1 (confluence of the two basins) has an average value of 2.2 mg/g; it shows very big fluctuations with sampling dates; the lowest value of 0.5 mg/g is obtained in sampling date of September and highest of 3.1 and 3.4 mg/g, in sampling dates of June and December, respectively.

TABLE I T-N content (mg/g) in the sediment of lake Pamvotis

Sampling station	*Sampling Date*							
(average)	*03/06/98*	*04/07/98*	*10/09/98*	*24/10/98*	*21/11/98*	*20/12/98*	*30/1/99*	*29/2/99*
1 (2.16)	3.10	2.25	0.50	1.80	2.00	3.40	2.06	2.17
2 (1.79)	2.25	2.80	1.75	1.63	1.80	0.04	1.98	2.10
3 (2.78)	2.25	2.40	3.75	2.50	3.70	3.30	1.94	2.40
4 (2.65)	2.10	4.00	4.10	1.70	2.30	1.94	2.25	2.80
5 (3.12)	2.80	2.10	4.20	3.90	3.00	3.60	2.33	3.03
average	2.50	2.71	2.86	2.30	2.60	2.50	2.10	2.50

Table II shows the values of T-P for each sampling station and date and the average within sampling stations at each sampling date. From Table II it is found that the average of T-P within sampling stations as well as the T-P content of individual sampling stations, shows a seasonal variation as follows:

The average T-P at sampling date of May and June was found less than 2 mg/g; at sampling dates in the period from July to September the average T-P content was increased to 8.0 mg/g; the T-P content fell down to an average of 2 mg/g in the sampling date of October; it increased to 8.0 mg/g in November and fell down to an average of 2.7 mg/g in December; finally, the average increased to around 12.0 mg/g in January and February.

The variation of T-P with the sampling dates at the individual sampling sites shows a similar pattern to that of the average within sampling stations with minor changes characteristic to each site, as follows:

- Sampling station 4 (agricultural inlet) has apart from November a lower value than the average, but the overall seasonal pattern is not changed
- Sampling station 5 (inlet) is usually higher or very close to the average at all sampling dates except those of November and December and the overall seasonal pattern is only slightly changed
- Sampling station 3 (shallow waters) shows in most cases higher levels of T-P content than the average except the sampling dates of November and December; and follows the seasonal pattern of sampling station 5
- Sampling station 2 (deep waters) has a T-P value less than the average in sampling date of September, and higher in sampling dates of July, November, and December, but the seasonal pattern of change is only slightly changed from that of sampling station 4
- Sampling station 1 (confluence of the two basins) in all sampling stations is close to the average values of all sampling dates.

TABLE II T-P content (mg/g) in the sediment of lake Pamvotis

Sampling station		*Sampling Date*						
(average)	*03/06/98*	*04/07/98*	*10/09/98*	*24/10/98*	*21/11/98*	*20/12/98*	*30/1/99*	*29/2/99*
1 (6.30)	1.03	8.00	6.50	1.00	7.60	3.60	12.30	10.40
2 (6.00)	1.03	10.40	0.00	1.20	9.50	4.90	9.90	11.10
3 (7.16)	2.12	9.30	8.65	2.80	5.90	2.60	11.00	14.90
4 (5.40)	0.34	8.20	5.10	0.90	9.30	2.00	9.70	7.70
5 (6.30)	1.58	8.80	10.10	1.20	5.00	1.10	10.30	12.30
average	1.22	9.00	6.07	1.40	7.50	2.70	10.60	11.30

The phosphate concentration of pore water was found around 10 to 20 mg/l except the sampling date of July which showed values above 50 mg/l for all sampling stations; the relative distribution among the sampling stations was almost equal (Figure 4).

The concentration of ammonia in pore water was very low (nearly zero for all stations) in September and October; it was rather high in May and in November (average within the stations 2.0 mg/g) and even higher in June and July (average between the stations 4.0 mg/g) (Figure 5).

