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Διαχείριση Παρακτίων Περιοχών

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- Το παρόν εκπαιδευτικό υλικό έχει αναπτυχθεί στα πλαίσια του εκπαιδευτικού έργου του διδάσκοντα.
- Το έργο «**Ανοικτά Ακαδημαϊκά Μαθήματα στο Πανεπιστήμιο Αιγαίου**» έχει χρηματοδοτήσει μόνο τη αναδιαμόρφωση του εκπαιδευτικού υλικού.
- Το έργο υλοποιείται στο πλαίσιο του Επιχειρησιακού Προγράμματος «Εκπαίδευση και Δια Βίου Μάθηση» και συγχρηματοδοτείται από την Ευρωπαϊκή Ένωση (Ευρωπαϊκό Κοινωνικό Ταμείο) και από εθνικούς πόρους.

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Chemical Characteristics of Aetoliko Lagoon, Greece, after an Ecological Shock

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A series of chemical parameters were studied in the water, particulate matter and sediments of Aetoliko lagoon, a wetland in western Greece, after an ecological impact at the end of November 1990, which resulted in massive death of fish.

The permanent anoxic conditions in the deeper water layer of the lagoon, with the simultaneous formation of hydrogen sulfide, are the main characteristics of the system. The dramatic reduction of the dissolved oxygen in the surface water which was substituted by the hydrogen sulfide of the near bottom water layer caused the sudden death of organisms.

This phenomenon also affected the nutrients. Ammonia was the main nitrogen form; phosphates and silicates were concentrated in near bottom waters, and the concentrations of nitrates and nitrites were much lower in December than 3 months later in the surface waters.

The behaviour of trace metals also indicated that in the extraordinary conditions studied, the main mechanisms of transport of metals among the main phases of the system (dissolved–particulate–sediments) were severely disturbed.

The Aetoliko lagoon is the northern part of an extensive wetland area in western Greece (Fig. 1). The main part of the system is the lagoon of Messolonghi. This wetland is of great ecological importance and is protected under the Ramsar convention. The system is polluted from sewage effluents from the small towns of Messolonghi and Aetoliko and from the intensive agriculture in the neighbouring area (Bonazountas & Kallidromitou, 1992).

Fisheries are a traditional activity in the lagoons and are very important for the local economy.

The area covered by Aetoliko lagoon is about 15×10^6 m² and its maximum depth is 25 m, whereas the maximum depth of the wider Messolonghi lagoon is about 2 m. The lagoons are connected through a narrow channel, about 1 m deep, under the bridge of Aetoliko.

Work is ongoing for the diversion of two rivers (Acheloos and Evinos) in the vicinity of the wetland, which may disturb the system.

A significant environmental disturbance in the Aetoliko lagoon had taken place during the 1970s when huge quantities of fresh water from the lake of Lysimachia were transferred to the lagoon after their use in irrigation. This caused an extensive alteration of the ecological characteristics of the area. This water transfer ceased in 1973 and the system returned gradually to its previous state (Avramidou-Kallitsi & Koutsoukos, 1990).

The morphology of the lagoon permits the development of a permanent pycnocline. The range of salinity in surface waters is 14–19‰ and in the near bottom waters 28–30‰ (Rigopoulos, 1988).

The isolation of high salinity water in the near bottom layer, in combination with the high primary productivity of the lagoon, have led to anoxic conditions in this layer (Danielides, 1991). The reduction of sulfates has led to the production of hydrogen sulfide (Scoullos, 1987).

At the end of November 1990 after a period of strong south winds, massive mortality of fish was observed in the Aetoliko lagoon along with an intense odour of hydrogen sulfide in the area. This phenomenon had been observed a few times in the past decades, it was mentioned by some fishermen but it had never been studied.

