

Particulate copper, lead and cadmium in Saronikos Gulf, Greece

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Effects of cadmium on the physiology and chemical composition of the green algae *Ulva rigida* (C. Ag.)

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Trace metals have been studied thoroughly in coastal areas of the Mediterranean. However the contribution of their particulate forms in marine pollution is still poorly understood. Saronikos Gulf, being in the vicinity of Athens, is an important area for the study of particulate metals which derive mainly from land based sources, namely, the Central Sewage Outfall (CSO) of Athens, direct industrial discharges and road traffic. In the northern part of the Gulf is located the enclosed Gulf of Elefsis, which receives high loads of metals by industrial activities.

Methods

Particulate Cu, Cd and Pb were studied on samples collected from an extended grid of stations that covered the entire area and water mass (to depths of 400 m) of the Gulf. Eight cruises, covered two annual cycles, carried out during June, September, December of 1988 and 1989 and March of 1989 and 1990. The water samples were collected by plastic Go-Flow bottles incorporated on a rosette system. The samples were filtered through prewashed and preweighed Millipore 0.45µm membrane filters, dried to constant weight, and treated with 1:1 aquatic solution of redistilled extra pure HNO₃ for 16 hr in covered PTFE beakers on a hot plate at 300°C. The solution was evaporated to near dryness, diluted with redistilled metal free water and quantitatively transferred to 50 ml prewashed polyethylene bottles. The final aliquots were analysed by a Perkin-Elmer 2380 GFAAS.

Results and Discussion

Cu : Higher concentrations were measured near the CSO and at the industrial zone of Elefsis. Lower values were found in the southern part of the Gulf. High concentrations were also measured during summer at the coasts of Elliniko and Vouliagmeni. A general decrease of concentrations was observed at greater depths with the exception of some deepest, near bottom, parts of the water column where the high suspended load is probably due to resuspension. No systematic trend was identified in the mean concentrations, during this relatively short two years period. However some extremely high values were observed in coastal samples. These values obviously influence the mean ones especially in March 1990 when high concentrations were found in a series of stations inside the Gulf of Elefsis.

Cd : In general with the exception of June 1988 and to a lesser extent September 1988, the concentrations were low with mean values below 0.01 µg/l. Clear systematic tendencies were not observed as far as it concerns the sources of particulate Cd or their distributions with depth, a fact indicating important contribution by diffused sources and eventually significant atmospheric inputs.

Pb : High concentrations of lead were found along the industrial zone and CSO and near coastal areas with heavy traffic. The contribution of each source is variable with clear indication that traffic contributes more during summer and autumn. Extremely high values were observed in the gulf of Elefsis (9/88,3/90) and in the plume of the CSO (9/89). The surface concentrations were in general higher than those of the subsurface layers but some high values were also measured at the near bottom depths. No systematic trends were identified during the study period.

		Cu (µg/l)	Cd (µg/l)	Pb (µg/l)
6/88	range	0.09 - 1.25	0.001 - 4.6	<0.01 - 0.79
	mean	0.34	1.4	0.12
9/88	range	0.01 - 11.6	<0.001 - 0.33	<0.01 - 3.3
	mean	0.32	0.025	0.14
12/88	range	<0.01 - 0.6	<0.001 - 0.056	<0.01 - 0.13
	mean	0.10	0.005	0.02
3/89	range	<0.01 - 0.13	<0.001 - 0.004	<0.002 - 2.7
	mean	0.03	<0.001	0.08
6/89	range	<0.01 - 0.19	<0.001 - 0.072	<0.01 - 0.21
	mean	0.05	0.009	0.03
9/89	range	<0.01 - 0.43	0.001 - 0.019	<0.01 - 0.17
	mean	0.10	0.004	0.05
12/89	range	<0.01 - 2.8	0.001 - 0.044	0.01 - 0.20
	mean	0.15	0.013	0.07
3/90	range	0.01 - 16	0.001 - 0.155	0.03 - 2.9
	mean	1.90	0.012	0.36

