

Geochemistry of heavy metals in the Moroccan Atlantic Coastline (Area of Safi City)

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Abstract

The Moroccan Atlantic coastline in the area of the city of Safi constitutes a province where concentrates important industrial activities. These activities are essentially implanted along the coast. The study heavy metals behavior shows concentrations overpassing their relative limits of contamination. granulometry sediments (especially fine fraction) play an important role in heavy metals concentration and complexation. The speciation, while using the sequential attack protocol of Tessier *et al.* (1979) between chemical fractions shows that large part of metals is carried by siliceous fraction and furthermore supports of contamination for metals.

Key words: Morocco, Atlantic coastline, Safi , geochemistry.

Introduction

This work aims the characterization of geochemistry quality of surface sediments in the Moroccan coastline in the area of city of Safi, by using the

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distribution of some heavy metals (Pb, Zn, Cu, Cd, Ni and Cr) in sediments of surface and in different chemical fractions forming the studied substrata.

Indeed, this coastline is the seat of an important urbanization and of chemical industrial complexes (transformation of phosphates, production of sulfur and sulfide products) and of fish canneries factories. Otherwise, industrial and urban wastes are poured directly in sea without previous treatments.

Studied area belongs on structural plan to western Meseta and precisely to Doukkala plain. Hinterland of this studied area is constituted by post paleozoic formations which can be described succinctly as follows:

- Jurassico-Cretaceous formed by pink clays and especially marly limestone with some gypsum levels surmounted by white limestone forming the cliffs of Safi;
- Miocene constituted by sandy marls containing oysters;
- Post Miocene formations are sandstone and marine limestone;
- Quaternary is formed of coastal cords and sandy dunes and by alluvial contributions.

The climate of Safi province is semi-arid. It is attenuated approaching the Atlantic Ocean. This zone shows low temperatures oscillating between 12°C and 26°C and a precipitation with an annual mean of 280 mm.

Morphologically, this zone is constituted of several beaches as Lalla Fatna, Cape Eddouza and Kasbet Hmiddouch. One notes the existence of several cliffs especially in the vicinity of Safi. A large part of landscape is formed of dunes and coastal cords.

Soils associated to cashing formations of this region cover a total surface of 712 000Ha and are as follows:

- a - R'mel: Constituted of sand and flint. It covers the whole inshore region of the province.
- b - Tirs: Characterized by the abundance of organic debris what explains its fertility. It covers the major part of Abda plain.
- c - Hamri: Constituted of clay, flint and sand. It is less fertile than Tirs but constitutes an important and wide formation in Ahmar plain.

Materials and Methods

The sectors chosen for this study are (Figure. 1):

- 1) Sidi Bouzid – Safi beach: Subject to urbanization and a confinement,
- 2) Ouassel - Sidi Rhouzia: Closed to industrial zone,

The forty three samples of surface sediments (Figure. 1) sampled following radials in supra - to intertidal zones in the three sectors, were subject to granulometrical (sands and clayey fraction), mineralogical (By RX diffractometry) and chemical (major elements and traces) analysis in total sediments and in different chemical fractions.

Previously to geochemical analysis, samples have been kept in low temperature ($T < 4^{\circ}\text{C}$) and dried on a Christ lyophilisator (Alpha 1-4 model) at 1,03mbar during 12 hours in a first time then to 0,01mbar during 12 other hours.

Besides acidic attack of total sediment, a sequential extraction has been done on the totality of sediment.

Schemes of sequential extraction are: Gupta and Chen (1975), Tessier *et al.* (1979), Quevauvillier *et al.* (1994), Maiz *et al.* (1997), Rauret *et al.* (1998), Veeken and Hamelers (2003) and Durand (2003). The kept scheme is Tessier *et al.*'s one (1979), because of different details given in this experimental protocol and also that the objectives of our work agree well with different studied phases, and aim rather a qualitative study.

The results of chemical analysis have been reported on radials (Figure. "3a" to "3g"), in order to show their spatial distributions.

Results

Distribution of metals in superficial sediments

Lead (Pb)

Lead concentrations vary from below detection values to 32 ppm. Most frequent values oscillate between 8,5 and 17,5 ppm. Highest values are recorded in Tensift Wadi and between the locality of Sidi Bouzid and the port of Safi. It is about either of sheltered zones, to outlet of river or to downstream of industrial areas (Figure. 2a). This variability of lead concentration reflects the existence of punctual sources of contamination that could be related to urban wastes. However this hypothesis doesn't explain

the elevated values met locally in sheltered zones and in Wadi Tensift outlet, what could be in relation with industrial activities.

