Dissolved and Particulate Mercury Concentration in Seawater collected during the *Discovery* and *Bannock* Cruises (EROS 2000 Project)

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This paper reports data on dissolved and particulate mercury in seawater samples collected during two field studies in the sea region of the Gulf of Lions, performed in the frame of EROS 2000 project (1988-1989).
As regards the study area, sampling station positions and notations, refer to the cruise and scientific reports prepared by Dr. Fauzi-Mantoura (Plymouth Marine Laboratory, UK) and by Dr. R. Ferrara / A. Seritti (CNR-Istituto di Biofisica, Pisa, I) respectively.

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EXPERIMENTAL

Seawater was filtered on 0.45 μm pretreated membrane filter (Sartorius SM11306) in a closed device, under nitrogen pressure.
400 ml of filtered seawater were photooxidized for 15 min by means of a U.V. immersion lamp (90 W), after an addition of 400 μl of an acid solution of $KMNO_4$. The ionic mercury was reduced by tin chloride and transferred on gold trap, as described elsewhere (1). Determination of mercury, electrothermally desorbed, was achieved by an atomic fluorescence spectrometer.
Filters containing particulate suspended matter, were mineralized with 3 ml of HNO_3 (Merck selectipur) in a pressure digestion system for 2 hours at 160°C. Mercury was determined as described for the dissolved form.

RESULTS

Table 1 and table 2 show the mercury concentration measured in the studied area during the two cruises.
From the tables it appears that the mercury levels are quite low and comparable with those measured for other areas of the Mediterranean basin (2,3,4), with the exception of the sampling station 8, where values are very high with respect to the mean value of the other stations. No variation of the metal concentration was noted as a function of the depth and in function of the season of collection.
Rather low values for the mercury associated to the particulate matter have been observed in the station 25 at about 40 miles from the coast.

DISCOVERY CRUISE Leg 1 (13-26 December 1988).

St	Depth	LatN	LongE	Hg D	St	Depth	LatN	LongE	Hg D
MA5	5	43 03.6	04 50.2	3.2	MC2	25	42 22.6	04 01.9	3.0
MA5	20			5.3	MC3	21	42 45.0	04 19.9	4.2
MA5	40			6.1	MD1	31	42 51.9	03 41.9	3.0
MA5	71			4.7	MD2	20	43 01.3	04 04.9	3.6
MA5	89			3.9	ME1	5	43 24.3	04 01.1	4.7
MA5	105			5.3	ME2	4	43 18.8	04 25.4	4.1
MA6	3	43.17.3	04 50.6	4.9	MF1	-	42 44.4	06 00.6	4.9
MA7	-	43 12.8	04 49.6	4.2	MF2	40	42 55.2	05 37.8	2.8
MA8	4	43 07.5	04 48.6	17.4	MF3	50	43 03.0	05 19.6	5.7
MC1	25	41 59.9	03 36.7	7.9	MF4	5	43 10.6	05 07.3	4.8

Table 1 - Dissolved mercury concentration in seawater (ng/l); Depth (m).

BANNOCK CRUISE (1-15 JULY 1989)

St	Depth	LatN	LongE	HgD	HgP	St	Depth	LatN	LongE	HgD	HgP
04	0	43 24.3	04 00.7	4.4	0.4	18	0	43 02.6	05 02.9	3.8	0.7
04	5			2.7	---	18	5			5.1	---
04	16			7.5	0.1	18	15			5.1	---
04	25			4.5	0.1	18	55			5.5	---
						18	145			5.7	0.9
05	0	43 20.3	04 17.9	4.8	8.4	18	295			5.4	0.5
08	0	43 15.9	04 57.4	13.6	13.3	20	0	41 45.4	05 37.1	19.1	0.3
08	5			13.5	2.4						
08	10			10.3	1.9	25	0	42 27.1	05 18.3	5.2	---
08	20			7.1	1.3	25	5			4.1	0.2
08	45			21.5	4.4	25	10			3.7	0.2
08	70			19.4	4.5	25	25			5.7	0.8
						25	35			5.7	0.1
09	0	43 13.5	04 51.1	8.5	3.9	25	50			4.2	0.8
						25	75			5.1	0.2
10	0	43 08.7	04 29.9	4.3	1.7	25	100			5.2	0.3
						25	150			4.2	0.2
11	0	43 02.4	04 09.2	4.7	1.3	25	300			4.3	0.2
						25	480			3.3	0.2
12	0	42 53.0	03 40.6	7.5	1.5						
12	8			8.7	3.5	**Samples in front of Rhone estuary**					
12	20			8.2	1.5	A	0			4.9	0.6
12	50			6.1	2.6	B	0			6.6	0.5
12	70			4.8	0.6	C	0			4.5	1.2

Table 2 - Concentration (ng/l) of dissolved mercury (HgD), mercury associated with particulate suspended matter (HgP) in seawater. Depth (m).