Sampling and Methods

In this study a series of chemical parameters were measured in two sampling periods, the first some days after the observation of dead fish (2-12-1990) and the second three months later (3-3-1991). The second sampling was designed to investigate any possible return of the system to its normal state. The examined area and the sampling stations are shown in Fig. 1. Station 1 has the greater depth of 25 m.

Temperature, dissolved oxygen, pH and salinity were measured *in situ*.

Water samples were taken with Hydro-Bios sampling bottles. The samples were filtered in succession through
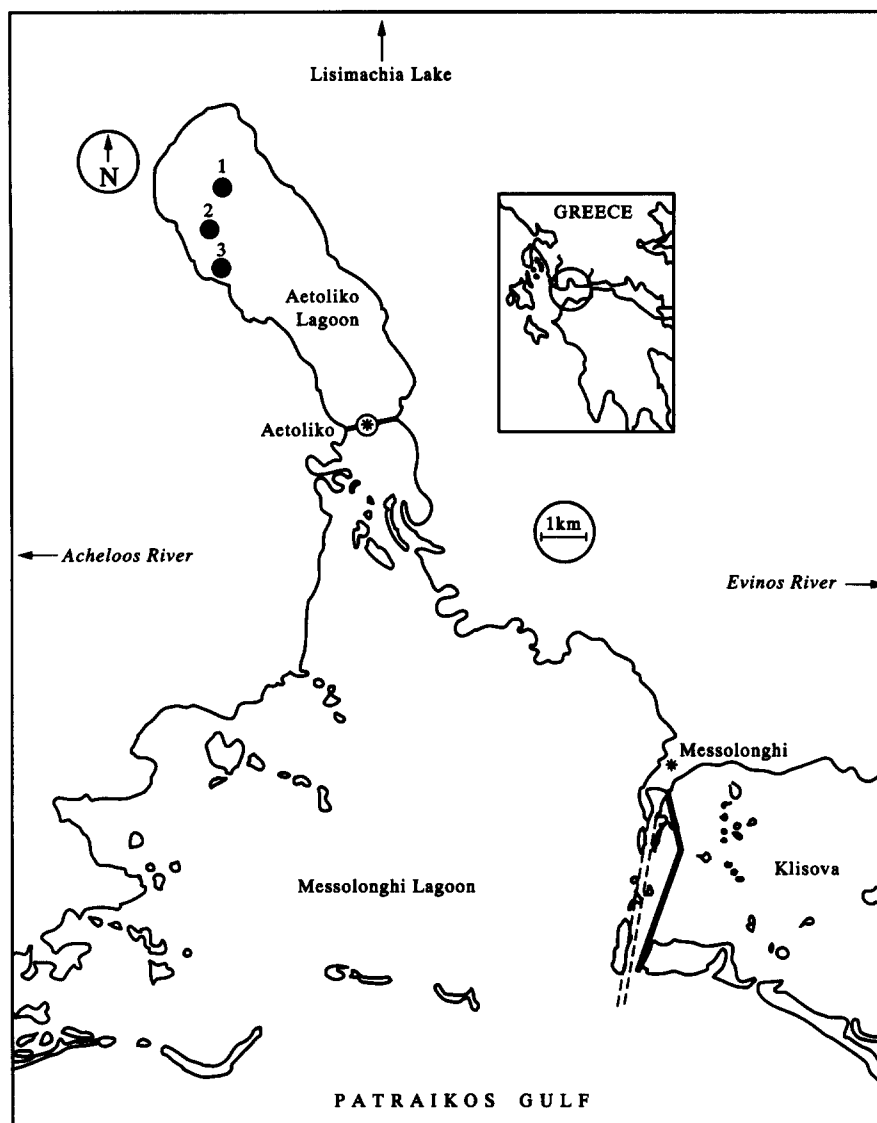
Fig. 1 The area of Aetoliko and Messolonghi lagoons with the sampling stations.

8 μm and 0.45 μm Millipore membrane filters using peristaltic pumps. All sample handling was carried out in a clean box.