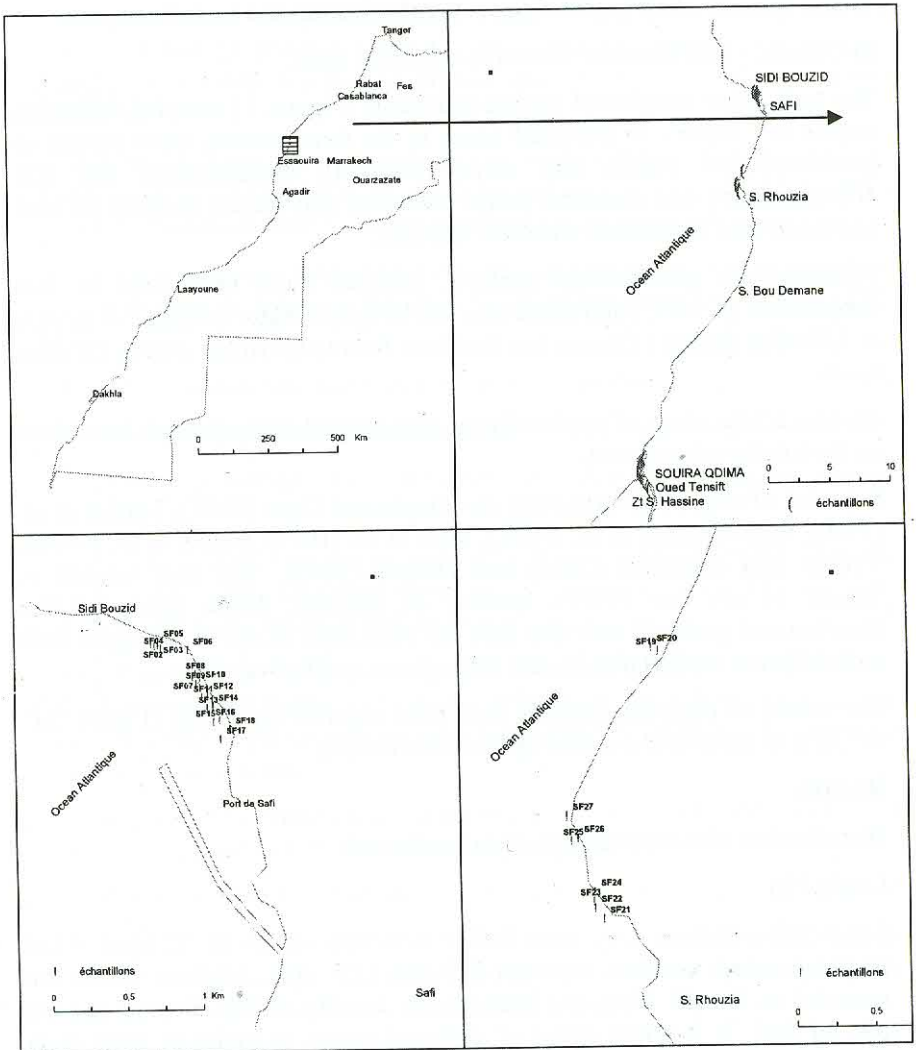


Figure 1. Situation of studied area and sampling zone

Table 1. Heavy metals composition in surface sediments

	Pb	Zn	Cu	Cd	Co	Ni	Cr
SF1	10	46	29	2	2	3	9
SF2	9	61	19	2	2	3	7
SF3	12	59	19	3	2	2	14
SF4	9	77	19	2	2	1	16
SF5	5	57	19	3	2	4	7
SF6	9	41	16	nd	nd	nd	6
SF7	11	97	44	3	3	4	19
SF8	28	203	155	3	2	2	15
SF9	32	268	189	3	3	1	8
SF10	20	189	133	2	2	nd	12
SF11	19	205	142	1	2	nd	7
SF12	15	32	18	nd	nd	1	4
SF13	19	71	25	nd	nd	1	2
SF14	17	107	62	nd	nd	2	5
SF15	30	155	124	4	2	3	19
SF16	27	148	176	5	4	6	22
SF17	32	165	142	4	4	2	17
SF18	9	123	32	3	3	2	16
SF19	9	41	27	2	2	4	10
SF20	6	50	29	2	2	2	7
SF21	9	59	21	2	2	3	5
SF22	21	99	24	nd	nd	nd	7
SF23	17	85	20	nd	nd	2	5

Zinc (Zn)

Results of zinc analysis vary also from below detection values to 268 ppm. Most frequent values vary from 49 to 133ppm. As for lead, highest values are recorded in Tensift Wadi and between Sidi Bouzid and the port of Safi (Figure. 2b). We note that more than 75% of the samples present

concentrations that pass the mean natural concentration of land (61ppm) and are superior to the doorstep of contamination evoked by Laurent *et al.* (1977). The variations of zinc concentration in different stations of sampling attest that it could be about a contamination of the coastline from alluvial sources.

