Global Nest: the Int. J. Vol 5, No 3, pp 127-133, 2003

NUTRIENT AND TRACE METAL DISTRIBUTION IN THE GULF OF ASTAKOS, AETOLOAKARNANIA, GREECE.

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Selected from papers presented at the 8th Conference on Environmental Science and Technology, 8-10 September 2003, Lemnos, Greece.

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ABSTRACT

The Gulf of Astakos is a very important embayment of the Ionian Sea, as it offers an ideal environment for extensive aquacultures with tourism, agriculture and commercial activities. In view of the need for sustainable development of the region, the state of the gulf's quality was assessed on the basis of determinations of nutrients (NO_3^-, NO_2^-, PO_4^{3-}, SiO_4^{4-}, and NH_4^+) and trace metals (Cd, Cu, Fe, Pb, Ni and Zn) along with physicochemical parameters in the seawater. The samples were collected in three sampling cruises during February 2000, May 2000 and July 2000 from ten sampling stations.

Nutrients were determined by standard colorimetric methods UV-Vis, using a Varian spectrophotometer. Dissolved metals were pre-concentrated using Chelex-100 resin. Particulate metals were digested following a hot plate digestion in teflon bombs. Metal concentrations were determined by Flame or Graphite Furnace Atomic Absorption techniques with a Varian spectrometer equipped with Zeeman background correction according to the concentration levels.

Seasonal fluctuations were recorded in both nutrient and metal concentrations presenting proportional fluctuations with those of the marine euphotic zones. The reduction of concentrations can be attributed to the low rainfall seasonal height, the reduced flow of the streams and in the bioaccumulation and consumption from the phytoplankton cells that bloomed during spring and early summer.

KEYWORDS: Astakos Bay, Nutrient Concentrations, Trace metals, Water Column

INTRODUCTION

Coastal areas of the Mediterranean are some of the most popular tourist destinations, but also suitable for a series of other activities, several of which may become mutually exclusive (Dassenakis *et al.*, 1999). Over the last two decades the development of aquaculture in cages in coastal marine areas, was very rapid in Greece. More than 200 units have been established producing over 20.000 tones of fish, bringing Greece to the first position as producer among the European Countries (Belias *et al.*, 1995).

The local authorities of Astakos were encouraged to assign a series of studies to the University of Athens in order to estimate the overall state of the environment of the Gulf as a background for a sustainable development plan for the region. The present paper reports the results obtained from the study of the marine environment carried out within 2000 and complements previous works of our team (V. Bikas, C. Belias, G. Kostopoulou).

STUDY AREA

Astakos Gulf was chosen for this study as an important area in the Ionian, with signs of slow growth rate but good perspectives as an important touristic, economical and transportation center for western Greece. It also exhibits the typical characteristics of a provincial area with lack of basic infrastructure such as waste treatment for the Municipality, organized solid waste deposition area, a controlling system for the primary production sector (especially for fertilizers, pesticides and fish meal) and the operation of stock-breeding enterprises (Eleftheriadou, 2001).

In the Astakos sea area 9 pisciculture enterprises are operating, two of them among the largest in Greece. Important, growing, agriculture and stock breeding facilities are located in the Astakos Gulf watershed. The touristic sector includes small-scale enterprises with only 200-bed capacity in the Municipality, with plans for exploitation of specific municipality coasts and the development of agro tourism. It is important to report that west of the Municipality is located a vast and modern merchant harbor, with infrastructure for the development of industrial and transportation zone, constructed by the Hellenic Bank for Industrial Development but not yet operating (Eleftheriadou, 2001).

SAMPLING AND ANALYSIS

Three samplings were carried out within the year 2000 in February, May and July using a grid of ten sampling stations. Five of the sampling stations were located along the seashore, three close to aquacultures one in the middle of the bay representing approximately a bulk and one in the Ionian Sea used as a reference station. At the deeper stations water and particulate matter samples were collected from two depths (surface and close to bottom).

