Identification of the northern Moroccan hot spots and contamination baseline of coastal sediments by heavy metals

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ملخص

تعريف النقط الساخنة بالسواحل المغربية وتلوث الرواسب بالمعادن الثقيلة

إن كمية تمركز المعادن الثقيلة برواسب السواحل المتوسطية المغربية، لها أهمية بالغة في تحديد النقط المهددة بالتلوث. لقد تمت دراسة ثمانية عناصر من المعادن الثقيلة (الزئبق، الكادميوم، الرصاص، الكروم، النيكل، الطاليوم، الزنك، و النحاس)، بغية تقييم التأثير المباشر لمخلفات المناطق الحضرية في نقل هذه العناصر إلى المحيط البحري.وقد بينت الدراسة أن سواحل طنجة و تطوان (مرتيل) هي الأكثر تلوثا بالمعادن الثقيلة، و هذا راجع إلى تمركز الصناعات بهذه المنطقة.

ABSTRACT

The quantification of the baseline of heavy metal content in coastal marine sediments is of great importance in determining hot spots. Eight heavy metals (Hg, Cd, Pb, Cr, Ni, Tl, Zn and Cu) are carried for monitoring programme of the coastal sediment contamination, in the objective to evualuate the direct impact of the urban areas on the heavy metal transfer to the marine medium. The study approach developed shows that the northern Moroccan coasts are relatively more contaminated by heavy metals, especially in the communes of Tangiers, Tetouan/Martil, Al Hoceima and Nador. Within Tangiers and Tetouan/Martil are the most industrialized zones, and their coastal sediments are consequently more polluted. However of that, for compliance purpose with human health regulations with regard to WHO/UNEP (1995) regulations, the northern Moroccan coasts are still without any risk to the human health. On the other side, the concentrations of the heavy metals analysed are lesser than those published in other Mediterranean coastal areas.

Key words: Mediterranean coast, Morocco, pollution, heavy metals, sediments.

RESUME

Identification des points chauds des côtes septentrionales du Maroc et contamination des sédiments par les métaux lourds. La quantification des concentrations des métaux lourds dans les sédiments des côtes a une grande importance dans la détermination des points menacés par la pollution. Huit éléments de métaux lourds (Hg, Cd, Pb, Cr, Ni, Tl, Zn et Cu) ont été étudiés dans le but d'évaluer l'impact direct des zones urbaines sur le transfert de ces éléments dans le milieu marin. L'étude a montré que les côtes méditerranéennes marocaines sont relativement plus contaminées par les métaux lourds : Tanger et Tétouan/Martil sont les plus menacés à cause de l'industrie développée dans cette zone. Néanmoins, les risques sanitaires sont insignifiants dans cette région.

Mots-clés : côte méditerranéenne, Maroc, pollution, métaux lourds, sédiments.

INTRODUCTION

In many countries, much attention has been paid to the baseline contamination of trace elements in sediments as a principal component of geochemical cycles of chemicals, especially heavy metals. The levels detected in sediments are used as an indicator parameter of the quality of the aquatic environment in which the organisms live. Furtheremore, it is very interesting to have knowledge of the presence of pollutants in the estuarian sediments of the northern Moroccan coasts to allow us the identification of the principal "hot spots" that have never been determined before.

The heavy metals studied: mercury (Hg), cadmium (Cd), lead (Pb), chromium (Cr), nickel (Ni), thallium (Tl), zinc (Zn) and copper (Cu), are classified as toxic agents here. They can be desorbed from sediment matrix, diffused in the water column, accumulated, and transferred in different levels of the marine trophic chain (RIBEYRE & *al*., 1979), reaching their highest levels in filter-feeders, such as bivalve molluscs, and in predatory fishes such as tuna and swordfish (RIBEYRE & BOUDOU, 1984; CUMONT, 1984; CHASSARD-BOUCHAUD, 1993).

Apart from the essential resources provided by the marine environment to human life, it should be taken into account in the overall toxicological evaluation that this environment is also an important source of protective factors, which in some cases may counteract hazardous agents (DE FLORA & *al*., 1991, 1994).