The nitrate concentration in the sediment was found beyond detection limit for all sampling dates and stations except that of October that appeared high (S1=62.3 μg/g, S2=15.4 μg/g, S3=89.4 μg/g, S4=267.6 μg/g, S5=22.4 μg/g); the

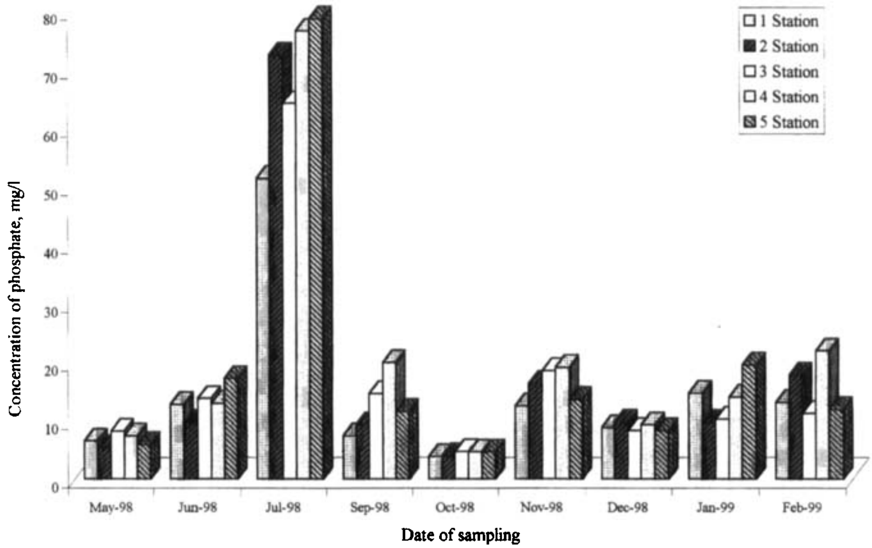

FIGURE 4 Temporal variation of the phosphate concentration in the pore water

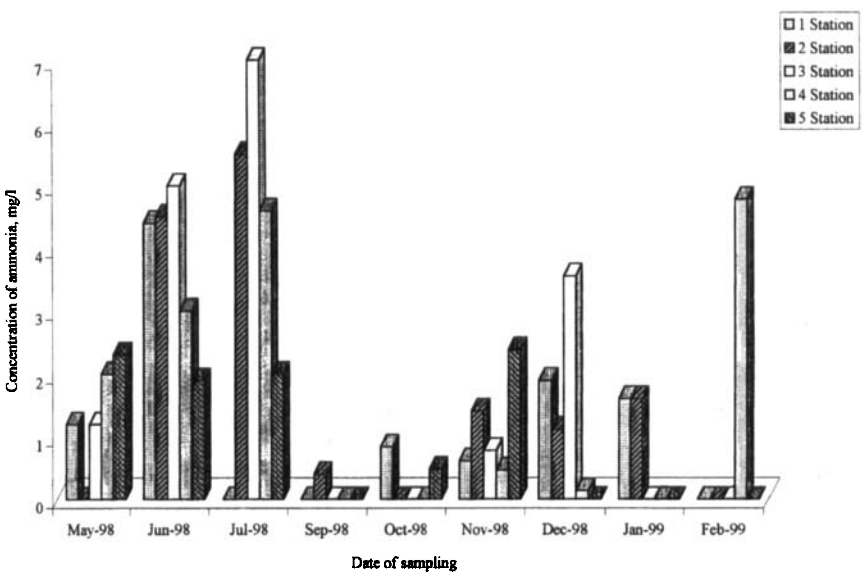

FIGURE 5 Temporal variation of the ammonia concentration in the pore water

nitrate content in pore water was found high at the same sampling date (S1=23.1 mg/l, S2=3.5 mg/l, S3=1.8 mg/l, S4=0.8 mg/l, S5=0.0 mg/l).

DISCUSSION

Some of the most important processes that result to the deposition of nutrients to the sediment in the basin of a lake are illustrated in Figure 6 and are summarized in the following scheme:

$$\text{P-N-nutrient}\left\{\begin{array}{l} \xrightarrow{\textit{suspended-solids precipitation}} \\ \longrightarrow \text{algae} \xrightarrow{\textit{feed}} \text{multicell-organisms} \xrightarrow{\textit{biomass}} \\ \longrightarrow \text{algae} \xrightarrow{\textit{dead parts}} \\ \xleftarrow{\textit{bacteria}} \end{array}\right\} \text{sediment}$$

At constant inflow of the nutrient elements from outside sources, T-P and T-N in sediment increases during eutrophic periods because of the rapid conversion of P, N-nutrient in water to algae and further production of biomass; on the contrary it decreases when the rate of action of bacteria is quicker than the rate of accumulation of P,N-nutrients in the sediment.