Seawater samples were collected using go - flo polypropylene sampling bottles and were filtered through preweighed 0.45 μm Millipore membrane filters. Temperature, Dissolved Oxygen, pH and Salinity were measured in situ. A few drops of $HgSO_4$ were added as preservative to the samples obtained for the determination of nutrients and were kept in the refrigerator (+4 ^oC).

Nutrients were determined with standard spectrophotometrical methods using a Cary 1E double beam spectrophotometer (UNEP, 1985)].

Trace metals were preconcentrated on Chelex - 100 resin columns and eluted with a mixture of 2N:1N HNO_3 and HCl (Riley *et al.*, (1968). Experiments at seawater concentration levels showed the yields resulted in average precision values from 5 % to 10 % and average recoveries of 95 % (Paulson, 1986). The particulate matter, retained in the filters, was dried to constant weight and treated with concentrated HNO_3 in covered PTFE beakers on a hot plate of 120 ^oC for several hours until total dissolution of the par-

Table 1. Sampling stations

	Sampling Station	Type	Sample Per station	Longitude	Latitude
1	Vliha	Stream	1	38^o 31’ 88”	21 ^{o} 05’ 78”
2	Ksiropotamos	Stream	1	38^o 32’ 03”	21 ^{o} 05’ 38”
3	Varagia	Spout	1	38^o 32’ 10”	21 ^{o} 05’ 08”
4	Mavrobalou	Spout	1	38^o 31’ 92”	21 ^{o} 04’ 91”
5	Louomeni	Coastal	1	38^o 31’ 78”	21 ^{o} 04’ 50”
6	Poseidon	Aquaculture	2	38^o 33’ 24”	21 ^{o} 00’ 08”
7	Podikos	Aquaculture	2	38^o 27’ 79”	21 ^{o} 04’ 02”
8	Ag. Panteleimon	Aquaculture	2	38^o 29’ 24”	21 ^{o} 05’ 58”
9	Gulf Center	Reference	2	38^o 31’ 17”	21 ^{o} 04’ 79”
10	Open Ionian	Reference	2	38^o 32’ 65”	21 ^{o} 06’ 62”

ticulate matter. Then the total metal content of particulate matter was determined employing a VARIAN 640-Z Graphite Furnace A.A.S. with Zeeman background correction and a VARIAN Spectra -200 Flame A.A.S..

The relative standard deviation of the measurements resulting from replicate determinations was < 10 %.

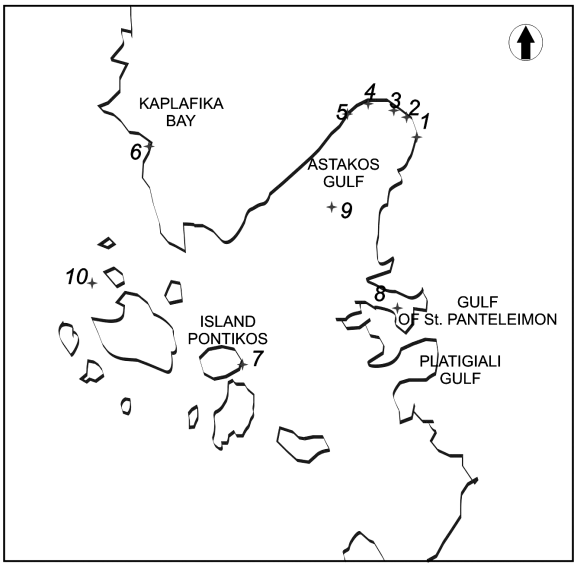

Figure 1. The study area of Astakos Gulf and the grid of stations sampled

RESULTS AND DISCUSSION

Physical Parameters

Temperature in the area was around 13 °C during winter and 23 °C during summer, whereas the range of Salinity was from 6,4 ‰ to 38,4 ‰, the range of Dissolved Oxygen 6,01 - 9,7 ml l^{-1} and the range of pH 7,02 - 8,32. Stratification was observed during summer while the saturation of dissolved oxygen exceeded 90 % in most cases. Below are demonstrated the values of the hydrological parameters measured in all stations and depths in all three samplings.