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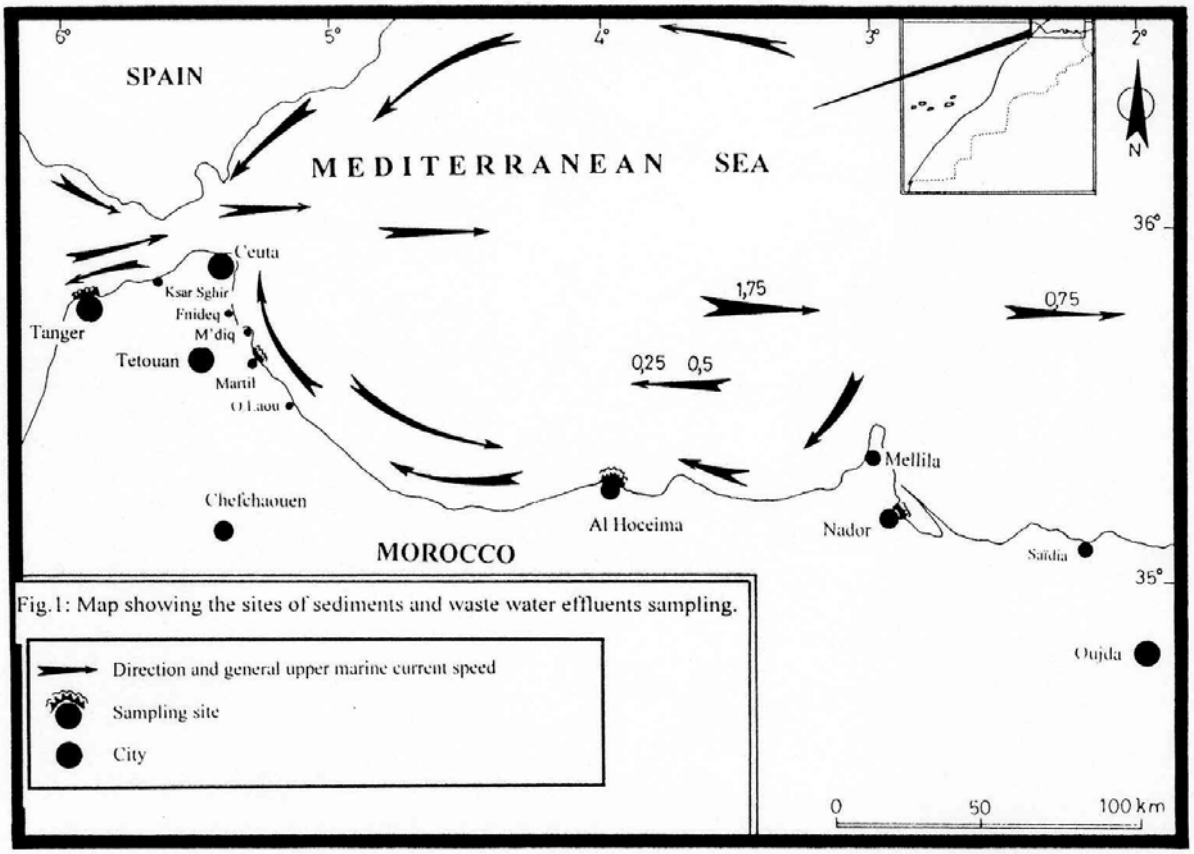

Fig.1: Map showing the sites of sediments and waste water effluents sampling.

Figure 1.

Pollution of the marine environment by heavy metals originates from various sources, the principal ones involved being the following:

(i) Municipal sewage: this is discharged directly into the immediate coastal zone, either untreated or subjected to various treatment procedures, through outfall structures of variable length, or reaching the sea by seepage as result of leaks in sewerage systems or other causes. Municipal sewage carries a large amount of heavy metals, other chemicals and microoorganisms. In cities and large towns, it usually contains a variety of chemical wastes both from households and from industries discharging directly into the public sewerage system.

(ii) Industrial effluents and emissions: industries located near the coastline discharge their wastes directly into the sea. Aerial emissions from industries located inland contain pollutants which can be transported out to sea through the atmosphere. Industrial effluents contain a large variety of chemical wastes, the type of pollutant depending upon the particular industry in question.

(iii) Rivers: polluted rivers carry a considerable amount of wastes to the sea. Apart from municipal and industrial wastes discharged upstream, rivers are also responsible for the transport of sometimes heavy loads of agricultural fertilizers and pesticides. Rivers contribute significantly to transboundary pollution, and effects can be felt at points comparatively distant from the origin. Run-off waters also contribute significatly on the transportation of particles from industry sources.

