Heavy Metal Levels and Eutrophication in the Saronikos Gulf

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Abstract: The influences of the waste water input on the eutrophication and the heavy metal levels (Cd, Pb, Cu) in the waters along the coast of Attika have been determined.

Résumé : L'influence de la contribution des eaux de rejet sur l'eutrophisation et la concentration des métaux lourds a été déterminée sur les eaux de la côte de l'Attique.

This study provides a first insight on the correlation between the toxic metals Cd, Pb and Cu and eutrophication caused by sewage discharge into the Saronikos Gulf. In the first week of April 1982 water samples (o.5-1 m below surface) have been collected at 9 stations located in a 15 km long sequence several miles off the coast of Attika (fig.1). The last station 9 was 5 km southeast from the main municipal waste water outfall of Athens and Piraeus and 2 km from Piraeus port entrance. The daily waste water input of over 2oo x $1o^6$ liters (1) is driven by the wind partially southeast along the coast of Attika against the continuous influx of very nutrient depleted water from the southern Aegean Sea.

The concentrations of Cd, Pb and Cu have been determined simultaneously by differential pulse anodic stripping voltammetry (2). Also the chlorophyll - a content and the phytoplankton biomass was determined. Moreover, microscopical studies with the Utermöhl technique provided the identification and cell numbers of the various phytoplankton species (viz.Tab.1). During the sampling time in April 1981 Dinoflagellates were the most predominant phytoplankton species.

One can distinguish (fig.1) 3 types of surface water masses prevailing in this part of the Saronikos Gulf: (a) unpolluted oligotrophic water with low biomass and low heavy metal levels at stations 2, 3 and 4 located more distant from the waste water outfall; (b) oligotrophic water with elevated levels of Cd and particularly Pb but not Cu at the most distant station 1 caused by the local pollution source of a large marina; (c) eutrophic water characterized by increasing phytoplankton biomass, particularly Dinoflagellates, with at the same time progressively increasing Pb- and Cu-pollution as the waste water outfall and the port area of Piraeus are approached (station 5-9). Station 4 represents with respect to the heavy metal levels a border case.

Yet the Cd-levels at station 6-9 remain rather low while there is Cd-pollution at station 5, 4 and 1. A probable explanation of the fate of Cd at station 6-9 in the municipal waste water plume seems to be the well known preferential uptake by bacteria of which a high population is to be expected in the municipal waste water. On the bacteria feeds zooplankton. As only rather small subsamples of o.5 l have been filtrated for heavy metal analysis and because the zooplankton density is much smaller than the phytoplankton density only an insignificant zooplankton content cen be expected in the filtered off material. The elevated Cd-levels at station 5 and 4 and also 1 support this conclusions, as here the municipal waste water plume with its high bacterial population is less or not effective and the existing Cd-pollution is either taken up to some extent by the non-eutrophicated phytoplankton level or remains in the dissolved state. High correlation coefficients between Cu in particulate matter and phytoplankton cell number were found. The correlation was independent of the fact whether living or dead cells were filtered and this indicates an adsorption of copper mainly on cell wall material. It might be possible to interpolate from the Cu values in particulate matter the magnitude of phytoplankton cell number. The heavy metal levels in Tab.1 are to be compared with the base line values in the Euboic sea (Cd 9; Pb 148 and Cu 138 ng/l) and the grand average in Ligurian and Tyrrhenian coastal waters: Cd 18; Pb 22o and Cu 74o ng/l (3), while in estuaries the levels are significantly higher (4) and in heavily polluted areas, as the port of Genova, the levels increase even severely to Cd 9oo; Pb 9ooo and Cu 34oo ng/l (3).