Nutrients were determined with standard spectro-photometric methods (Strickland & Parsons, 1968), in a Hitachi 100-60 spectrophotometer with a 5 cm length cuvette.

Trace metals in the dissolved phase were preconcentrated on a chelex-100 resin column, according to a slight modification of the Riley & Taylor (1968) method (Scoullos & Dassenakis, 1984). Standard addition experiments showed the following recovery of trace metals: Cu: 95%, Pb: 94%, Mn: 90%, Ni: 92%.

The filters with the particulate matter were treated with boiling concentrated nitric acid in covered Teflon beakers.

Undisturbed sediment minicores (10-60 cm long) were collected from a rubber boat by a SCUBA diver using Perspex tubes. After sampling, each core was sliced into subsamples of 2 cm thick. The slices were wet sieved through a nylon screen of <61 μm mesh and dried at 40°C. All chemical treatments were performed on the <61 μm sediment fraction, which is

the most interesting fraction for trace metals studies (Forstner & Salomons, 1980).

For the extraction of the total metal content of sediment the samples were treated with a mixture of concentrated HNO_3-$HClO_4$-HF in covered PTFE beakers placed on a hot (200°C) plate, (UNEP, 1985). For the extraction of the non-lattice held metal content the samples were leached for 12 h with 0.5 N HCl (Agemian & Chau, 1976).

Trace metal concentrations were determined in a Perkin-Elmer 403/HGA-400 Graphite Furnace Atomic Absorption Spectrophotometry (GFAAS) system for the dissolved and particulate metals and a Varian AA-775 Flame AAS system for the metal content of the sediments.

Organic carbon in sediments was determined by using the Gaudette et al. (1974) method.

The relative standard deviation of the measurements $[S_r=(S/\bar{x})\times100]$ was <5% for nutrients and trace metals in sediments and <10% for dissolved and particulate trace metals.

Our laboratory participated successfully in the international intercalibration exercise of IAEA (Inter-

national Atomic Energy Agency) (IAEA/AL/053, IAEA/MEL/49, 1991), and now is participating in a project for Quality Assurance of Information for Marine Environmental Monitoring in Europe (QUASIMEME), which is co-ordinated by the Scottish Office Marine Laboratory.

Results and Discussion

Hydrological parameters

The vertical distributions of dissolved oxygen, temperature, and particulate matter at Station 1, for the two samplings, are shown in Fig. 2.

The main characteristics of the first period were the very low concentrations of dissolved oxygen throughout the water column (Fig. 2A) and the existence of hydrogen sulfide in elevated concentrations (> 100 ppm) even in surface samples (Vougioucalakis et al.,

(A) Dissolved oxygen

(B) Temperature

(C) Suspended matter

Fig. 2 Distributions of dissolved oxygen, temperature and particulate matter in the water column of Station 1.

1991). This caused the massive death of the fish. At the second sampling period the saturation of water in dissolved oxygen was > 75% in depths < 10 m, suggesting that the system had almost returned to its normal state in this respect.

Another characteristic of the system was the lack of thermocline in December (Fig. 2B). In the March sampling the temperature of the near bottom layer had remained quite high, while the 5–15 m layer was much colder, due to the lower atmospheric temperatures of December and January. The halocline was also weak in December as the surface salinity was 16.6‰ and the near bottom one 21.8‰ since in March the range was 18.4–27.5‰.

pH in surface waters was lower in December (7.4–7.8) than in March (7.8–8.2) due to the partly anoxic conditions. In depths > 20 m the pH was < 7 (6.7–6.9) in both samplings.

A conclusion that could be obtained from these observations is that a stirring of water masses of the lagoon took place at the end of November, which resulted in the substitution of dissolved oxygen in surface waters by the hydrogen sulfide found in great concentrations in the bottom water layer.

From Fig. 2C it becomes clear that the suspended matter which had been stirred up during the end of November had settled down in March as its maximum concentration was observed in the near bottom layer.