Copper (Cu)

Concentrations of Copper are widely variable and vary from below detection value to 189 ppm in totality of studied area. Most frequent concentrations are between 19 and 62 ppm for about 80% of analyzed samples (Figure. 2c). These concentrations are close to natural concentrations mean value in dried sediment which is about 45ppm (Illou, 1999). This large disparity between values would not be explained by differences in the physico-chemical conditions of the area, but rather by the existence on the coastline of punctual sources of contamination in copper.

Indeed, most elevated concentrations are found Sidi Bouzid and the port of Safi. This relatively sheltered zone is recognized by industrialization. High concentrations vary from 123 to 189 ppm. We remark also that at Tensift Wadi outlet, elevated concentrations have been recorded and vary 74 to 98 ppm. These concentrations remain, for a part of samples, elevated, first, to those described in non polluted sediments (Illou, 1999) and, second, to the doorstep of contamination proposed by Laurent *et al.* (1977) which is about 30 ppm.

Nickel (Ni)

This element presents low concentration non detectable in the majority and don't exceed 6ppm. Detectable values of nickel are recorded at the Tensift Wadi outlet where clays are dominant (Figure. 2d). All concentrations recorded for nickel are lower or analogous to described concentrations for non polluted marine sediments (4 to 7ppm) and as extensively below the doorstep of contamination given by Laurent and *al.* (1977) which about 5ppm.

Cobalt (Co)

Concentrations of cobalt revealed by studied surface sediments vary from less 1ppm to 4ppm (Figure. 2nd). Most frequent concentrations are between 1,3 and 2,9ppm, about 95% of samples, and therefore slightly superior to normal mean concentration estimated around 2ppm. Elevated concentrations

are situated, as for Ni, at Tensift Wadi outlet and to the front of the port of Safi. (South of Sidi Bouzid). These results would reveal an anthropic origin of the contaminations.

Cadmium (Cd)

The results of Cd analysis in superficial sediments show some concentrations comparable to those described by Illou (1999) in sediments of non polluted zones. Obtained concentrations present a big homogeneity and don't reflect any sources of contamination at least for this element with the exception of Debra zone (to the North of Safi) characterized by industries activities of sulfur and phosphate transformation of for which one sample showed a relatively raised concentration in Cd (4,7ppm) and that slightly passes the doorstep of contamination fixed by Laurent *et al* (1977) to 3ppm (Figure. 2f).

Chromium (Cr)

This element gives same configuration of distribution that recorded cadmium. Concentrations form certain homogeneity and vary from 9 to 22ppm (Figure. 2g). Also, concentrations in chromium revealed by surface sediments analysis of studied zone in the present work remain lower to the limit of contamination by this element, and this denotes the absence of a source of pollution by Chromium. Unusually and relatively to the rest of prospected localities, Debra zone (to the North of Safi) showed concentrations relatively raised in Cr (22ppm) dealing maybe, in the absence of industrial activities using Cr (e.g. chromium-plating, dry cleaning, etc...), with sulfur industries wastes and transformation of the phosphate.

Affinities of metals with the nature of substratum in studied area

To understand the behavior of metals, it was necessary to see their affinities regarding to the substratum nature its composition in total organic carbon (TOC). The results of this description are given by Table 2.

Table 2. Correlation Coefficients de between heavy metals concentrations, Total organic Carbon (TOC) and the fine fraction (Fr<63µm)

	COT	Fr < 63µm
Pb	0,49	0,62
Zn	0,82	0,61
Cu	0,49	0,56
Ni	0,79	0,57
Co	0,65	0,27
Cd	0,81	0,65
Cr	0,70	0,30

It appears that the majority of analyzed elements show a good interrelationship with the rate of fine fraction in studied sediments. Besides, linear interrelationships established between chemical elements and total organic carbon (Bouasria, thesis in progress) and particularly couples of Zn-TOC, Ni-TOC, Co-TOC, Cd-TOC and Cr-TOC are very strong. To this consideration, it agrees to note the effect of organic matter and fine fraction in complexation and concentration of metals, in superficial sediments, as metallico-organic complex and / or metallico-organo-clayly complex.

Affinities between metals and interrelationships

Relations between the different analyzed metals have been determined with the help of calculation of total interrelationship matrix (Table 3).

The study of linear interrelationships between elements permits to show metallic associations. Considered metallic couples, show meaningful interrelationship coefficients varying between 0,52 and 0,93 are Pb-Zns, Pb-Cu, Zn-Cu, Cu-Cd, Cu-Co, Cd-Co, Cd-Ni and Cd-Cr. These good interrelationships indicate a well geochemical association of these elements and especially the existence, of a same source of feeding these elements.