General observations

The study of particulate trace metals in the Saronikos gulf showed that they contribute considerably to its pollution. Main sources are the CSO, the industrial zone, the coastal traffic and runoff, as well as the ships. The important variations in particulate metal inputs are due to the effect of rainfalls and meteorological conditions and also to the intensive "patchy" planktonic blooms which are important to contribute to the high metal concentrations found at the surface layers. The highest values were measured near the point land based sources. The water circulation and atmospheric inputs influence the distribution of metals throughout the area. The concentrations at the southern part of the Saronikos were relatively low compared to values reported for other polluted areas of the Mediterranean.

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The green algae of the genus *Ulva* are among the species commonly found in polluted and eutrophicated coastal marine areas. In sea waters with high nutrient concentrations *Ulva* sp. have exhibited increased growth rates and elevated mineral nutrient content in their tissues². It was also found during field and laboratory experiments that they demonstrate the ability to accumulate heavy metals, when exposed to high concentrations³. Therefore they can play a significant role in the food chain as well as in the biological and physicochemical transfer of metals from seawater to sediments⁴.

The present study is part of an ongoing program with the principal aim to investigate the effects of different concentrations of heavy metals on the physiology and chemical composition of *Ulva rigida*, and understand the mechanism of uptake and release of metals.

Ulva rigida atoms were collected from a polluted bay near Athens (Gulf of Elefsis). The specimens were treated with increased concentration of cadmium (200 ppb) for 15 days⁵. The water was replenished every day with new quantities of cadmium enriched seawater from the same area. Individual algae were removed after 1,2,4,7 and 15 days and their cadmium content was determined by Atomic Absorption Spectrophotometry⁶. Portions of the samples removed, were kept for different periods of time in clean seawater (6 and 15 days), and at the end of these periods the remaining cadmium content was measured (see Table 1).

It was found that the metal uptake is faster during the first days of the exposure to high cadmium concentrations. Usual concentrations in algae ranged from 21.71 to 111.34 µg/g dry weight. When placed in clean seawater the algae releases most of the accumulated metal within the first 6 days. The remaining amount of metal depends on the originally accumulated quantity but never reaches the metal content of the untreated algae which is around 0.06 µg/g d.w.

It is known from the literature that *Ulva* sp. are rich sources of sterols and glycoproteins⁷. The production of chemicals during the metal treatment period, was used as an indicator of the algal physical condition. Unexposed algal samples as well as specimens treated with cadmium (200 ppb), were taken, air dried and extracted with organic solvents (chloroform/methanol). The extracts were concentrated under vacuum, and the residue was dissolved in ethyl acetate. Solutions of known concentration (10 mg/ml) were prepared and chromatographed by High Pressure Liquid Chromatography (Techsil 110sil column with a gradient hexane/ethyl acetate solvent system).

It was observed that the two chromatographs exhibited some marked differences. The organic extract of the treated algae showed the presence of some intense peaks (Techsil 110sil column with a gradient 70% hexane, 30% ethyl acetate → 10% hexane, 90% ethyl acetate, 30 min. run, 2 ml/min, UV 254 nm detector) eg. peaks with retention time 6.93, 9.10, 9.40, 13.64 min. absent in the extract of the unexposed to cadmium samples. From the aforementioned results, we can assume that, under the intense stress conditions caused by the increased cadmium concentration, some metabolic processes in the algae were altered. This is the result of chemical adaptability observed also in other marine organisms when exposed to modified environmental conditions.

Table 1

Sampling days	Days in clean seawater	Metal content of the algal tissue (µg/g dw)
1	0	21.71
	6	5.23
	15	30.34
2	0	24.72
	6	6.85
	15	4.16
4	0	36.64
	7	73.86
	6	11.43
15	15	10.02
	0	111.34

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