Nutrients

High concentrations of phosphates (> 10 μg at l⁻¹), silicates (> 200 μg at l⁻¹) and ammonia (> 400 μg at l⁻¹) are usually observed in the anoxic water layer of the lagoon (Danielides, 1991). The decomposition of organic matter is the main cause of this, but the dissolution of some sediment fractions in the lower pH of anoxic waters might also contribute (Stumm, 1973).

The concentrations and chemical behaviour of nutrients in the examined period were affected by the changes in the hydrological conditions.

The vertical distributions of ammonia, nitrates and phosphates in Station 1, for the two samplings, are shown in Fig. 3.

In the Aetoliko lagoon, ammonia is the main form of nitrogen especially in greater depths, a condition found also in other anoxic lagoons (Wollast, 1983). The maximum concentration of ammonia was measured in December at 15 m depth as a result of the disturbance of the system. The corresponding concentrations in March were lower at 15 m depth whereas at 20 and 25 m depth they were higher than those found in December (Fig. 3A) as the system had partly returned to its steady state.

Nitrate concentrations were very low during the December period (Fig. 3B) since the oxygen depletion caused their reduction to ammonia (Scoullos, 1987). In the March period their concentrations were increased in the 0–10 m depth interval but remained very low in greater depths which remained anoxic. The behaviour of nitrites was the same as that of nitrates but their concentrations were much lower (0.04–0.90 μg at l⁻¹ in December and 0.55–5.90 l⁻¹ in March).
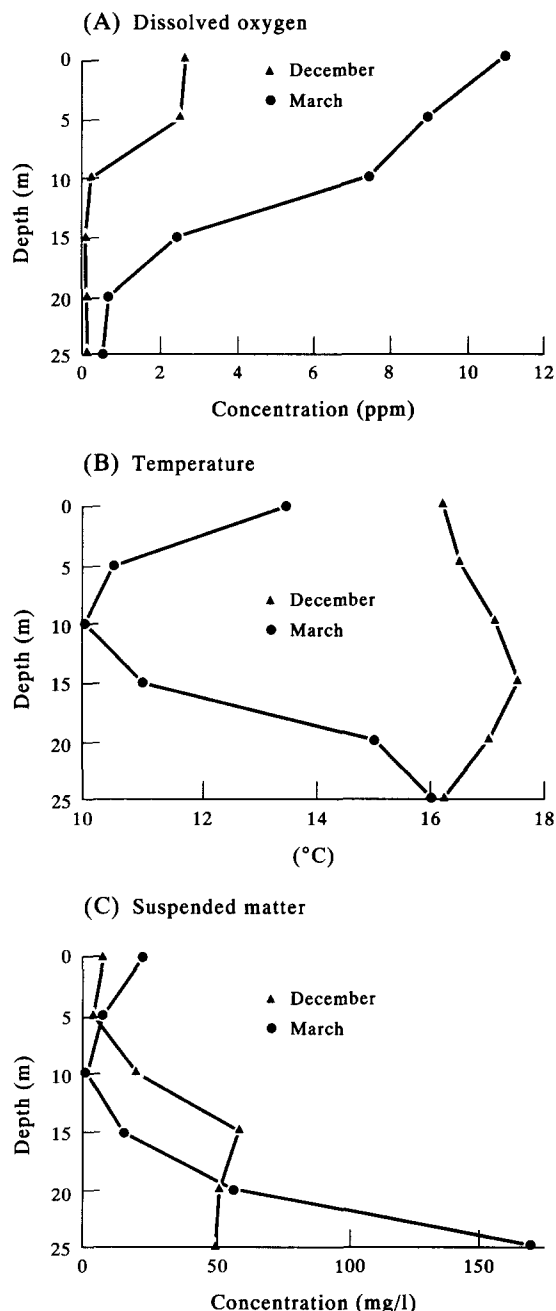
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(A) Ammonia