Table 3. Interrelationship Matrix between heavy metals in superficial sediments

	Pb	Zn	Cu	Cd	Co	Ni	Cr
Pb	1,000						
Zn	0,699	1,000					
Cu	0,795	0,858	1,000				
Cd	0,385	0,420	0,520	1,000			
Co	0,325	0,429	0,529	0,931	1,000		
Ni	0,130	-0,023	0,122	0,654	0,560	1,000	
Cr	0,265	0,319	0,386	0,776	0,722	0,461	1,000

Distribution of metals in different chemical fractions of samples

The results of extractions have been reported by elements in the corresponding figures. Values of chemical fractions obtained by these extractions according to Tessier *et al's* (1979) experimental protocol are as follow:

- F1 - exchangeable metals (Acido - soluble and soluble in water)
- F2 - metals related to carbonates
- F3 - metals related to oxides and hydroxides of iron and manganese
- F4 - metals related to the organic matter and sulphides
- F5 - metals related to crystalline networks

Lead (Pb)

Obtained results for Lead indicate that fractioning is nearly identical for all samples. In exchangeable fraction (F1), it is almost absent from 0 to 7% (of total Pb). In the non residual, lead is in majority taken by F3 fraction (oxides of Fe and Mn.) whose rates vary between 7 and 31% (of total Pb) what is in agreement with results of Span and Strong (1984). Carbonates and the exchangeable fraction only participate little in lead concentration. It is necessary to note also that organic matter and sulphides (F4) contain a considerable part of Pb (Figure. 3a).

Zinc (Zn)

Results of relative analysis to Zn fractioning show that this element is carried extensively by the residual fraction with rates varying from 45 to 82% (total Zn). Among non residual fractions, the one of iron and

manganese oxides shows very elevated rates of Zn (of 4 to 39% of total Zn). This affinity of Zn to oxides has also been confirmed by Lena and Gade (1997), Kuo *et al.* (1983) and Ramos *et al.* (1994). We also note the role played by carbonates in fixing Zn and that concentrate it with rates (until 26% of total Zn) (Figure. 3b).

Copper (Cu)

Results of relative analysis to Cu fractioning, in superficial sediments, show that this element is distributed between three chemical compartments that are by order of decreasing importance: silicateous residual fraction (F5), fraction related to organic matter and to sulphides (F4) and exchangeable fraction (Figure. 3c).

Nickel (Ni)

Ni distribution in different chemical fractions shows that this element is essentially concentrated in the silicateous residual fraction (F5). This association has been demonstrated elsewhere by Brannon *et al.* (1976), and Illou (1999). The proportion of nickel recovered in the non residual fractions (F1, F2, F3 and F4) is oscillating between 22 and 59% of total Ni. Among those non silicateous fractions, exchangeable fractions contain, in general, most elevated rate in Ni. We also note that retained part of Ni by organic matter and sulphides remained non negligible (Figure. 3d). This association can be in favor of a bio-availability of the Ni conjugated to its strong mobility.

Cobalt (Co)

As for Ni, cobalt distribution in different chemical fractions reveals that this element is essentially concentrated in the silicateous residual fraction vestigial (F5). Proportion of nickel recovered in non residual fractions (F1, F2, F3 and F4) is situated between 21 and 40% of total Co. Among those non silicateous fractions, exchangeable fractions contain, in general, the most elevated rate in Co. We also note that the part of the Co kept by organic matter and sulphides remained relatively negligible (Figure. 3rd).

Cadmium (Cd)

This element is found in non negligible concentrations in exchangeable fraction (F1) that concentrates until 34% of total cadmium. Otherwise, concentration of cadmium kept by carbonates (F2) is substantial with rates that oscillate between 19 and 73% of total Cd. Furthermore, we remark that

the part of Cd extracted from organic fraction and sulphides remained low (Figure. 3f).

The association of cadmium with non residual phase, and mainly with carbonates, suggest that Cd is potentially available, to see even ingested, for fauna and flora (Xian 1989). This association between Cd and carbonates, in marine sediments, has been demonstrated by several authors, as Förstner *et al.* (1978), Salmons and Förstner (1980), Cenciarini and Fernex (1980) and Rifaat *et al.* (1992).

Chromium (Cr)

Cr distribution in chemical fractions of studied coastal sediments shows its fixing by iron and manganese oxides (F3) and organic matter (F4), and that it is carried extensively in silicateous residual phases (F4) (Figure. 3g). The role played by organic matter in the complexation of chromium is also demonstrated by the good linear interrelationship of this element with rate of total organic carbon (TOC).

Discussions

The distribution of metals traces in different litho-geochemical fractions of inshore sediments of the Moroccan Atlantic coastline permitted to put in evidence the preferential associations between these metals and sedimentary supports.

- The exchangeable fraction especially concentrates a good part of metals Cd, Ni, Pb, Co and Cu. These metals would be concentrated by adsorption to the surface of clays, or by infiltration through plans of their crystalline networks.
- The carbonated fraction especially retains zinc and cadmium. These elements can be associated to carbonates during their precipitation or they are introduced to the site as unsteady metallic carbonates. Indeed, the origin of biogenic carbonates under kinds of tests cannot be neglected.
- The fraction of iron and manganese oxides and hydroxides concentrate a good part of Pb and the Zn.
- The fraction dealing with organic matter plays a non negligible role in concentration and complexation of all metals and especially Cu, Cr, Cd, Co, Ni and Co. These associations would depend on physico-chemical conditions of the site and would have a chemical origin by formation of an

organo-metallic complex, as well as a biogenic origin. This affinity to organic matter has been demonstrated also by the good interrelationships "Metals - COT.

