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Arsenic in the Marine Environment of Five Gulfs of Greece

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Arsenic (As) is considered a toxic trace element for plant, animal and human organisms. As, and certain arsenic compounds, have been listed as carcinogens by the Environmental Protection Agency of USA. As enters the marine environment through various industrial activities as well as insecticide production and use.

Neutron activation analysis (NAA) is a very sensitive, precise and accurate method for determining As. This paper is a review of research studies concerning As in the marine environment of five gulfs of Greece by NAA performed at our Radioanalytical Laboratory. The objectives of these studies were: (a) to determine the levels of As concentrations in marine samples from 5 gulfs of Greece, (b) to pinpoint As pollution sources and, if possible, to estimate the extent of As pollution, (c) to find out whether edible marine organisms from the Gulfs of Greece receiving domestic, industrial and agricultural wastes have elevated concentrations of As in their tissues that could render them dangerous for human consumption.

A radiochemical NAA method (GRIMANIS 1969) was mostly applied for determining As in seawater and marine organisms. Seawater filtered through 0.45 μm pore size filter. Instrumental NAA was used for As determination in bottom sediments.

Arsenic in the marine environment can be methylated by anaerobic organisms to dimethylarsine (McBRIDE and WOLF, 1971). It appears that in marine organisms the main form is organic As which is much less toxic than inorganic As.

Arsenic has been determined in marine samples collected from 5 Gulfs of Greece (Saronikos, Evoikos, Korinthiakos Gulfs, Kissamos Gulf in Crete and Gera Gulf in Lesbos) shown in the map of Greece (Fig. 1). Saronikos Gulf was the most extensively studied within the framework of the United Nations Environment Programme for Mediterranean Pollution Monitoring Research Project (UNEP/MED POL).

The discharge of industrial and domestic wastes entering Northern Saronikos Gulf through the Athens Sewage Outfall (ASO), a Fertilizer Plant (F.P) and other industries outside Piraeus harbor has led to elevated concentrations of As in seawater and sediments over at least 100 km^2 of the Northern Saronikos Gulf seafloor.

The distribution of As in the water column (total particulate and dissolved) and in sediment core samples (total, [all chemical forms of As present in sediments], 0.5N HCl extractable [anthropogenic As], and residual [non anthropogenic]) from N. Saronikos Gulf was determined:

In seawaters most of the As was found in dissolved form (94-99.9 per cent) with a trend of increasing concentration with depth. Concentrations ranged as follows: 2.4-7.2 μg/l for total As, 2.3-7.2 μg/l for dissolved As and 0.01-0.27 μg/l for particulate As. Maximum values of As were found near the ASO.

In sediments As concentrations (total) increase from background levels of about 10 μg/g to 570 μg/g near the ASO up to 2900 μg/g near the F.P (Perhaps to intermittent dumping of arsenopyrites) Total As concentrations tend to increase with sediment depth. Residual As concentrations are the predominant form in core samples near the ASO; near the F.P extractable As is the predominant form. In sediments from stations not under the influence of the pollution sources As was found to be mainly in residual form.

The partitioning of As (ANGELIDIS and GRIMANIS, 1987) into three fractions (reducible by acidified hydroxylamine hydrochloride [As scavenged by Fe/Mn hydrous oxides), oxidizable by acidified hydrogen peroxide [As contained in organic matter and sulfides] and the residual after the previous extractions [detrital As] of Saronikos Gulf surface sediments was determined by using a sequential extraction technique (SALOMONS and FORSTNER, 1980). The arsenic content in the reducible and oxidizable fractions increases in polluted sediments near the ASO and the FP. In non-polluted sediments the residual fraction is the most important carrier of As.

At a distance of about 5 km from ASO seawater and sediments contain total As concentrations which can be considered natural background levels for Saronikos Gulf.

Fig. 1. GREECE

Gulfs investigated are shown with No.:

1 = Saronikos
2 = Korinthiakos
3 = Evoikos
4 = Gera (Lesbos)
5 = Kissamos (Crete)

Seawater and sediment samples showed higher concentrations of As southwest than southeast of the pollution sources. This distribution suggests a westward transfer of As, probably due to the cyclonic movement of the water masses of the Saronikos Gulf.

No strong accumulation has been detected in seawaters and sediments of Evoikos, Korinthiakos, Kissamos and Gera Gulfs.