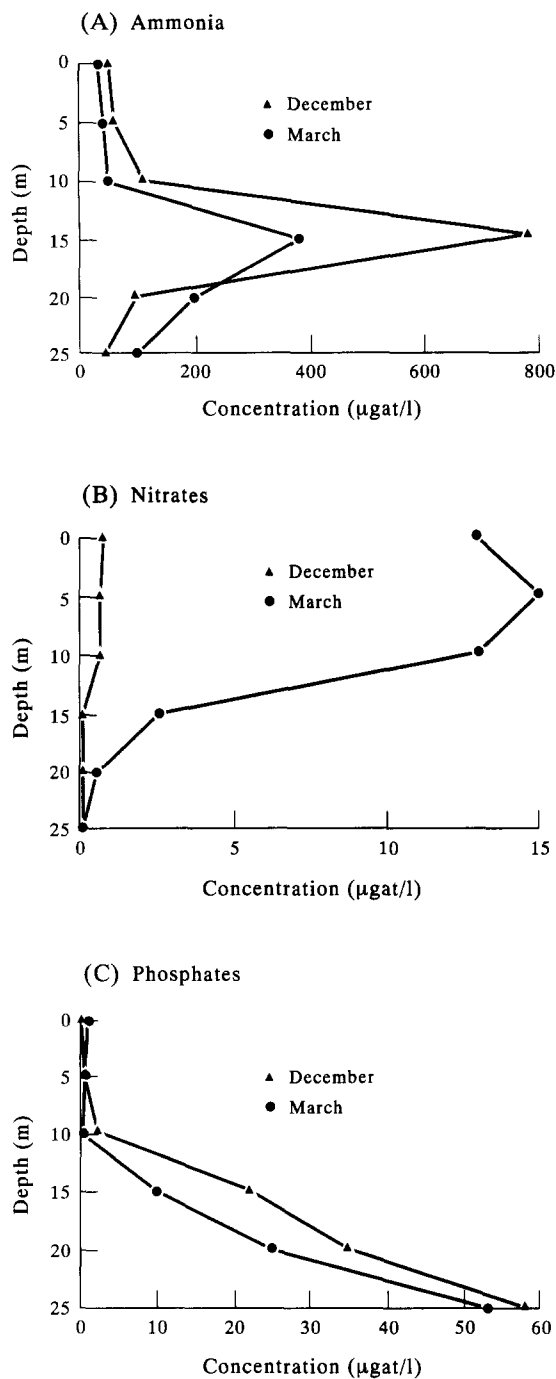## (B) Nitrates

(C) Phosphates

Fig. 3 Distributions of ammonia, nitrates and phosphates in the water column of Station 1.

The concentrations of phosphates and silicates were increased in the deeper, near bottom, water layer as shown in Fig. 3C for phosphates. Silicate concentrations in the > 20 m depths were greater than 500 μg at l⁻¹ while in surface samples were lower than 50 μg at l⁻¹. The slightly increased concentrations of phosphates at 10–20 m in December were the result of the disturbance of the system.

The ratio NO_3/NH_4 was < 0.02 in December throughout the water column of Station 1 and about 0.1 at Station 2. The corresponding values in March increased to 0.05–0.34 for the surface layer (0–15 m depth) at both stations as the system returned gradually to its normal state. The ratios still remained very low in comparison with non-polluted sea areas (Friligos, 1980).

Trace metals

The concentrations of trace metals in Aetoliko lagoon are generally elevated due to the morphology of the area but also due to pollution (Scoullos *et al.*, 1992).

The vertical distributions of concentrations of dissolved and particulate Mn, Cu and Ni at Station 1 are shown in Fig. 4.

The main difference in the behaviour of dissolved and particulate Mn was that the higher concentrations of the dissolved forms of the element were observed in the deeper water layer and the higher concentrations of the suspended forms were observed in the surface layer (Fig. 4A).