The siliceous residual fraction incorporates the major part of studied metallic elements with exception of cadmium that would be carried more by the F1 fractions and F2.

The granulometry of sediments has a determining role in metals fixing; so the relatively thin sediments localized in sheltered zones (South of Sidi Bouzid, in Debra zone (North of Safi) and to the outlet of Tensift Wadi) arrive to concentrate strong concentrations of heavy metals.

Concentrations of total metals pass somewhere the doorstep of contamination defined for marine sediments. This contamination especially affects harbor zone at the South of Sidi Bouzid, Debra zone, and to least the outlet of Tensift Wadi. Besides the non residual fractions, and particularly organic matter, constitute important sources of traces metals potentially available of which it is necessary to take account explicitly at time of evaluation of the bio-availability of metals.

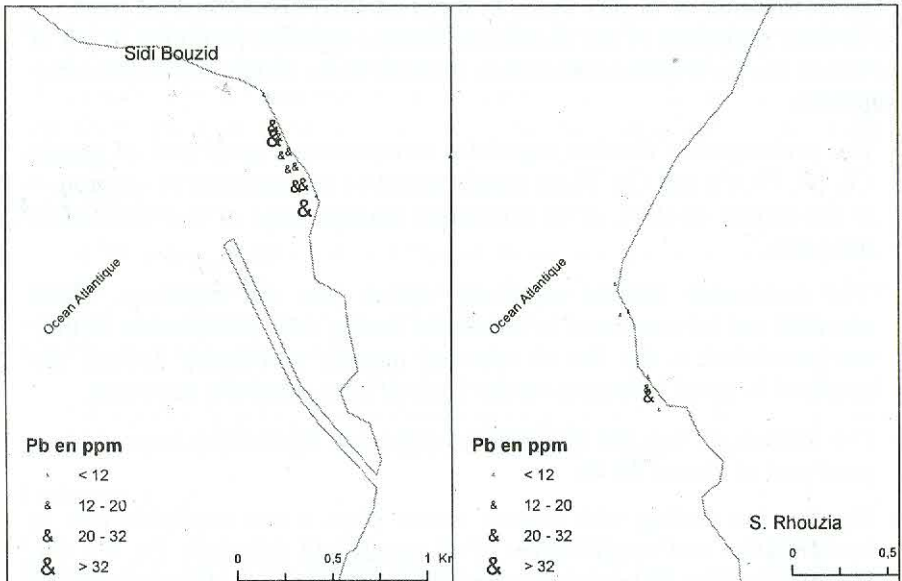


Figure 2a. Distribution of Pb concentrations in surface sediments

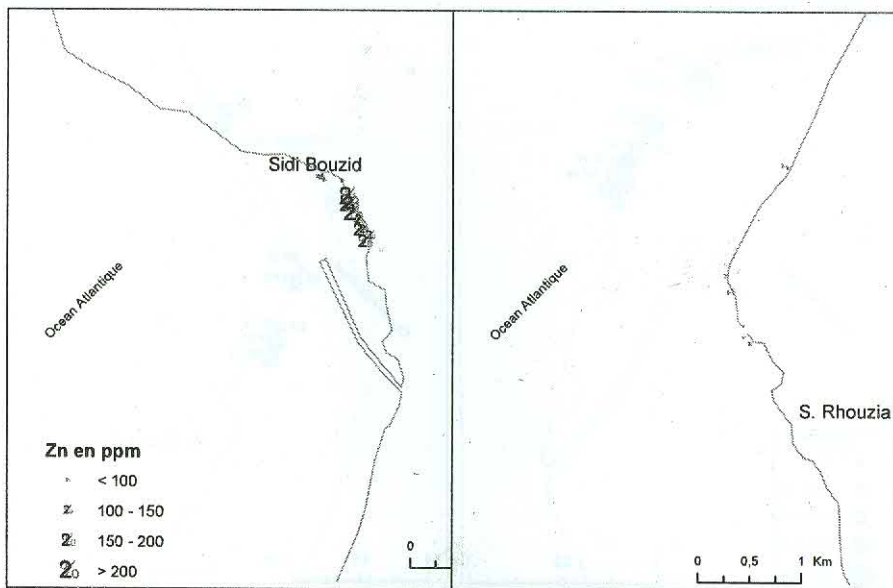


Figure 2b. Distribution of Zn concentrations in surface sediments

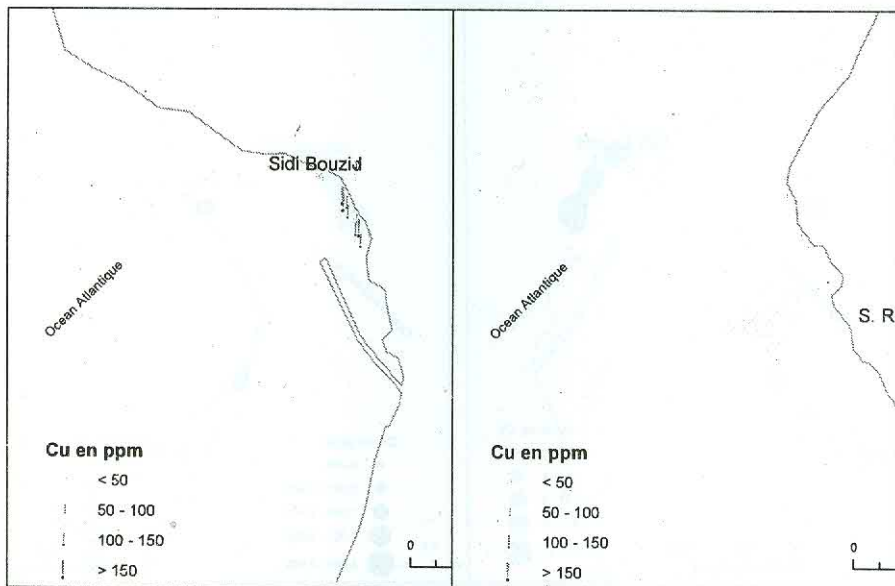