Nutrient Concentrations

From the values given on table 2 it is obvious that nitrates is the main observed form of nitrogen pollution in the area throughout the year while some elevated concentrations of ammonia were also observed mainly during spring and summer. The concentrations of nitrites, and the rest of the nutrients in a lesser degree, are also high in comparison to the levels of other Greek Gulfs. Very high values for all nutrients were measured in stream and spout stations. This indicates that runoff and washout of agricultural lands brings to the gulf considerable loads of nutrients.

The levels of phosphate concentrations are rather low suggesting phosphorus as the limiting factor

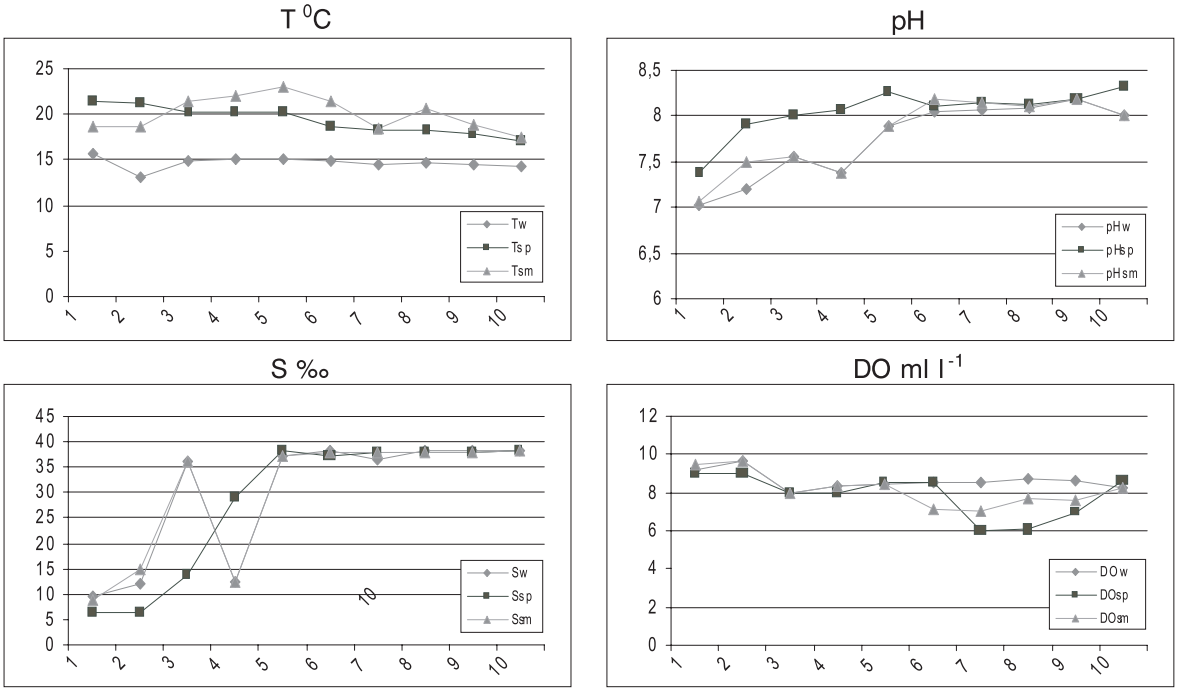

Figure 2. Physical Parameters

for these waters. According to the eutrophication scale by Karydis (1999) the gulf could be characterized as a mid-eutrophicated system. The values of silicates are elevated near shore.

The reduction of nutrient concentrations during summer especially closer to the shore is firstly attributed to the consumption of nutrients by phytoplankton and secondly to the reduction of flow rates and dry out from the streams and spouts which contribute directly to the system. The nutrient concentrations measured in all stations and depths in all three samplings are plotted in figures below.