Table 1: Phytoplankton cell number and total heavy metal levels in the investigated area of Saronikos Gulf

Station	Water Type	Chlorophyll-a (μg/l)	Phytoplankton (cell numbers/ 1o ml)	Dinoflagellates (cell numbers/ 1o ml)	Cd (ng/l)	Pb (ng/l)	Cu+) (ng/l)
1	b	o.1o	4o8	394	48	672	59
2	a	o.11	131	81	6	128	83
3	a	o.18	225	155	5	147	73
4	a	o.13	169	134	8o	182	134
5	c	o.55	1597	1494	1o9	315	152
6	c	1.38	2121	1764	16	311	211
7	c	1.81	4777	2885	7	394	381
8	c	2.77	3697	2534	22	397	383
9	c	1.23	4o52	3445	17	731	676

+) for the heavy metals the total levels in 1 l surface water are listed

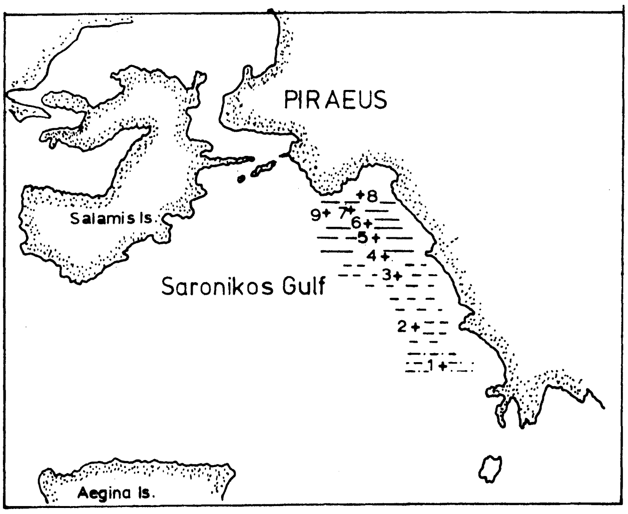

Fig.1 Sampling stations in different water masses
.-.-.- oligotrophic heavy metal polluted, stat.1
------ oligotrophic heavy metal unpolluted, stat. 2-4
——— eutrophicated heavy metal polluted, stat. 5-9

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Paper presented by H.J.W. v. Gudenberg (FRG)

Discussion

M. Branica:

a) In your 1st. sheet one can read that various values of metals may depend on the methodology applied, as well as the additional contamination during sampling procedures. On the other hand, the reported values may also be influenced by sample pretreatment (pH, UV irradiation, etc.).

b) How can you explain good correlation between copper and the number of cells?

H.J.W. v. Gundenberg:

a) Samples have been taken according to the well known expertise or our institute at Jülich concerning the elimination of contamination in sampling and sample pretreatment. Therefore, the reported metal data are to be considered as genuine.

b) Copper values in particulate matter show no differences whether living or killed cells were filtered and analysed. This fact indicated a great capacity for copper adsorption on the outside of cell walls and membran substances. The correlation coefficient between phytoplankton cells and copper in particulate matter r = o.8 confirms this observation.

<u>V. Žutić:</u> a) In an eutrophicated aquatorium, as the one you considered is, it would be very important to know not only the total heavy metal concentration but also the free and labile fraction (as determined by ASV at natural pH) which seems to be more interactive with phytoplankton. DOM could dramatically change the metal speciation.

b) As to the Cd(II) uptake by phytoplankton our experiments with a microflagellata <u>Dunaliella t.</u> we found very important accumulation into the cell while the cell membrane remained intact. Ionic Cd(II) seems to be taken through the Ca-channel.

<u>H.J.W. v. Gundenberg:</u> a) We agree but in the reported exploratory study only the total metal content in the water samples has been determined.

b) We assume that in the particular case studied the high bacteria concentration from the municipal waste water competes efficiently with the phytoplankton for the Cd. This is not in contradiction with your findings on Cd-uptake by a phytoplankton species in a model experiment.

H.W. Nürnberg: Concerning the question if a heavy metal has to be present in the form of labile ionic species to be taken up by phytoplankton no generalisation seems possible. It will depend on the stability of the heavy metal complex with organic ligands L and the specific properties of the cell membrane of the studied planktonic species if the heavy metal uptake is favoured or not. There are experimentally observed examples that even EDTA-complexation favours the uptake of Cd and Ni, e.g. for the diatom Thalassiosia rotula (viz. G. Dongmann, H.W. Nürnberg, Ecotoxicol. Environm. Safety, 6 (1982) 535).

B. Raspor: Based on the experience of S. George with bioaccumulation of Cd-EDTA in mussels it can be concluded that if Ca is complexed by EDTA in solution, the organism is going to take up Cd, due to the chemical similarity between Cd and Ca, and therefore it will seem as if Cd-EDTA is accumulated by the organisms.