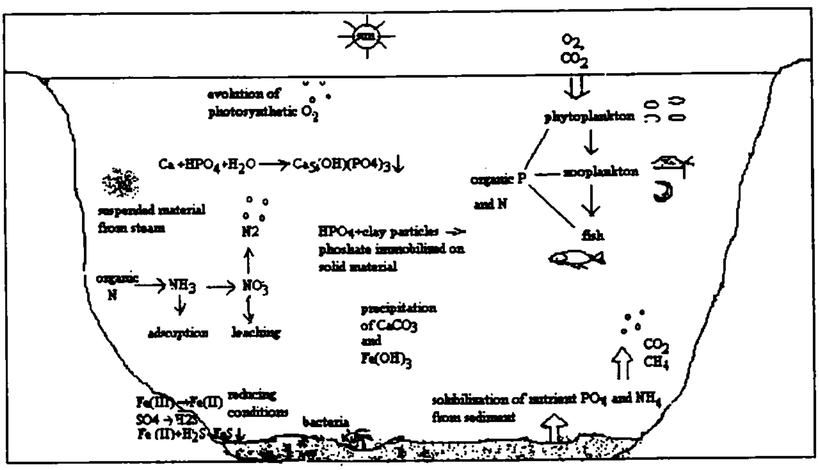

FIGURE 6 Schematic representation of the most important chemical processes in a lake basin

The suspended solids of the inflow are another source of nutrient that is deposited in the sediment. The precipitation of suspended solids is more effective at peaceful waters and major pollution takes place in the area around the inlet at a distance that depends on the particle size of the suspended solids. On the other hand in deep waters the fishes find shelter and when they are poisoned by chemicals leave their carcasbiomass.

Ammonia production is characteristic of the septic processes of lake waters and occurs mostly in deep waters and in case of eutrophic periods at the whole aqueous phase of the lake; the quantity formed is an indicator of the extent of the reducing capacity of the lake waters. On the other hand nitrate is a product of the oxidative conversion of dissolved and organic nitrogen that takes place in surface waters; its quantity may be used as indicator of the oxidative capacity of these waters. The temperature difference between the surface and the deep waters of the lake separates it into three aqueous layers that are distinct at winter and summer and are called epilimnion (surface), thermocline (intermediate zone), and hypolimnion (deep waters)[5,6]. During the spring and autumn, inversion of temperature takes place and the temperatures of hypolimnion and epilimnion tend to be equalized. In addition, during autumn and spring the weather becomes windy and the mixing and homogenization of the layers becomes effective. Such an effective mixing reduces the ammonia concentration of the hypolimnion waters and the increases its nitrate concentration.

The difference between the incoming and outgoing nutrients gives a measure of the converted nutrient to bio-mass and/or transported to sediment. Differences between the T-N and T-P content of residue as well as in the seasonal pattern of change are reasonable since the sources of the two nutrients are different, i.e. atmospheric N_2 - through the biochemical action of certain waterplants – and lake inflows for nitrogen, while lake inflows only for phosphorous. Therefore, the time pattern of T-P content change in the sediment depends on the load change of inflows alone while the T-N time pattern content change depends on the N_2 uptake from the atmosphere as well as from the nitrogen seasonal load of inflows. On the other hand differences on the time pattern of changes of T-N content and T-P content of the sediment between the sampling stations near inflows and the sampling station in deep waters gives a measure of the extent of lake pollution by the inflows. Finally, several isolated events like storms can bring nutrients in various ways from urban areas, from marshes and from agricultural land which may produce high values of T-P and T-N in the sediment[7,8].