Figure 2c. Distribution of Cu concentrations in surface sediments

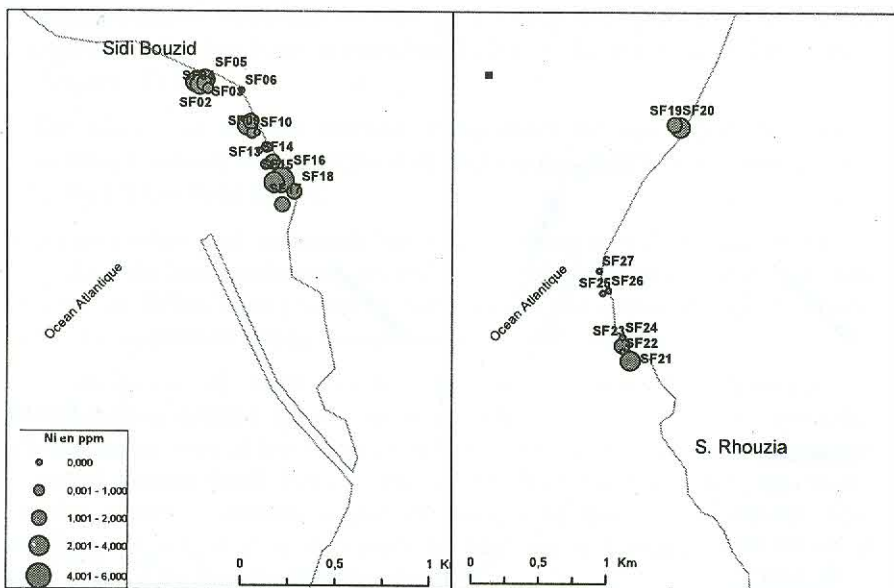


Figure 2d. Distribution of Ni concentrations in surface sediments

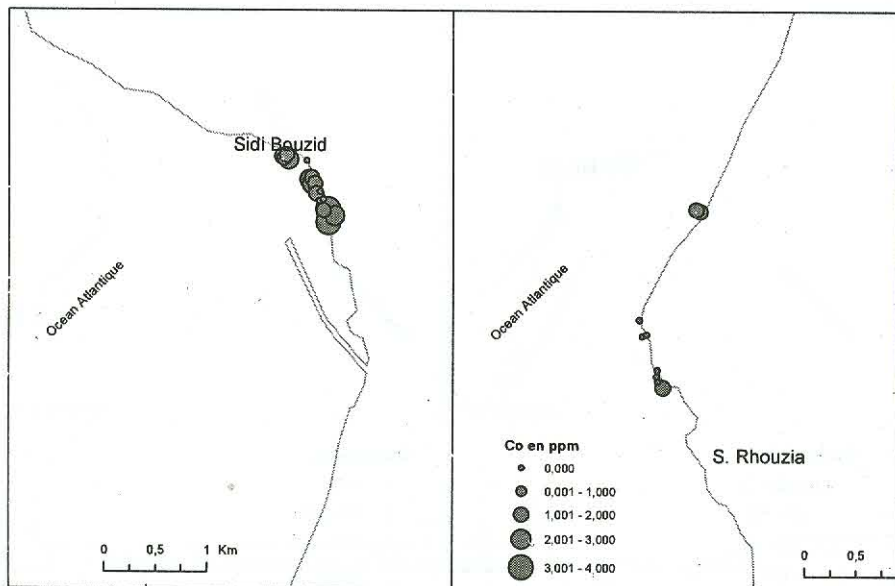


Figure 2e. Distribution of Co concentrations in surface sediments

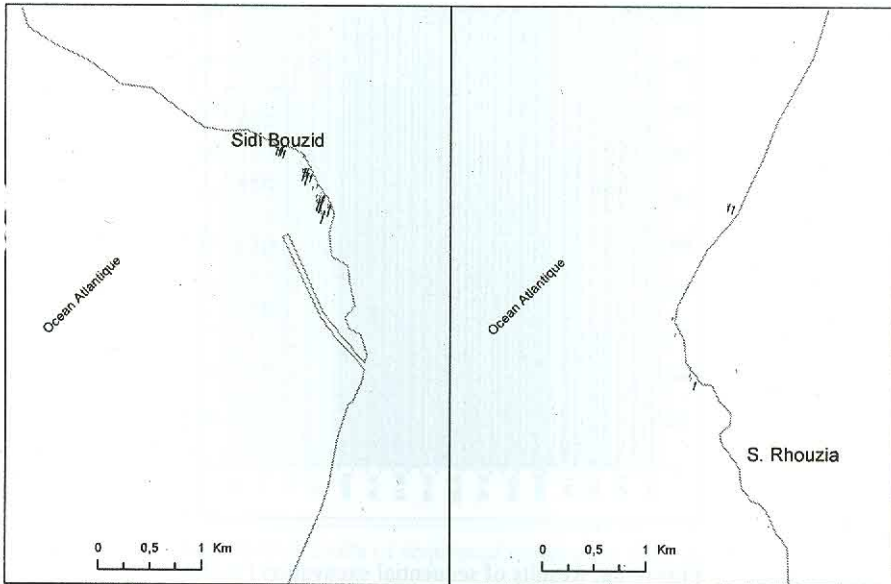


Figure 2f. Distribution of Cd concentrations in surface sediments

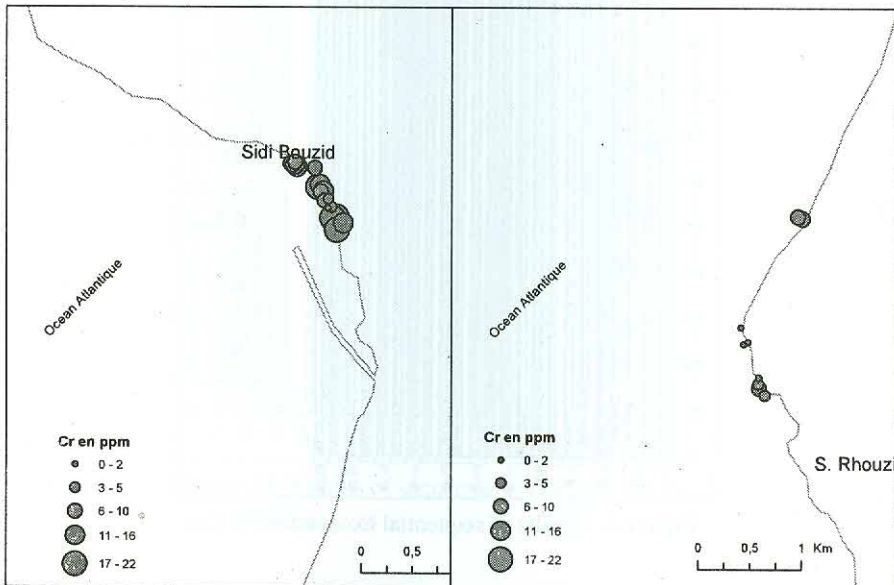


Figure 2g. Distribution of Cr concentrations in surface sediments

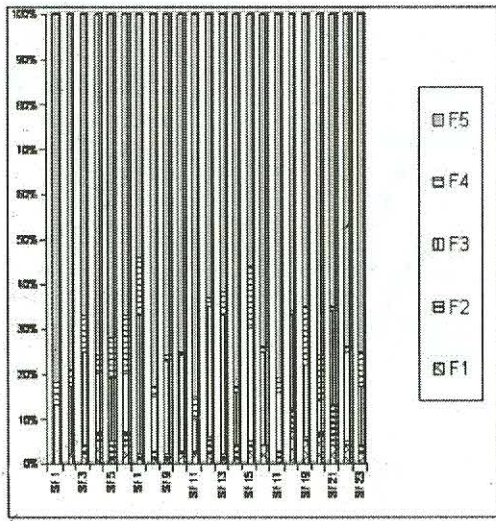


Figure 3a. Results of sequential excavation (% Pb)