Table 2. Nutrient Concentrations

	Nutrient	PO_4^{3-}	SiO_4^{4-}	NO_3^-	NO_2^-	NH_4^+
Winter	Average	1,87	42,86	35,23	0,27	0,74
	Min- Max	0,02-7,36	5,02-137	2,85 - 102,4	0,02-0,74	2,4-4,7
Spring	Average	0,65	29,50	54,12	0,11	14,83
	Min- Max	0,04-2,35	0-108,5	0,2 - 158,3	0,002-0,42	2,72-57,50
Summer	Average	1,06	12,64	29,74	0,36	4,07
	Min- Max	0,02-7,36	5,02-137	0,25 - 100,25	0,02-0,74	0,9-17,2

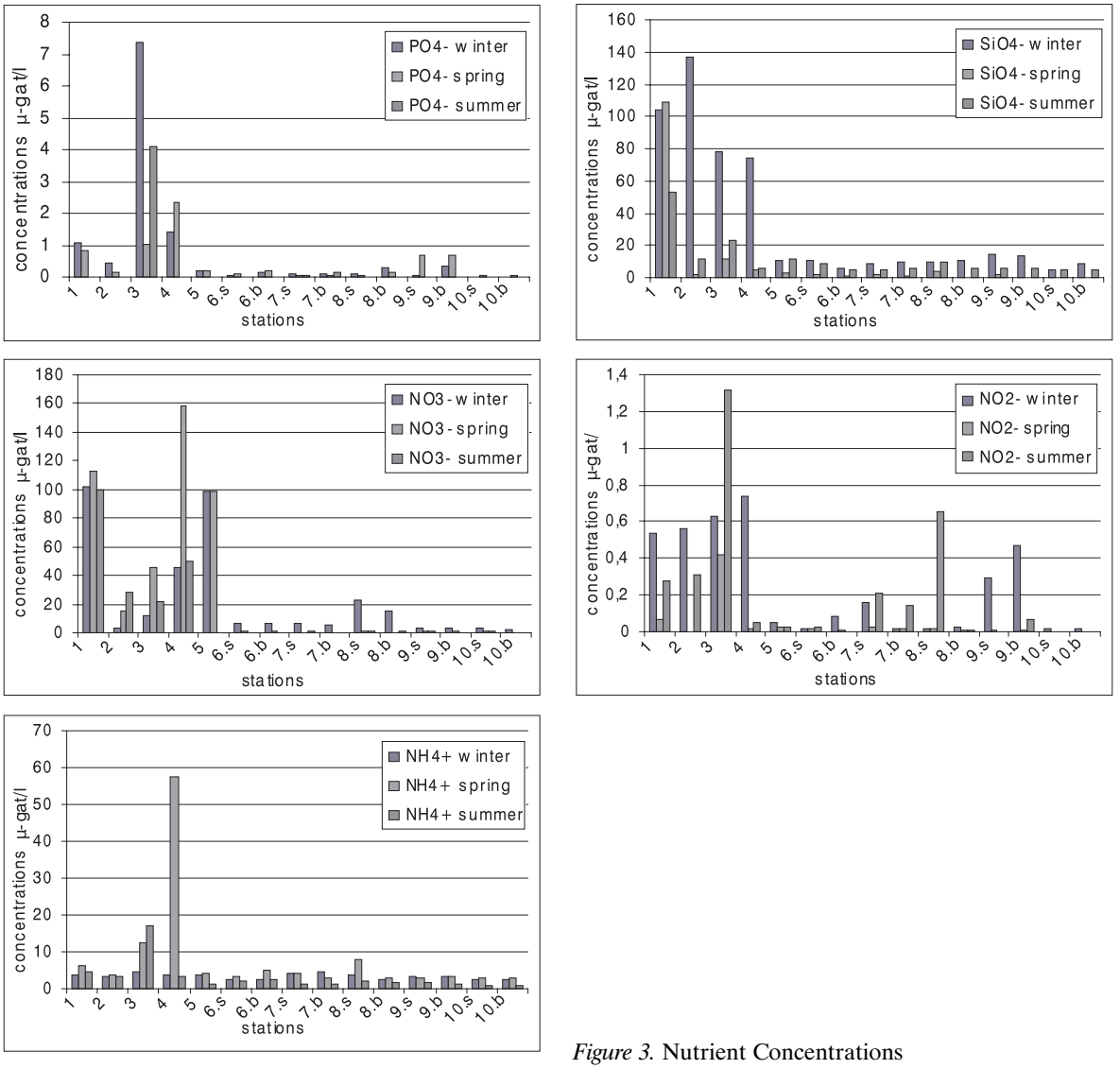

Figure 3. Nutrient Concentrations

Trace metal concentrations

The average value and the value width of the trace metals examined are given in tables 3 and 4. All metals exhibit high concentrations in comparison to the reference station (10). A comparison of the concentrations calculated for the gulf of Astakos to values calculated for Ahelloos Estuary (Dasenakis *et al.*, 1997) and Evripos straits (Dasenakis *et al.*, 1996) reveal a small pollution problem.

The dominant form for all metals except Iron (Fe) is the dissolved. High concentrations of Zinc were observed while Cadmium, Copper, Lead and Nickel had pretty much the same value width. Higher concentrations were observed at the coastal stations and at the deep samples of the aquacultures. A strong relation between Cadmium and Phosphates (comparison coefficient = 78,5 %) indicates the contribution of the use of phosphatic fertilizers to the pollution of the watershed and the sea.

High concentrations of particulate Nickel and Zinc were observed at the streams because of the corrosion brought material and wash of fertilized lands. The observed high concentrations of particulate lead (Pb) are given to land wash off for the coastal stations and for the distant stations at the intense movement of petrol engine boats from the function of aquacultures.