The abundance of the dissolved Mn^{2+} in anoxic conditions is expected, due to the reduction of the particulate forms of MnO_2, which prevails in well oxygenated coastal waters (Wollast *et al.*, 1979). This phenomenon has also been observed in other areas

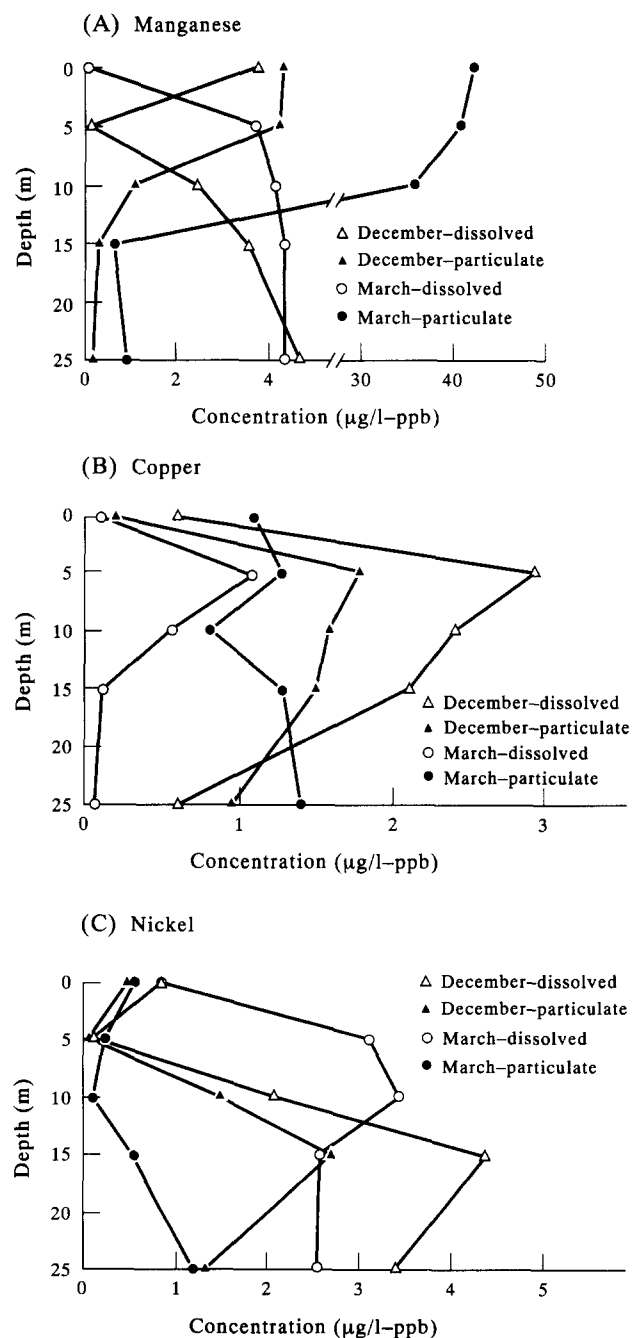### (A) Manganese

(B) Copper

(C) Nickel

Fig. 4 Distributions of dissolved and particulate Mn, Cu and Ni in the water column of Station 1.

with intermittently anoxic conditions like the Gulf of Elefsis (Scoullos, 1979). The above are also followed by lower concentrations of particulate Mn in December, mainly in the surface water layer (0–10 m) (Fig. 4A).

In both periods the maximum concentrations of dissolved and particulate Cu were measured at 5 m (Fig. 4B). The concentrations of dissolved copper increased in December but in both periods were minimized at the near bottom water layer as a consequence of the absorption of dissolved Cu on the organic matter and of the formation of CuS. The conversion of dissolved to particulate Cu was more clear in March when the disturbance of the system had almost disappeared (Fig. 4B).