(iv) Coastal waste disposal: other forms of disposal of solid and liquid waste in or near the marine environment contribute to the direct pollution of the sea in various ways, depending on the type and amount of the material disposed of.

(v) Maritime (offshore) sources: the pollutant discharged in greatest amounts is ballast oil from tankers. In many cases, beaches suffer a variable amount of damage. Ships also dispose of waste materials overbroad.

In very general terms, the majority of the social-economic consequences of marine pollution can be

expressed as immediate of long-term effects on human health. In this context, the two main types of human exposure to pollutants in the marine environment are through direct contact with polluted seawater and/or beach sand, and consumption of contaminated seafood. In some cases where the seawater, after being treated in desalinization plants, is used for drinking purposes, pollution may constitute a potential health risk (WHO/UNEP, 1995).

The estimated turnover time for Mediterranean waters is 80 years (WHO/UNEP, 1995). The basic nature of the Mediterranean circulation system contains components of strong vertical convections which determine the distribution of salinity and produce vertical recycling of nutrients and other dissolved substances (MOLLER & *al*., 1983). When winter storms lower surface temperature in the western Mediterranean to 12°C, deep convection can take place; in the Algerian-Provençal basin it was traced to the depth of 2,000 m (UNEP/FAO, 1989).

In the present paper, Hg, Cd, Pb, Cr, Ni, Tl, Zn and Cu concentrations are analysed in principal mixed effluents and in the coastal sediments of the four largest northern Moroccan cities: Tangiers, Tetouan/Martil, Al Hoceima and Nador. The sampling was carried out during 1993 and 1994.

The fundamental objectives of our work are: (i) the establishement of the actual baseline levels of contaminants in marine sediments ("baseline"); (ii) the identification of heavy contaminated sites ("hot spots"), where levels of contaminants are at least an order of magnitude higher than levels in clean or uncontaminated areas; (iii) the measurement of contaminant levels in marine sediment with regard to the provision of a continuing assurance of the coasts quality with respect to public health.

MATERIALS AND METHODS

According to such programme, the levels of Hg, Cd, Pb, Cr, Ni, Tl, Zn and Cu were analysed especially in effluent discharges and in marine sediments of the nearest estuaries and beaches submitted to the effluent inputs of the considered cities (Fig. 1).

The sampling method, size number of the samples and temperature of storage in icebox, the determination of trace elements in marine sediment were carried according to the Reference Methods for Marine Pollution N°26 (UNEP/IAEA, 1994). In the case of the effluents discharges, the determination of the heavy metals is similar to that of the sediment case, except the digestion step which is carried out by HNO_3/H_2O_2 (2/0.5 ml/ml) mixture in microwave oven, and the use of the modifier matrix concentration.

Samples were taken at various periods of the year. Then our sampling, from 1993 to 1994, were carried out when possible, each quarter, due to the absence of significant seasonal influences on sediment contamination by heavy metals (SABHI, 1990; EL HRAIKI & *al*., 1992).

With regard to the annual concentration fluctuations, eventual temporal trends, were carried out according to sampling, storage, extraction, analysis and interpretation of the results, we have considered for the same site the homogenate of different samples collected during the monitoring programme.

Sediment samples were dried and mixed until obtaining homogenate. Then the aliquotes of 250 mg were carried for extractions and prepared for analysis according to UNEP/IAEA (1994) procedure.

For each considered metal analysis in marine sediment, one standard blank, three sample blanks and certified materials of sediment (BCSS-1 and PACS-1) (NRCC, 1990) were used as control materials. To avoid any contamination, and in the objective to obtain data of good quality, the handling is systematically used according to the Assurance Quality Control System (AQCS) of the IAEA (1995). Control samples or "standard blanks", and the certified materials, were analysed at the same time as that of samples collected in the goal to control the exactitude of measurements.

The digestion steps (Table I) are carried out by making 50 ml of waste water in nitric acid (HNO_3) and dihydroxid (H_2O_2) mixture (2/0.5 ml/ml), in microwave oven "mls1200" under high pressure (Table III). In the case of mercury, digestion of samples was carried out in 2 ml of concentrated nitric acid alone in the microwave oven under low electromagnetic power, to avoid evaporation of mercury.