Seasonal fluctuations were recorded in metal concentrations presenting proportional fluctuations with those of the marine euphotic zones. The reduction of concentrations can be attributed to the low rainfall seasonal height, the reduced flow of the streams and in the bioaccumulation and consumption from the phytoplankton cells that bloomed during spring and early summer.

Regarding the partitioning between dissolved and particulate phase, in average 54 % of Cd, 49 % of Cu, 35 % of Fe, 54 % of Pb, 66 % of Ni and 58 % of Zn were found in the dissolved phase.

CONCLUSIONS

The economic development of Astakos watershed was not accompanied by the application of antipolluting techniques. The high concentrations on stream waters and spouts indicate a thoughtless use of fertilizers and pesticides in the area in addition to the release of crude municipal wastes, as there is not a wastewater treatment plant at the municipality. A more correct use of food and medicine is proposed for the many aquacultures of the area to prevent heavy pollution problems at the immediate seabed area.

Table 3. Dissolved Trace Metal Concentrations

	Trace Metal	Ni	Cu	Cd	Zn	Fe	Pb
Winter	Min- Max	0,35-2,34	0,38-4,59	0,35-0,9	6,42-30,5	9,88-150,7	0,38-2,3
	Average	0,87	1,32	0,53	13,75	28,96	1,86
Spring	Min- Max	0,23-2,79	0,58-2,4	0,2-1,24	6,95-27	2,58-36,69	0,28-1,99
	Average	0,71	1,17	0,57	15,74	7,35	0,85
Summer	Min- Max	0,17-0,79	0,04-0,86	0,22-1,30	1,14-14,66	4,93-28,03	0,31-1,70
	Average	0,34	0,15	0,38	5,48	8,56	0,64

Table 4. Particulate Trace Metal Concentrations

	Trace Metal	Ni	Cu	Cd	Zn	Fe	Pb
Winter	Min- Max	0,2-0,53	0,31-2,95	0,05-1,69	8,14-38,56	4,88-106,07	0,52-2,02
	Average	0,32	1,09	0,64	15,96	34,03	1,07
Spring	Min- Max	0,10-0,95	0,22-0,94	0,01-0,92	1,48-12,59	1,85-65,02	0,28-1,93
	Average	0,34	0,59	0,44	4,77	18,83	1,06
Summer	Min- Max	0,06-1,88	0,22-0,85	0,02-0,91	1,41-10,07	6,3-293,77	0,22-1,74
	Average	0,34	0,48	0,36	4,03	63,55	0,48