The vertical distributions of dissolved and particulate Ni concentrations in Station 1 (Fig. 4C) were similar in December with minimum values at 5 m depth and maximum at 15 m depth. In March the corresponding distributions showed a relative reduction of the dissolved Ni in the deeper water layer and an increase of particulate Ni. This indicates that a conversion between the two forms takes place in this depth with mechanisms similar to those existing for Cu.

The vertical fluctuation of Pb concentrations in Aetoliko lagoon was rather limited. The concentration range was 0.11–0.82 ppb for December and 0.24–0.36 ppb for March, for the dissolved Pb, and 0.19–0.41 ppb for December and 0.05–0.41 ppb for March for the

particulate Pb. A small increase was observed in the surface samples, most probably due to the well known atmospheric origin of Pb.

In Table 1 are shown the percentages of concentrations of particulate trace metals which were collected on 8 and 0.45 μm pore size filters for the December sampling.

The percentages of trace metal concentrations of the > 8 μm fraction were generally (with few exceptions) higher than the corresponding percentages of suspended matter although; it is generally considered that the main fraction of trace metals is connected with small size particles (Duinker, 1980).

Another interesting observation which becomes clear from the data of Table 1, is that the percentages of the 15 m water layer of Station 1 were similar to those of 10 m depth of Station 2 (except Ni) since the percentages of the surface waters were different. That is an indication of the different origin of particles in surface waters of station 1 (at the centre of lagoon) and 2 (nearshore). It is also an indication that the stirring of waters during the period studied caused the homogenization of the suspended matter at the intermediate depths.

Sediments

The concentrations of organic carbon and of the extractable and total Zn, Ni, Cr, Cu, Mn and Fe in three sediment cores are shown in Table 2.

The sediments of Aetoliko lagoon mainly consist of

TABLE 1
Fractionation of suspended matter and particulate trace metals.

Station	Depth	Suspended matter A %	B	Cu A %	B	Mn A %	B	Ni A %	B	Pb A %	B
1	0	53.8	46.2	90.0	10.0	85.5	14.5	98.0	2.0	71.2	28.8
	15	28.9	71.1	46.0	54.0	32.0	68.0	6.3	93.7	51.7	48.3
	25	41.9	58.1	42.8	57.2	64.3	35.6	44.4	55.6	65.0	35.0
2	0	68.5	31.5	61.2	38.8	51.4	48.5	65.7	34.3	64.0	36.0
	10	24.8	75.2	40.4	59.6	34.6	65.4	32.0	78.0	45.8	54.2

Fraction A: Particles > 8 μm.
Fraction B: 8 μm > particles > 0.45 μm.

TABLE 2
Extractable and total trace metals in sediments of Aetoliko lagoon.

Station	Depth	Organic carbon %	Zn Extr. ppm	Tot. ppm	Ni Extr. ppm	Tot. ppm	Cr Extr. ppm	Tot. ppm	Cu Extr. ppm	Tot. ppm	Mn Extr. ppm	Tot. ppm	Fe Extr. ppm	Tot. ppm
1	0–2	3.1	59.0	122.2	35.5	75.6	42.3	140.0	47.6	88.0	497	837	10 350	41 700
	2–4	3.7	60.6	99.8	43.4	64.9	46.4	105.8	47.6	82.6	464	621	9920	32 500
	10–12	2.6	62.8	91.6	52.4	57.3	50.4	122.3	50.7	82.3	371	522	9920	29 550
	20–25	2.9	57.4	136.3	49.0	82.2	46.4	145.7	52.0	110.9	517	886	11 600	45 600
	55–60	3.3	62.3	132.9	42.2	79.6	48.4	188.2	39.5	96.6	537	947	9490	47 200
2	0–2	3.8	67.2	113.3	52.4	79.8	54.5	114.8	143.2	114.3	796	938	10 800	28 400
	2–4	3.6	63.9	92.2	55.7	73.8	56.5	111.2	86.4	108.6	623	726	9920	26 500
	10–15	2.9	59.0	102.2	45.6	59.0	44.3	114.3	69.5	84.3	603	761	9490	26 300
	19–21	2.7	67.2	120.9	44.5	70.5	52.4	125.8	68.9	98.8	616	905	10 800	39 600
3	0–2	0.3	50.8	108.6	56.8	71.1	48.4	67.1	66.1	68.9	499	517	6050	9400
	2–4	0.3	59.0	86.8	53.4	67.0	56.5	57.9	61.4	78.9	397	524	7340	8690
	8–11	0.4	49.2	103.4	60.3	73.5	50.4	70.6	70.1	120.0	431	528	6480	12 900
% Extr./Tot.	Range		42.1–69.3		47.0–91.4		25.7–97.7		40.9–95.9		56.7–96.5		20.1–84.5	
	Mean		55.9		70.1		49.4		67.0		74.3		39.7	