The processes of digestion protocols of both Hg and Cd, Pb, Cr, Ni, Tl, Zn and Cu in sediments were carried out with respect to prescriptions of UNEP/FAO/IAEA/COI (1984b, 1984c) digestion methods respectively and those of AQCS (1995) protocols.

After mineralisation processes, three measurements were loaded for each sample. Only mean measurements of each aliquote with low standard deviation (<5%) were recorded.

Table I: digestion steps in microwave oven

	Mercury		Cd, Pb, Cr, Ni, Tl, Zn, Cu	
Step	**Power (Watt)**	**Time**	**Power (Watt)**	**Time**
1	100 (without pulse)	1 min	250 (without pulse)	2 min
2	0 (pause)	30 sec	0 (pause)	30 sec
3	130 (without pulse)	5 min	250 (without pulse)	10 min
4	0	1 min	0	30 sec
5	150	5 min	450	5 min
6	0	1-2 min	0	30 sec
7	170	5 min	600	3 min
8	100	2 min	500	1-2 min
9	-	ventilation 10 min	-	ventilation 5 min

Analysis of Cd, Pb, Cr, Ni, Tl, Zn and Cu was carried out with Atomic absorption spectrophotometer 5000 Perkin Elmer with graphite furnace system HGA600 using palladium nitrate as matrix modifier. In the case of cadmium, ammonium nitrate is used as matrix modifier.

The analysis of Hg is loaded by Mercury Hydrid System (MHS10) COLMAN MASB50.

Because of the large number of samples, only mean results of analysis from mixed samples are reported for each species.

RESULTS AND DISCUSSION

HOT SPOTS SITES

From the northern Moroccan Mediterranean coast, we have conducted studies on the impact of discharge of Hg, Cd, Pb, Cr, Ni, Tl, Zn and Cu, analysed in the urban and industrial waste water in the nearest coasts of Tangiers, Tetouan/Martil, Al Hoceima and Nador (Fig. 1). According to our results of 1993 (Table II), seashore bottom is less contaminated than the immediate coastal sediment sampled from the intertidal zones in front of the considered cities. The high levels of heavy metals detected in sediments prove that trace metals coming from the nearest effluents or from elsewhere deposit and are adsorbed to the sediment particles in the water column. On the other hand, the levels of the heavy metals detected in the seashore sites are in accordance with the high ability of heavy metals to be dissolved in the sea water and are easy to be dispersed by marine currents. The other main explanation is the non-consistent effects of effluents coming from the coastal cities "Hot Spots" on immediate receptor (marine medium). In our previous research (SABHI, 1990), the results of analysis carried in the sediments of the intertidal area were strongly different from those of samples in the seashore, one mile from of the selected coasts (Table II). From our previous and present data analysis of heavy metals (SABHI, 1990) and pesticides (El ALAMI, 1991; EL HRAIKI & *al*., 1992) in sediment collected in immediate coasts and seashore, we have been conducted to underline the considered cities of the northern Moroccan coast, as major sources of urban and industrial discharges (hot spots).

TEMPORAL TRENDS ON SEDIMENT CONCENTRATION BY HEAVY METALS

Analysis of the results of three years of sediment monitoring (1992 to 1994) showed that:

(i) there are significant sample-to-sample variations in contaminant concentrations in sediments of the same area, caused certainly by nearest hot spots outflows, where major changes in contaminant inputs occur before the metals reach the marine bottom;
(ii) there are relatively significant differences in mean contaminant levels between samples of different sites (Tables II and III).

These environmental trends (time and location changes) can be related to two types of factors : (1) the high ability of the heavy metals to diffuse in aqueous medium; (2) the large effects of oceanographic parameters as current directions, speeds, temperature, salinity, pressure... and factors related to handling samples and their resultant data (e.g. improper sample selection and handling). These observations are in agreement with those reported by CHAN (1989), MISRA & *al*. (1989, 1990), UTHE & *al*. (1991a, 1991b), NICHOLSON & FRYER (1992), FRYER & NICHOLSON (1993).

As sampling of sediments was carried out in the same coordinates respectively, thus reducing variability and improving the homogeneity of response among test environment, we are able to deduce by the results and those reported by CHAN (1989) , that , processes that might influence the

Table II: Concentrations of mercury, cadmium, nickel, chromium, thallium, lead, zinc and copper in effluents ($mg.l^{-1}$) and sediments ($mg.g^{-1}$ D.W) sampled in front the hot spots and reference areas (seashore).

