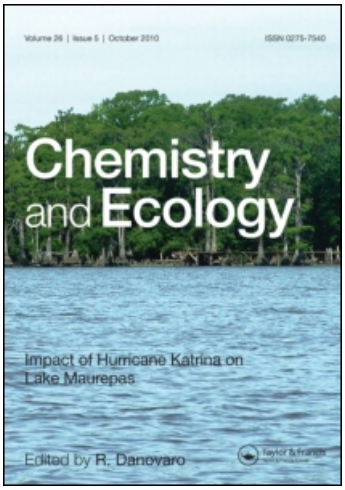

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Trace Metals in Marine Environment in Relation to the Study of Their Biogeochemical Cycle

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Concentrations of cadmium, copper, lead and zinc are measured in the waters of the Tyrrhenian Sea in relation to waste sources and the biogeochemical cycle. These concentrations were not significantly elevated in the abiotic components of the marine environment and it is concluded that they have a low residence time in these waters.

INTRODUCTION

The study of the presence and speciation of trace metals such as Zn, Cd, Pb, Cu and Hg in the abiotic components of the marine environment represents a fundamental topic in relation to the interaction between these elements and the biosphere. At present, it is widely demonstrated that the chemical form of metals (free ions, complexes, organo-metals etc.) strongly affects their availability to aquatic organisms (Davies, 1978; Smies, 1983). In sea water the concentrations of Zn, Cd, Pb, Cu and Hg range from ng/l to μg/l. These low levels need accuracy and standarization of methods

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of sampling, storage and measurement in order to avoid contamination which would otherwise give completely wrong analytical results (Mart, 1979).

As regards to the analytical technique, in the last ten years the development of electrochemical techniques such as the Differential Pulse Anodic Stripping Voltammetry (DPASV) using solid electrodes allows both high sensitivity levels and very reliable data to be obtained (Sipos *et al.*, 1974; Nürnberg, 1979).

The Atomic Fluorescence Spectrometry (AFS) allows detection limits of 10 pg to be reached for mercury (Ure, 1976; Ferrara *et al.*, 1980).

In this paper Zn, Cd, Pb and Cu concentrations are reported both in the dissolved and particulate fractions of sea water. The data refer to a field study carried out with the Oceanographic Ship "L. F. Marsili" belonging to the C.N.R. on the Tyrrhenian Sea from December 1981 to May 1982. Furthermore, apparent Copper Complexing Capacity (L_t) and Stability Constants (K_s) of particularly interesting areas are reported. Finally, mercury levels in sediments waters and air are reported.

Experimental

The DPASV measurements were performed both with a PAR 174A Polarographic Analyzer and an Amel 472 Multipolarograph equipped respectively with a Hanging Mercury Drop Electrode (HMDE) for Zn measurements and a rotating Mercury Film Electrode (MFE) for Cd, Pb and Cu measurements. The filters with particulate matter were digested by low temperature ashing in an oxygen plasma induced by microwaves. The determination of apparent copper complexing capacity was performed as described by Plavsic *et al.* (1982). Mercury measurements were performed by an Atomic Fluorescence Spectrometer built for this purpose and reported elsewhere (Ferrara *et al.*, 1980). Water samples were analyzed as previously reported (Seritti *et al.* 1980). Sediments were treated as reported by Agemian and Chau (1976) and analyzed by a mercury analyzer (Coleman MAS 50). Air samples were collected and analyzed as described by Ferrara (Ferrara *et al.*, 1982).

RESULTS AND DISCUSSION

In Table I the average concentrations and ranges of total dissolved Zn, Cd, Pb and Cu referring to 54 sampling stations along the Tyrrhenian Sea are reported.

TABLE I
Total concentration (ng/l) of metals in the dissolved fraction. (*n*: number of sampling stations)

	Zn	Cd	Pb	Cu
Average	2650	5.70	48.8	70.3
Range	250–14000	2.4–12.1	7.8–141.63	14.03–183.5
n	54	54	54	52

The values reported here are comparable to those found by other authors in the Mediterranean (Mart *et al.*, 1978) and other parts of the world (Mart *et al.*, 1982).