From the above discussion and the obtained results as reported in the results section it is obvious that:

(A) the T-N content in the sediment remains nearly constant during the whole year to an overall average value of 2.0 to 3.0 mg/g and this suggests that the biomass formed during the period of measurements is almost equal to the biomass converted to ammonia and nitrogen through the action of bacteria and fungi in the sediment. A small scale seasonal variation is also observed as follows:

- A small increase of the average value is observed during the dry months of July up to September which may be justified by the increase of agricultural runoffs as evidenced by the relatively higher T-N content in sediment of the sampling stations near the inflows and by the significant decrease of underground clean inflow through the shallow holes.
- A small decrease of the average value is observed during the January samples due to the clean up of the lake waters from the rain water of previous months.
- The T-N content changes considerably between sampling stations; that is more pronounced during eutrophic periods (September, October and November) where it

  (i) increases considerably at the sampling station 5 and less in sampling station 3

  (ii) remains nearly constant between 1.6 to 1.8 mg/g at the sampling station of 2

(B) the average within sampling stations T-P content of the sediment shows a seasonal variation and follows the trend of changes of the T-P content of sediment that is found in sampling stations that are close to the inflows. The specific trend is as follows:

- The rainy months of January and February increase the level to around 11.0 mg/g
- The dry months following period of spring rains like May and June show very low levels, less the 2.0 mg/g
- The highly eutrophic month of October shows a very low level due to rapid conversion of T-P content of sediment to orthophosphates to satisfy the great demand for the formation of phytoplankton
- The rainy month of November brings phosphorous from the agricultural runoffs as is evidenced by the relative high increase of T-P content of the sediment in sampling station 4
- Finally the low levels of the month of December suggest a clean up procedure as evidenced from the results of sampling stations 4 and 5

(C) The ammonia content of the pore water of the sediment shows a relatively high level for nearly all sampling stations during the dry months June and July showing the rather increased septic activity of bacteria and fungi in this period. During September and October, which are months of temperature inversion, the ammonia level is decreased to almost zero; the eutrophic behavior during these months is also contributing to this decrease. The increase of the level in November and December is very low suggesting the low septic activity of bacteria and fungi during these cooler months. Finally, in January and February there is only at specific sampling stations evidence for the formation of ammonia.

(D) The orthophosphate content of the pore water of the residue is worth noticing because it is relatively constant all over the seasons at 10–20 mg/g, except of July which is very high at the level of 75 mg/g at almost all sampling stations suggesting either an inflow of large quantities of orthophosphates or that the pH in the sediment pore water is decreased which is rather unlikely since the ammonia content at this month is found to be high.

(E) The nitrate content of the pore waters is found to be zero during the whole period of the year except the month of October and especially in sampling station 1 (25.0 mg/g). This is due to an isolated event from the shops of the nearby coast or the boats that go to the island; a rather large quantity of nitrates was found in the residue, also, at the same month (270 μg/g) but this was found at sampling station 4 which is far away from the station 1. The high value of nitrate in sediment of station 4 can be justified by the agricultural runoffs since this station is close to the agricultural inflow and the autumn rains are more likely to bring nitrates.

CONCLUSIONS

1. The average T-N content of the residue remains constant all over the period.
2. The average of T-P content of the sediment is seasonal and increases from July.
3. The T-P content is mainly due to the inflows from the agricultural runoffs and the trench of Kosmira.
4. The high level of sediment T-N and T-P content in September gives rise to the eutrophic behavior of the lake.
5. The high population of bacteria and fungi decompose the nitrogen and phosphorous compounds from the sediment to provide the nutrients for the formation of phytoplankton.
6. When the T-P content of the sediment is largely consumed the eutrophic behavior decreases.
7. The drop of temperature from December decreases bacterial activity and the T-P in the sediment starts increasing and reaches a rather high value.
8. The sediment of the lake has a septic activity during the late spring month.
9. Isolated events beyond control have also been observed from the exceptional high levels of orthophosphates in the pore water at specific sampling dates, and from the existence of ammonia and nitrates in pore water at specific sampling stations.

Acknowledgements

This study is part of a project under the title Evaluation of Restoration Measures of Lake Pamvotis. The project has been supported by the Ministry of Environment of Greece, the office of the Mayor of Ioannina and A.S. Onassis Public Benefit Foundation and has been carried out by the University of Ioannina and Jorg Imberger, Director of the Centre for Water Research (CWR) at the University of Western Australia.

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