These data confirm the difficulty of finding an explanation for the problem of the high mercury concentrations in pelagic fish in the Mediterranean basin, as the concentration measured in the Mediterranean are quite comparable to those in the oceans (5).

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Mercury Speciation in Water of the Krka River Estuary

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Research studies concerning the mercury cycle in the Krka River Estuary have been carried out since 1983. Preliminary results showed relatively low mercury levels in sediments and mussels *Mytilus galloprovincialis* from this area (1). The mercury levels in estuarine water and seawater are comparable with the values found recently in unpolluted coastal areas and open ocean waters (1). The vertical distribution of mercury concentraction in this highly stratified estuary indicates the mercury accumulation at the fresh/saline water interface (1,2). A proportion of organic mercury in various samples has also been measured. The methylmercury was found in sediments, mussels and fish, but not in water (1). Further investigations will be focused on the study of mercury speciation in water, especially at the fresh/saline water interface.

During 1988 and 1989 distributions of reactive and total as well as dissolved and particulate mercury in estuarine waters were investigated. Reactive mercury-$(Hg)_R$ concentration measurements represent those Hg species that are readily reducible by $SnCl_2$ in acidified water. It is composed of dissolved inorganic Hg species; certain mercury associations with organic ligands and in unfiltered water sample the mercury which is easily leached from particulate matter. Total mercury-$(Hg)_T$ refers to the amount of Hg measured after UV-photochemical destruction of samples and will also include stable organomercury associations. It was found that the reactive mercury in unfiltered water generally corresponds to the values of the dissolved mercury fraction. This is in accordance with the fact that the dissolved mercury was mostly inorganic, both in fresh and saline water. A positive correlation between the difference of total and reactive mercury concentrations and quantity of suspended matter, as well as with the concentration of particulate mercury has been found in unfiltered estuarine water. From this it can be concluded that particulate mercury is predominatly bound in organic complexes.

In the deeper saline water layer, over 80 % of the total mercury is reactive Hg. However, this percentage changed in the upper layer, depending on hydrological and/or biological conditions. For example, the portion of reactive mercury in unfiltered samples from the upper layer at the low river discharge

Table 1. Concentrations of reactive and total mercury (ng dm^{-3}) in unfiltered samples from the upper water layer (0.5 m) of the Krka River Estuary

	January 1989 (Q = 16 $m^3 s^{-1}$)				July 1989 (Q = 51 $m^3 s^{-1}$)			
L(km)[a]	S(‰)	$(Hg)_R$	$(Hg)_T$	$\%(Hg)_R$	S(‰)	$(Hg)_R$	$(Hg)_T$	$\%(Hg)_R$
0	0	0.3	0.8	38	0	0.3	1.0	30
1	-	-	-	-	1	0.1	0.5	20
4	3	0.7	0.7	100	2	0.1	0.9	11
10	10	0.4	0.7	57	5	0.2	1.0	20
17	16	1.3	1.9	68	7	0.1	1.2	8
22	25	1.1	1.4	79	14	0.3	1.5	20
32	38	0.8	0.9	90	38	1.2	1.2	100

[a] Distance from the begining of the estuary in seaward direction

(January 1989) was significantly greater than at the high river flow in July 1989 (Table 1), reflecting the influence of hydrological conditions.

Speciation of mercury along the vertical water profile showed a minimum of the particulate mercury at the interface of fresh and saline layers. This finding is in accordance with the presumption that particles accumulated at the interface (3) release mercury owing to dissolution as a result of increased salinity (aglomeration of organic matter, competition of macrocations and complexation by chloride).

Further investigations on the mercury speciation in water will contribute to a better understanding of the biogeochemical cycle of mercury in stratified estuaries as well as of mechanisms regulating mercury behaviour at the boundary conditions which are prevailing at the fresh/saline water interface.

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