Coast	Metal analyzed	Statistical parameters	Tangiers	Tetouan (Martil)	Al Hoceima	Nador
	Hg	x	0.001	0.002	0.007	0.011
		s_{n-1}	0.001	0.007	0.001	0.008
	Cd	x	0.07	0.035	0.001	0.011
		s_{n-1}	0.017	0.007	0.001	0.001
	Ni	x	0.007	0.080	0.001	0.001
		s_{n-1}	0.002	0.009	0.001	0.002
Major effluent discharges	**Cr**	x	0.215	0.318	0.030	0.110
		s_{n-1}	0.070	0.002	0.007	0.007
	Tl	x	0.001	0.001	0.001	/0.001
		s_{n-1}	0.001	0.001	0.001	0.007
	Pb	x	0.070	0.115	0.016	0.100
		s_{n-1}	0.006	0.003	0.002	0.038
	Zn	x	0.130	0.250	0.070	1.15
		s_{n-1}	0.007	0.005	0.008	0.112
	Cu	x	0.030	0.115	0.033	0.019
		s_{n-1}	0.001	0.008	0.01	0.005
	Hg	x	0.09	0.120	0.007	0.055
		s_{n-1}	0.015	0.070	0.002	0.007
	Cd	x	0.253	0.125	0.03	0.110
		s_{n-1}	0.009	0.050	0.008	0.015
Coastal sediments	**Ni**	x	0.030	0.110	0.007	0.060
		s_{n-1}	0.005	0.007	0.002	0.005
in front of the major effluents	**Cr**	x	0.417	0.517	0.150	0.111
		s_{n-1}	0.020	0.050	0.013	0.007
	Tl	x	0.020	0.007	0.009	0.030
		s_{n-1}	0.003	0.003	0.002	0.002
	Pb	x	0.215	0.417	0.175	0.520
		s_{n-1}	0.02	0.03	0.007	0.015
	Zn	x	12	30	9.2	37.7
		s_{n-1}	1.2	1.3	1.6	0.7
	Cu	x	4	3.5	1.2	6.7
		s_{n-1}	0.5	0.7	0.7	0.8
	Hg	x	0.002	<0.001	<0.001	0.08
		s_{n-1}	0.002	0.001	0.001	0.005
	Cd	x	0.020	0.009	<dl	0.05
		s_{n-1}	0.003	0.009		0.005
Offshore sediment	**Ni**	x	0.007	0.015	0.004	0.01
		s_{n-1}	0.002	0.003	0.001	0.004
1 mile from coast line	**Cr**	x	0.05	0.025	0.01	0.07
		s_{n-1}	0.007	0.005	0.007	0.002
	Tl	x	<0.001	<0.001	<0.001	0.015
		s_{n-1}	0.001	0.001	0.001	0.008
	Pb	x	0.055	0.017	0.020	0.022
		s_{n-1}	0.005	0.006	0.004	0.007
	Zn	x	3.5	1.17	2.2	1.7
		s_{n-1}	0.007	0.003	0.007	0.15
	Cu	x	0.10	0.070	0.330	0.120
		s_{n-1}	0.003	0.002	0.1	0.007

Table III: Baseline contamination trends over 1992 to 1994, by mean of linear regression coefficient analysis.

	Heavy metals	**Hg**	**Cd**	**Ni**	**Cr**	**Tl**	**Pb**	**Zn**	**Cu**
Effluents	Tangiers	-	0.96	0.94	0.96	-	0.97	0.99	0.99
	Tetouan/Martil	0.96	0.99	0.96	0.99	-	0.98	0.99	0.99
	Al Hoceima	-0.94	-0.97	-	0.99	-	0.97	0.99	0.99
	Nador	0.96	0.96	-	0.99	-	0.90	0.98	0.99
Coastal sediments	Tangiers	0.97	0.99	0.99	0.99	0.99	0.93	0.99	0.94
	Tetouan/Martil	0.90	0.95	0.92	0.92	0.86	0.90	0.99	0.99
	Al Hoceima	-0.99	-0.99	0.86	0.99	0.98	0.97	0.99	0.98
	Nador	0.99	0.98	0.94	0.97	0.99	0.99	0.99	0.94

temporal variation of metal concentrations in aquatic environment include : (i) variable metal input into the aquatic environment, (ii) speed of deposition, and (iii) changes in the physical-chemical characteristics of the surrounding waters.

