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Heavy metal concentrations in superficial sediments from the Gulf of Olbia, Sardinia

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The city of Olbia and its hinterland discharge their untreated and partially treated sewage into the Gulf of Olbia in the North East of Sardinia. The most higly polluted area is a channel (Fig.1), where the Olbia harbour is located, flanked by several sites for the production of shellfish. In 1985 a significant algal bloom occurred in the channel. The aim of the present paper is to measure the level of heavy metals (Cd, Cu, Cr, Zn, Pb) in the superficial sediments of the channel, both to evaluate the potential hazard to the shellfish themselves and to obtain significant information in view of the forthcoming dredging operations to improve navigation in the channel. This information will help to select an adequate disposal site for the dredged sediments.

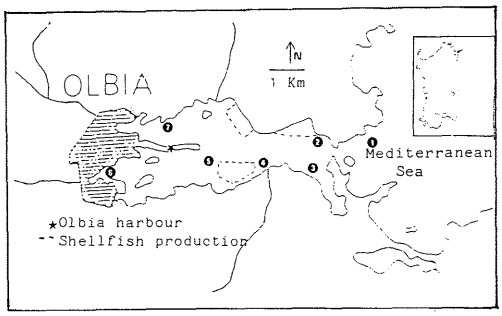

Fig.1. Location of the sampling sites .

Seven sampling stations were selected along the channel. Core samples of the sediments were collected in October'86 by divers. The samples were immediately frozen after collection. The upper part of the core (1-5 cm) was removed, air dried, grounded in an agate mortar, and sieved at 100 mesh. Aliquots were digested in an nitric-perchloric acid mixture, according to the method suggested by IRSA-CNR (1985) Analysis were carried out on a Perkin Elmer atomic absorption spectrophotometer. An NBS River Sediment Standard (1645) was used to check the analytical procedure.

Sampling site	Pb	Cu	Cr	Cd	Zn
1	1.1	5.2	1.6	0.2	40.2
2	6.1	5.0	11.0	1.6	70.5
3	7.2	5.0	3.5	2.1	55.2
4	8.0	22.0	12.0	2.0	105.3
5	10.2	9.0	9.0	1.6	86.1
6	17.1	15.1	6.0	3.1	104.0
7	16.0	5.0	2.0	0.7	70.0

Tab.I. Mean concentrations (µg/g dry wt) of heavy metals in surface sediments.

The metal concentrations do not vary significantly along the channel. Sampling station 1, at the point where the channel communicates with the open sea,showed the lowest values for all metals considered. The highest Pb concentrations were found at stations 6 and 7, which are the nearest the harbour and the city. The values were lower than those found in other harbour areas in the Mediterranean and are in the range of those found by other authors in coastal areas (Tab.II).

	Pb	Cu	Cr	Cd	Zn	References
Olbia Gulf	6.1-17.1	5.0-22.0	2.0-12.0	0.2-2.1	40.2-10	This study
Cagliari Gulf,Sardinia:						
-Harbour zone	21-860	4.9-180	22-100	__	60-65	Contu et al ,
-Outer harbour	8.8-44	3.1-8.8	1.3-7.2	__	10-25	1983
Coastal areas of Israel	3.9-19.7	0.3-2.9	1.7-12.4	0.3-2.2	2.1-18.2	Roth and Hornung,1977
Bay of NIce	4-112	2.1-35.4	__	0.7-2.4	__	Flatau et ., al, 1982
Sicily Channel Coast	5-20	4-15	2.5-16.2	0.2	7-26	Castagna et al, 1987
Venice Lagoon	3.1-278	21-463	14.7-46.4	1.1-25.4	61-5930	Pavoni et al.,1987

Tab.II. Heavy metal concentrations (µg/g dry wt) in sediment collected in different areas of Mediterranean.