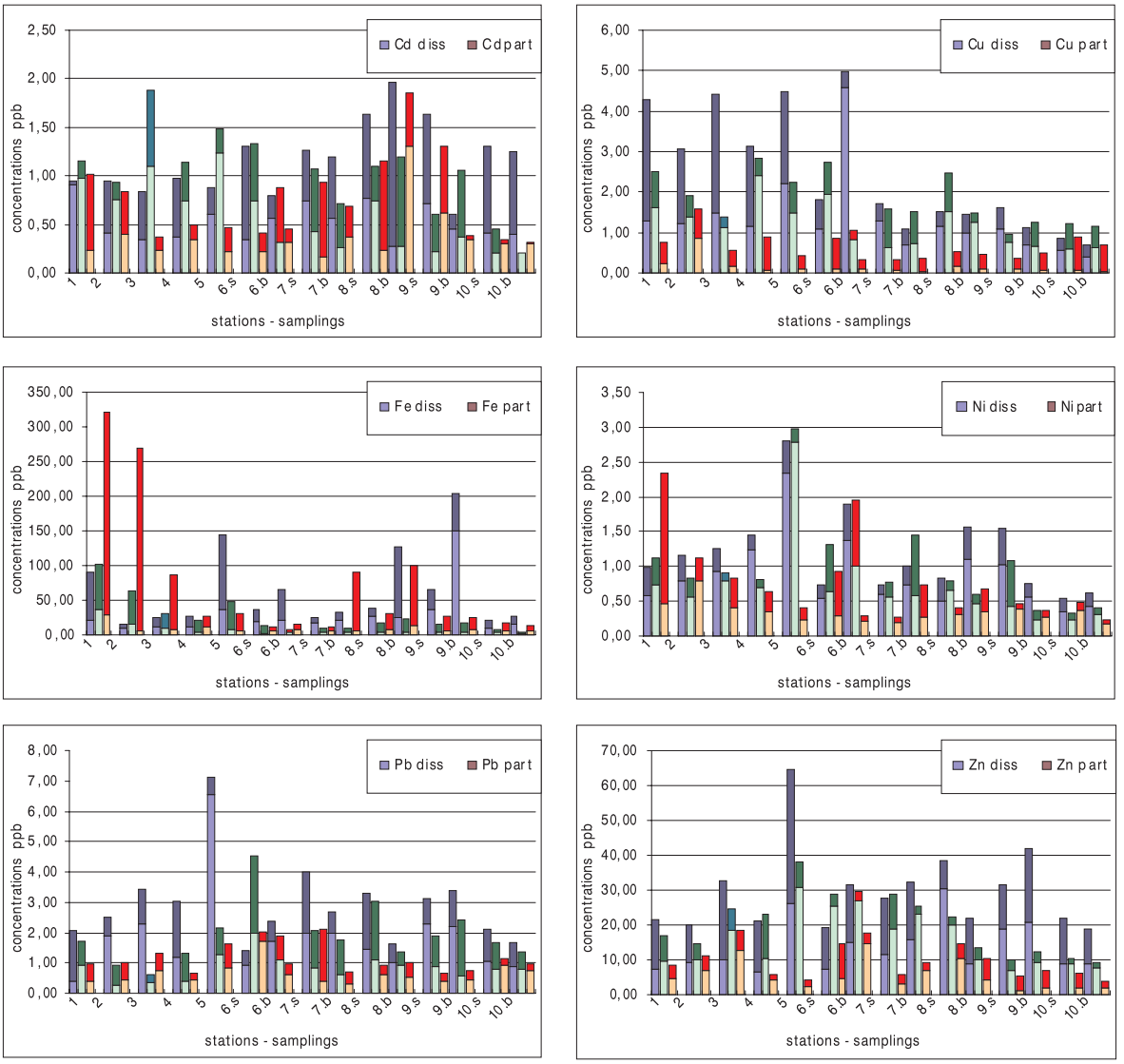

Figure 4. Trace and Particulate metal Concentrations

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