In Table II average concentrations and ranges of metals associated with particulate matter are reported.

TABLE II
Total concentration (ng/l) of metals associated to particulate matter. (*n*: number of sampling stations)

	Zn	Cd	Pb	Cu
Average	740	1.23	43.0	59.7
Range	150–1660	0.54–9.0	1.5–314.3	1.5–311.3
n	12	49	53	52

The average concentration of metals in this fraction seems to be in general particularly low. The ranges are wider than those reported for waters and in particular for Pb and Cu. This can be attributed to the relevant role of particulate matter in the Pb and Cu cycle.

The L_t and K_s values of different areas of the Tyrrhenian Sea are reported in Table III.

TABLE III
L_t and K_s of waters collected in different areas

Sampling stations	L_t(mol/l)	K_s(l/mol)
Isola di Montecristo	9.3×10^{-8}	2.35×10^{7}
Foce dell'Arno	9.66×10^{-8}	7.30×10^{7}
Foce del Tevere	24.3×10^{-8}	13.2×10^{7}
Golfo di La Spezia	9.6×10^{-8}	1.5×10^{7}
Golfo di Napoli	16.5×10^{-8}	3.9×10^{7}

The data are similar to those reported by Plavsic for the Adriatic Sea (Plavsic *et al.*, 1982) and those reviewed by Hart (1981) and show different nature and amount of ligands in the chosen areas.

Tables IV, V and VI report mercury levels in air, waters and sediments.

TABLE IV
Mercury concentration in air

Sampling area	No. of samples	Hg° concentration (ng/m^3) Range	Mean
Open sea	200	0.9–3.6	2.1
Rural area	100	1.2–4.1	3.2
Urban area	300	2.2–31.5	10.1
Mineralized area (cinnabar deposits)	120	8.2–86.3	12.4
Industrial area (chlor-alkali plant)	65	12.1–35.5	22.2

TABLE V
Mercury concentration (ng/l) in waters of the Tyrrhenian Sea

	Hg-Total	Hg-Reactive	Hg-Particulate
Average	8.8	3.7	2.1
Range	2.9–19.7	0.9–11.1	0.1–12.9
n	46	41	46

TABLE VI
Mercury concentration in sediments

Sampling area	No. of samples	Averag (μg/g)	Range (μg/g)
Open sea	17	0.06	0.01 ÷ 0.16
Coastal area	18	0.27	0.04 ÷ 0.79
River estuaries coming from cinnabar deposits	8	0.84	0.55 ÷ 1.15
Estuary areas	6	0.39	0.02 ÷ 1.10
Coastal zone in front of a choralkali plant	10	0.75	0.13 ÷ 1.51

From these data, it appears that mercury levels in the abiotic components of the studied environment do not appear to be significantly elevated. Even if an influence of natural and anthropogenic sources can be observed, the highest values found don't seem to be responsible of biological perturbation such as the high content of mercury found in fish caught in the Mediterranean Sea (Bernhard and Buffoni; 1981; Stoeppler *et al.*, 1979). However, other information is needed to clarify the cycle of this element in the marine environment. In particular, data on fluxes and exchanges among all the pools of the system must be acquired in order to reach a conclusion.

CONCLUSIONS

From the data here reported it can be concluded that: the concentrations of heavy metals in all the abiotic components of the marine environment do not appear to be significantly elevated. This enhances the hypothesis that the residence time of heavy metals in waters is quite low because of physico-chemical and biological conditions. If the metals are stripped rapidly, one would expect elevated concentrations in the sediments, but this is limited and suggests that anthropogenic effects are not the sole or possibly even the major cause of the biological perturbations noted. It follows that more dynamic data such as the evaluation of the fluxes and changes are needed to clarify the biogeochemical cycle of these elements in the Mediterranean.

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