In general, the analytical results obtained from covariables, time and concentrations of the heavy metals (Hg, Cd, Pb, Cr, Ni, Tl, Zn and Cu) show significant positive correlations (Table III) between accumulation in the sediments versus time, where these increased contaminations baselines along the time should be due to the continuing processes of inputs within these eight heavy metals.

The analysis of temporal trends using a linear regression between concentrations of metal versus the years of the monitoring had shown that, in general, the trend of increasing contaminant levels in most sites studied here should be corroborated by increased inputs from nearest hot spots or by those far from Moroccan coasts from there, by oceanographic currents (C.E.R.B.O.M., 1982). Other data had shown that atmospheric transportation contribute to 2/3 of heavy metal input in Mediterranean sea (UNEP/OCA, 1993).

From the results analyzed in Table III, it is clear that covariables within population (and thus sample) differ among individual sampling and during different time periods within their lifetimes. In this field of investigations, UTHE & *al*. (1991a, 1991b) reported that, with few exceptions, yet concentrated levels of coastal sediments demonstrate transfer fluxes to the sea. In addition, aquatic medium is submitted to the control of environmental factors such as temperature and is thought to be affected by chemical and other types of contamination sources. Many of those covariables are less obvious, e.g., physical-chemical process, while in other cases the relationship is only suspected, e.g., input status or discharge intensity.

In order to account for the effect of covariables on contaminant levels, we have introduced linear regression as statistical model to demostrate the trends of contaminant concentrations with regard to the time of input disharges.

These results are conform to those reported by UNEP/IAEA (1994) and UNEP/IAEA/IOC (1986) by data collected in an international monitoring programme.

This step function in heavy metal levels arise because of change in the contaminant, that is immediatly reflected in the levels in the considered site of sampling. In this field, NICHOLSON & FRYER (1992) reported that, however, changes in contaminant levels will not necessarily have this form; they introduced six stylized scenarios of possible patterns of changes that are in agreement with our data analysis:

(i) change in load with immediate uptake,

(ii) change in load with gradual uptake,

(iii) linear change in load/uptake (same scenario than ours),

(iv) exponential change in load /uptake,

(v) incident with immediate recovery, and

(vi) randomly fluctuating levels.

In the other studies reported in by MISRA & UTHE (1987), more covariables were introduced to handle data of temporal trends monitoring in both marine biota or sediments as: fork length, total weight, age (otolith), sex, liver, weight, and percent extractable fat in liver and muscle were recorded for each specimen. So the importance of clearly defining the objectives of the study must be emphasized. Most of the sites monitored showed relative high levels of Zn, Cu, Cr and Pb, especially in Tangiers and Tetouan/Martil sites (Table III).

Given the complex biochemical/physiological nature of living organisms and the complex nature of the processes influencing a contaminant in the environment, it is difficult to determine how much of any observed trend in a sediment analysed reflects environmental change. The abiotic compartments (sediments, suspended particulate material, and seawater) have to be more studied in the objective to throw further light on this relationship. On the other side, many studies had confimed these comments (UTHE & *al*., 1991a, 1991b; NICHOLSON & FRYER, 1992; UNEP/IAEA, 1994).

TRENDS OF SPATIAL CHANGES

From the same area during the three years of the monitoring (Table III), or at the same period of monitoring (Tables II and III) we have recorded large interspecific changes in both concentrations of the metals analysed. On the other side, high variations and wide range of metal concentrations were observed with regard to geographical changes, especially in Tangiers and Tetouan/Martil.

Most of the cities monitored showed relatively high levels of Zn, Cu, Cr and Pb, especially in Tangiers and Tetouan/Martil zones (Table III). On the other side, the coast of Nador was remarkably contaminated by lead. The relatively high concentrations in both Tangiers, and Tetouan/Martil's coasts (Fig. 1; Tables III and III)) is related to manufactories, and industrial and urbanistic activities. These results show that Tetouan/Martil coast is relatively the most contaminated area in the northern Mediterranean coast of Morocco. In all samples of sediments analysed from the four cities, the contamination levels of Hg, Cd, Ni and Tl were low in comparison to informations of WHO/UNEP (1995); it should be certainly due to the particular geographic situation of this city between the Atlantic ocean and the Mediterranean sea, that certainly contribute to the fast natural diluting of the Mediterranean outer currents.