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C-I10

Chromium fluxes through Mex Bay inshore waters*

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Introduction: The first survey of chromium in inshore waters of Alexandria was conducted by Aboul Dahab and Halim (1986) in Mex Bay West of Alexandria. The Bay has a mean depth of 9.8 m. It's surface area is of 19.4 Km^2 and its volume 190.3 X 10^6 m^3. The Bay receives several effluents: agricultural drain water (6 X 10^6 m^3 day^{-1}), waste water from a chlor-alkali plant (35 X 10^3 m^3 day^{-1}) and also from the Western Harbour of Alexandria (3.1 X 10^6 m^3 day^{-1}, El Gindy, 1986). The Western Harbour receives 90 X 10^3 m^3 day^{-1} of brackish water from a navigation canal (Noubaria Canal) and 1.2 X 10^3 m^3 day^{-1} of waste water from 16 tanning factories.

The daily average total chromium input from the respective effluents to Mex Bay was quantified by Aboul Dahab and Halim (1986).

Table (1): Average daily discharge of chromium from the Main effluents to Mex Bay

Effluent Cr species	Umum drain	Chlor-alkali effluent	Western Harbour outlet
Particulate Cr	324	4	25
Dissolved Cr	132	3	16
Total Cr	456	7	41

El Gindy et al., (1986) estimated the residence time of the fresh water input to Mex Bay as 2.08 days. Aboul Dahab and Halim recently determined the sedimentation rate in Mex Bay (0.85 Cm yr^{-1}) by studying sediment cores from the area (unpublished data).

The scope of the present work is to estimate the amount of chromium deposited to Mex Bay sediments, the amount of chromium leaving the Bay by water exchange with the open sea and to investigate chromium accumulation in marine organisms belonging to different trophic levels from the Bay.

Material and Methods: Sediment: Sediment samples were taken by a core device from the stations shown in Fig. 1. The superficial layer of sediment (0-2 cm) was analysed. Samples were air dried, ground in a agate mortar and sieved to pass 63 µm mesh to normalize all samples. Samples were dissolved totally with HNO_3, HF and $HClO_4$ acids and the dried residue taken up in 0.1 M HCl acid. GFAAS technique was used for the measurement of Cr concentrations.

Biota: Donax trunculus, Penaeus kerathurus, Neptunus pelagicus, Boops boops, Mullus barbatus, Sardina pilchardus and Rhinobatus halavi were collected on two occasions from Mex Bay by commercial trawlers (Winter and Summer 1986). Samples were identified and prepared in view of the method recommended by UNEP, 1984. Digestion was done by concentrated HNO_3.

To check the analytical method, NBS River sediment (1645) & Bovine liver (1577) were analysed for Cr. The efficiency ranged from 97 % to 102 %. All manipulations were carried out in a laminar flow hood in a dust-free room.

Results: Density, organic carbon, chromium concentrations and the index of relative pollution potential are given in Table 2. Chromium concentrations in the sediments from Western Alexandria fluctuated between 42 $\mu g g^{-1}DW$ and 751 $\mu g g^{-1}DW$ (station 1 and 14, respectively) with an average of 243±213 $\mu g g^{-1}DW$. Significantly high chromium concentrations were determined at station 14, within the outlet of the Western Harbour (978 $\mu g g^{-1}DW$) and at station 13 immediately downstream from Umum Drain outlet (543 $\mu g g^{-1}DW$). Stations 10 and 11 also showed relatively high chromium concentrations (311 $\mu g g^{-1}DW$ and 382 $\mu g g^{-1}DW$, respectively). The minimal value of 42 $\mu g g^{-1}DW$ at station 1 is assumed to be the background level for the area. The percentage of organic carbon in the sediments of Mex Bay ranged between 0.1 % and 3.3 % with an average of 1.4 ± 1.1 %. In the inner part of the Western Harbour outlet it was 4.2% and 3.3 % in outer part (station 14* & 14, respectively).