muddy sand and clay. The <61 μm fraction represents more than 95% of the entire sediment. The concentrations of organic carbon at the surface sediments were lower than the corresponding concentrations of the neighbouring Messolonghi lagoon which ranged between 4–6% (Voutinsou-Taliadouri, 1989).

In most cases, a downcore reduction of the total metal content of the sediments was observed in the upper 10 cm of the cores indicating recent pollution, although this trend was not followed by the concentrations of extractable metals. The values increased again at the 20 cm sediment layer.

Fluctuations of the values of the ratio [extractable]/[total] metal were also interesting. The ratio was elevated (mean values >65%) for Mn, Cu, and Ni. This indicates increased mobility of those metals in the system, which was also confirmed from the behaviour of their dissolved and particulate forms and is of great ecological importance. This behaviour has also been observed in other coastal systems too, mainly for Mn (Scoullos *et al.*, 1988). Zinc showed an intermediate trend, whereas the concentrations of the non extractable fraction are dominant for Cr and Fe.

The concentrations of trace metals in the sediments of the Aitoliko lagoon are elevated in comparison with other non-polluted Mediterranean areas (indicative values: Cu < 30 ppm, Cr < 40 ppm, Ni < 50 ppm). These are lower than the polluted areas in Greece and the Mediterranean (indicative values Cu > 80 ppm, Ni > 100 ppm, Cr > 100 ppm, Zn > 200 ppm) (UNEP 1989).

The discharge of urban effluents, the atmospheric inputs and the washout of cultivated land are possible causes of the enrichment of sediments in trace metals.

Conclusions

The massive extinction of fish in the Aetoliko lagoon during the end of November 1990 was the result of an intense disturbance of the system which led to the substitution of the dissolved oxygen in the surface water with hydrogen sulfide of the anoxic water layer of the lagoon. This disturbance affected almost all the chemical parameters, e.g. pH, nutrients, trace metals.

High concentrations of ammonia at 15 m depth, and phosphates and silicates at the near bottom layer in combination with the low concentrations of nitrates and nitrites were the main characteristics in December. The system returned to its previous state in March.

A disturbance of the normal vertical distributions of trace metal concentrations in the water column of the lagoon was apparent for Mn, Cu and Ni. Transport of metals between sediments and their dissolved and particulate forms was also indicated.

The return of the system to its previous 'normal' state was rather quick, since 3 months later the distributions of the parameters studied showed an almost complete re-establishment of expected physiological seasonal conditions.

The positive repetition of such a massive extinction of fish in Aetoliko lagoon when meteorological conditions permit, as at the end of November 1990,

cannot be excluded and this fact has caused increasing anxiety in the local population as fishing is an occupation of great importance for the local economy. Technical arrangements which will facilitate the water movement between the Aetoliko and Messolonghi lagoons may make a positive contribution to the environment of the area but all the ecological dimensions of such arrangements must be studied.

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