The contamination magnitudes of Hg, Cd, Ni and Tl were low in most of the monitoring areas, with comparison to data reported in other Mediterranean countries (UNEP/FAO, 1989; WHO/UNEP, 1995).

COMPARATIVE STUDY OF BASELINE SEDIMENT CONTAMINATION BY Hg, Cd, Pb, Zn AND Cu

Mercury

In general, the levels of Hg (0.007 to 0.120 µg Hg/g D.W.) detected in different Moroccan coastal areas are lower than the typical background value for the Mediterranean (WHO/UNEP, 1995). Levels higher than background were observed in sediments of the Tiber delta which is not far away from the well known mercury anomalies of the Monte Amiata area. Much higher than background levels have been observed near the Idrija mercury anomaly which drains through the Isonzo river into the Gulf of Trieste. Concentrations up to 50 mg Hg-T/Kg D.W. were observed in sediments from the river mouth (WHO/UNEP, 1995).

Cadmium

The results of cadmium concentrations analysed in the Moroccan coastal sediments (0.03 to 0.253 µg Cd/g D.W.) are lower in comparison to those of the earlier publications. The concentrations in Mediterranean marine sediments range between 0.1 and 2.3 µg/g D.W. (UNEP, 1978). DONAZZOLO & *al*. (1984) report a probable background cadmium concentration, as calculated from core samples, of 1.2 µg/g D.W. FRIGNANI & GIORDANI (1983) report concentrations of 0.5-2.5 µg/g D.W. in offshore sediments, whereas VOUTSINOU-TALIADOURI (1983) quote a value of 0.4 µg/g D.W. for Aegean sea sediments. A probable background cadmium concentration should be in the range of 0.1 to 2.5 µg/g. D.W. WHITEHEAD & *al*. (1985) suggested a background concentration of 0.15 µg Cd/g DW of sediment.

The results of the Calypso cruise around the Mediterranean coastline give a mean of 0.13 µg Cd/g D.W. (range: 0.035 to 0.56 µg Cd/g D.W.) (WHITEHEAD & *al.*, 1985).

In other cases, where samples were taken from areas close to source inputs, industrial or urban, cadmium concentrations have been reported to range from 0.3 to 10 µg Cd/g D.W. The various lagoons along the French coast of the Gulf of Lyons are heavily polluted with cadmium (étang Salses-Leucate >5 µg Cd/g D.W.; étang Bages-Sigean >6 µg Cd/g D.W.; étang de Thau >4 µg Cd/g D.W.; BUSCAIL & *al*., 1985).

Very high concentrations (32-64 µg Cd/g D.W.) have been reported in sediments of Spanish lagoons (DE LEON & *al*., 1983), in Izmir Bay (0.2-40 µg Cd/g D.W. (UYSAL & TUNCER, 1985) and in the harbour of Alexandria (7-64 µg Cd/g D.W., SAAD & *al*., 1981).

Lead

The levels of Pb in sediments ranged between 0.175 and 0.520 µg Pb/g D.W, that are lower than

those reported in sediment core samples (12 to 32 µg Pb/g D.W; OREGIONI, 1980). DONAZZOLO & *al.* (1984) have reported background values for Pb, derived from core samples to be around 23 µg Cd/g D.W. Offshore sediments have Pb concentrations ranging from 15 to 94 µg Cd/g D.W. (FRIGNANI & GIORDANI, 1983; VOUTSINOU-TALIADOURI, 1983).

In coastal sediments, relatively high Pb concentrations (100-330 µg Cd/g D.W.) have been reported near inputs in coastal lagoon, Spain (200-2000 µg Cd/g D.W.), coast of Spain (23-3300 µg Cd/g D.W.), Marseille (28-1250 µg Cd/g D.W.), Cagliari (64-670 µg Cd/g D.W.), Gulf of Trieste (18-470 µg Cd/g D.W.), and Thermaikos Gulf (25-130 µg Cd/g D.W.).