Concentrations of As found in the flesh of benthic fish species such as Pagellus erythrinus, Sargus annularis and Mullus barbatus collected from Northern Saronikos Gulf were twice as high as those from other Gulfs of Greece (Evoikos, Korinthiakos, Kissamos and Gera Gulfs). These high concentrations of As were comparable to natural "background" levels so that these benthic fish species do not reflect the very high As concentrations found in seawaters and sediments of N. Saronikos Gulf.

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Factors controlling secondary productivity (Level 1 and 2) of polluted temperate coastal waters (Izmir Bay, Aegean Sea): a multivariate model

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In coastal areas that are characterized by well-mixed water column depending on the continuous water movements, inputs of nutrients by rivers and sewages cause a complexity in the planktonic food web. Typically, there exist excessive amounts of phytoplankton in such waters. However, this high primary productivity has not reflected to level 1 and 2 secondary productivity just enough because of complex relationships among species and eu- or hypertrophicated environment such as pollution caused high mortality in certain development stages, different tolerance to different pollutants, variations in feeding habits during the pollution process, pollution controlled competition and even the decreasing of zooplankton filtration rates due to dense phytoplankton cells etc. (BOUGIS, 1976).

In the present study, it was analyzed and discussed how far the eutrophication or hypertrophication have affected zooplankton abundance. The results were represented as a multivariete model.

The samples evaluated in this study were collected with a 5 liter universal series water sampler down to 15 m. depth by 0.5, 2.5, 5.0,10 and 15 m. intervals from 6 stations on a 6 km. line monthly or bimonthly.

As summarized in Table I, individual number of total zooplankton which were mainly produced by nauplii, copepodites and adults of Oithona nana, Acartia clausi and veliger larvae of bivalves, were statistically related with orthophosphate phosphorus, dinoflagellate abundance, density, diatom abundance, total inorganic nitrogen and silica respectively (Figure 1).

In accordance with multiple regression function, the fact that the orthophosphate phosphorus was the most significant parameter, proved that the importance of phosphorus excretion by zooplankton in eu- or hypertrophicated environments. It was clearly determined that the zooplankters feed both dinoflagellates and diatoms due to the phytoplankton succession and variations in density but preferably consumed dinoflagellates. There existed an inverse relationship between total inorganic nitrogen in which the most important ammoniotelic zooplankton excretion products were found, and zooplankton individual number because these compounds were basically included in the system as toxic non-ionic ammonia form by sewages, riverine inputs and degradation of biological materials in such environments.

Silica that might be an important selective factor affecting the ecology of estuarine and coastal phytoplankton (HECKY and KILHAM, 1988) was the least important factor for the zooplankton abundance.

Table I:Statistical parameters of the multiple regression of Zoopl.nb $=(PO_4^{-3}-P^{1.424})(Din.^{0.129})(10^{0.117\sigma_t})(Dia.^{-0.057})(\Sigma N^{-0.660})(Si^{-1.014})$

Variables	Regression coefficient	Standard errors	Lower limit	Upper limit	F
PO_4^{-3}-P(μg-at l^{-1})	1.42397	0.16030	1.10636	1.74159	141.41
Din.(cells nb.l^{-1})	0.12874	0.03471	0.05996	0.19751	11.76
Density(σ_t)	0.11701	0.00772	0.10171	0.13231	28818.07
Dia.(cells nb. l^{-1})	-0.05719	0.02479	-0.10631	-0.00807	5.32
ΣN(μg-at l^{-1})	-0.65952	0.09763	-0.85296	-0.46607	172.26
Si(μg-at l^{-1})	-1.01405	0.08366	-1.17982	-0.84828	1143.40
Full regression	F=5048.7	$p<0.0000$	$R^2=0.996$		$\sigma_{\bar{y}}$=0.1521

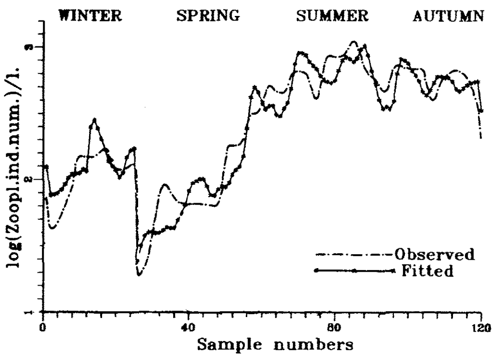

Fig. 1: Graphic representation of the model.

The assimilation of soluble silica by diatoms before each grazing period must give rise to the negative relationship.

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