No significant correlation was found between chromium concentration and organic carbon ($r = +0.25$) in Mex Bay sediments. For this reason we assume that the incorporation of chromium in the Bay sediments was done largely by inorganic processes.

Biota: The mean chromium concentrations in the marine organisms from Mex Bay are very scattered (Table 3 and Fig. 2). The relatively high concentrations of chromium in the soft parts of the bivalve Donax trunculus (255 µg $Kg^{-1}FW$) compared to fish levels (70 to 153 µg $Kg^{-1}FW$), suggests a higher rate of accumulation. There was a considerable difference between chromium concentrations in the flesh of the crab Neptunus pelagicus (465 µg $Kg^{-1}FW$) and the shrimp Penaeus kerathurus (222 µg $Kg^{-1}FW$). There were wide differences between chromium concentrations in the flesh of the four fish species studied. The level increased in the following order: Boops boops (70 µg $Kg^{-1}FW$) < Mullus barbatus (94 µg $Kg^{-1}FW$) < Sardina pilchardus (127 µg $Kg^{-1}FW$) < Rhinobatus halavi (153 µg $Kg^{-1}FW$).

Discussion: The sedimentation rate (0.85 cm yr^{-1}) in Mex Bay can be converted to a weight basis using the formula:

Bulk sedimentation rate = $F = R(1-P)d$ (Hamilton-Taylor, 1979)

where R = sedimentation rate, 0.85 cm yr^{-1}, P = porosity, 0.844 and d = density, 2.596 g cm^{-3}. $\therefore F = 0.85\ (1-0.844)2.596 = 0.3442$ g $cm^{-2}yr^{-1} = 9.43$ g $m^{-2}day^{-1}$. Using the chromium concentration in the sediments of the inner Mex Bay (452 $\mu g g^{-1}DW$, average of the stations in the inner Bay, and given the surface area of the Bay (19.4 X $10^6 m^2$), the chromium sedimentary flux for the whole Bay would be 9.43 X 19.4 X 452 X 10^{-3} = 83 Kg day^{-1}. The average annual rate of rainfall over the investigated area (19.4 Km^2) is 192.1 mm, and the total amount of rainfall therefore is 192.1 X 10.4 X 10^3 m^3 yr^{-1} = 10.2 X 10^3 $m^3 day^{-1}$. This is a negligible value compared to the fluxes from the land-based sources.

Aboul Dahab and Halim (1986) found a rapid decrease in suspended chromium concentration in a seaward direction in Mex Bay. Approximately 95 % of the suspended chromium is deposited and remains within the Bay. They also found that the dissolved chromium concentration at the Mex Bay outer boundary is 1.054 $\mu g l^{-1}$ and at the discharge points is 4.345 $\mu g l^{-1}$. The net export by water exchange (E) of a dissolved component from A to B can be approximately expressed as: $E = W(X_A - X_B)$ where W is the water exchange rate due to the mixing and X_A and X_B are concentrations of the component at A and B respectively.

$$W = \frac{\text{Basin volume}}{\text{Fresh water residence time}}$$

$$\therefore W = \frac{190.3 \times 10^6}{2.08} = 91.49 \times 10^6 m^3\ day^{-1}.$$

Since no considerable vertical gradient for chromium is observed (Aboul Dahab and Halim, 1986), the average concentration for the water column is taken:

$$E_{\text{dissolved chromium}} = 91.49 \times 10^6 (4.345 - 1.054) = 301.1\ Kg\ day^{-1}.$$

From the total amount of chromium flux to the Bay, 474 Kg day^{-1} (Table 1), flushing of the Bay to the open sea removes 301 kg day^{-1} and sedimentation within the Bay 83 Kg day^{-1}.It is apparent that the main process of chromium removal, is by water exchange.Sedimentation accounts for 22 %. Although this budget is crude, it provides approximations of the inputs, outputs, and of the standing stock of chomium in the water and biota of the Bay, which is about 90 Kg.

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