Copper

The levels observed in our study (1.2-6.7 µg Cu/g D.W.) are very low with regard to those recorded as background of Mediterranean sediments (10-30 µg Cu/g D.W). On the other side, concentrations in coastal sediments from different Mediterranean areas are considerably higher than background values. Thus, high concentrations have been reported from Cartagena, Spain (mean 226 µg Cu/g D.W.), Valencia, Spain (mean 118 µg Cu/g D.W.; DE LEON & *al*., 1985), Catalonian coast (7-229 µg Cu/g D.W.; MODAMIO, 1986), Gulf of Lyons (50-200 µg Cu/g D.W.; NOLTING, 1990), Izmir Bay, Turkey (33-866 µg/g D.W.; YARAMAZ & *al*., 1990), Saronokos Gulf, Greece (mean 364 µg Cu/g D.W.; ANGELIDIS & *al*., 1983), the river Rhone delta (20-55 µg Cu/g D.W.; ADDED & *al*., 1981), in the Ligurian Sea (14-145 µg Cu/g D.W.; COSMA & *al*., 1979, 1982, 1983), gulf of Trieste (9-139 µg Cu/g D.W.; MAJORI & *al.*, 1979), in the western harbour of Alexandria (SAAD & *al*., 1981), where a value of 1890 µg Cu/g D.W. has been reported.

Zinc

The values of zinc reported in this study (9.2-37.7 µg Zn/g D.W.) are very low compared to the background concentration for total zinc in Mediterranean sediments (20 µg Zn/g D.W.) and to those of Portman and other coastal sites in Spain (up to 6480 µg Zn/g D.W) (WHO/UNEP, 1995), in the vicinity of Marseille (2550 µg Zn/g D.W), in the Gulf of Elefsis and the upper Saronikos Gulf, Greece (2100-2400 µg Zn/g D.W), in the Venice lagoons (up to 5930 µg Zn/g D.W), and at various sites in the Ligurian sea, the Kastela bay, Croatia (1300 µg Zn/g D.W.), inner Izmir bay, Turkey, the lake Mariut, the abu Kir bay, the Alexandria harbour in Egypt. Offshore sediments have zinc concentrations ranging usually between 20 and 80 µg Zn/g D.W. (FRIGNANI & GIORDANI, 1983; VOUTSINOU-TALIADOURI, 1983). However, SHAW & BUSH (1978) reported average zinc concentrations in deep sea sediments of around 117 µg Zn/g D.W. In sediment cores, the zinc levels usually range between 20 and 85 µg Zn/g D.W. (WHO/UNEP, 1995).

RISK ASSESSMENTS ON HUMAN HEALTH

In general, the heavy metals Hg, Cd, Pb, Ni, Tl and Cr concentrations observed (Table III) are lower than those of Zn and Cu analyzed in the same samples at the same conditions. This should be caused by high environmental Zn and Cu levels and their high affinity to be adsorbed to sediment particles. In contrast, the data of waste water analysis of all of the Hg, Cd, Ni and Tl, showed that most of them have concentrations beneath detection limits (<0.1 µg Hg/Cd/Kg D.W.).

CONCLUSION

The determination of trace metals in marine sediments is an important aspect of ecotoxicological and geochemical marine pollution studies and for assessing the levels and pathways of marine pollutants.

In general, the heavy metal content in sediments of northern Moroccan coasts is comparable to those reported from many other countries around the Mediterranean sea. Only small changes in metal contents of various samples was observed, which is mainly due to the analysis of mixed samples. A clear increase or decrease in the metal content was observed for many of the investigated fishery products during the reported period of monitoring. Thus, temporal trends showed an increase of both of Hg, Cd, Pb, Cr, Ni, Tl, Zn and Cu concentrations in most samples of sediments coming from different areas analyzed, and clear significant annual influences were observed.

With concern to investigations in other Mediterranean areas, the sites of Tangiers and Tetouan/Martil, can be actually classified with regard to local conditions (national urbanistic and industrial developments) in the list of hot spots as pollution sources.

All of the potentially toxic elements investigated in the present work showed lower levels than those usually found in the marine sediments collected from

other coastal areas of the Mediterranean, with exception to local hot spots (Tangiers and Tetouan/Martil), characterized by relatively high urban and industrial activities.

On the basis of what is decided, our future investigations will be focused on the dynamics of the heavy metal transfer from marine water and sediment interfaces using individual and mixed heavy metal concentrations, to evaluate the desorption of the these toxics from sediment particles and their effect on marine biota.

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