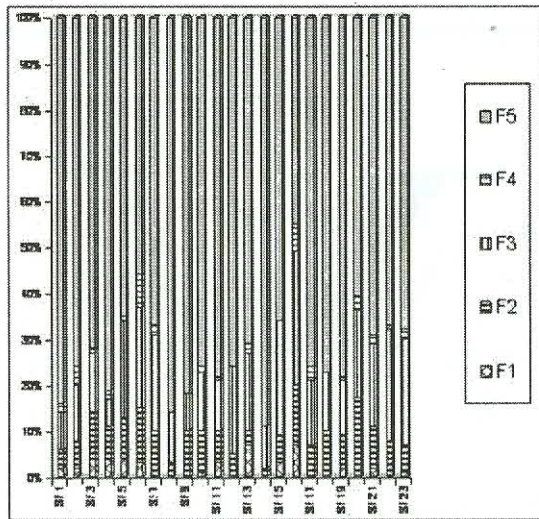


Figure 3. Results of sequential excavation (% Zn)

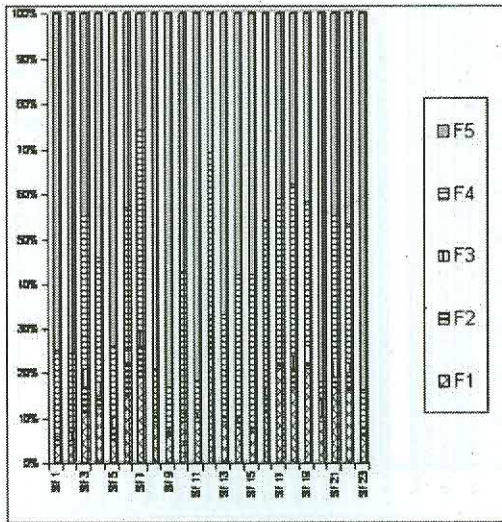


Figure 3c. Results of sequential excavation (% Cu)

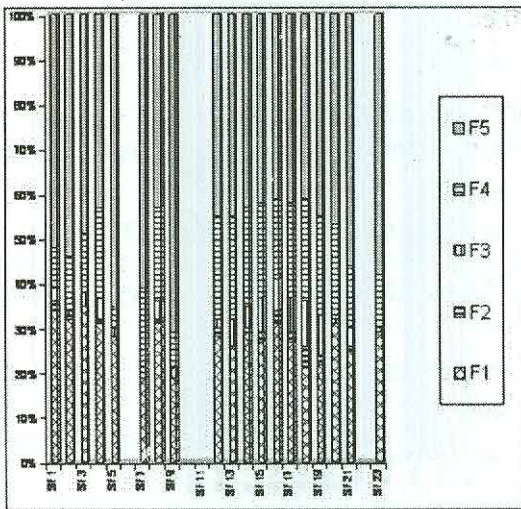


Figure 3d. Results of sequential excavation (% Ni)

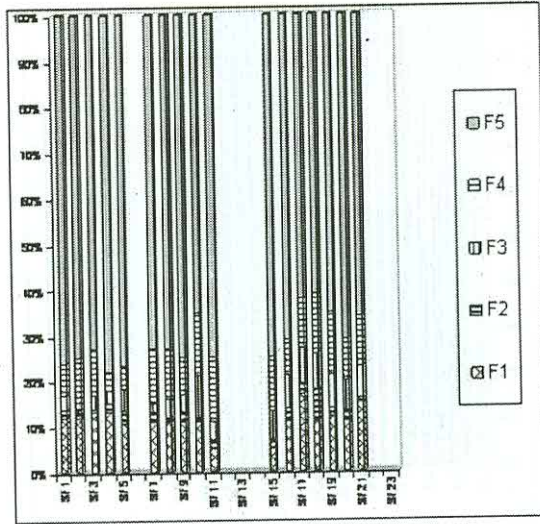


Figure 3e. Results of sequential excavation (% Co)

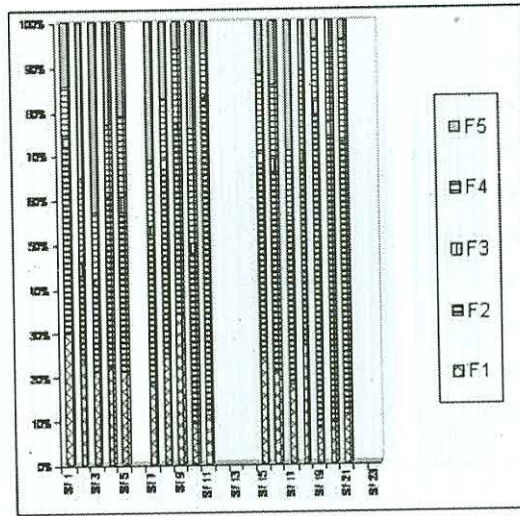


Figure 3f. Results of sequential excavation (% Cd)

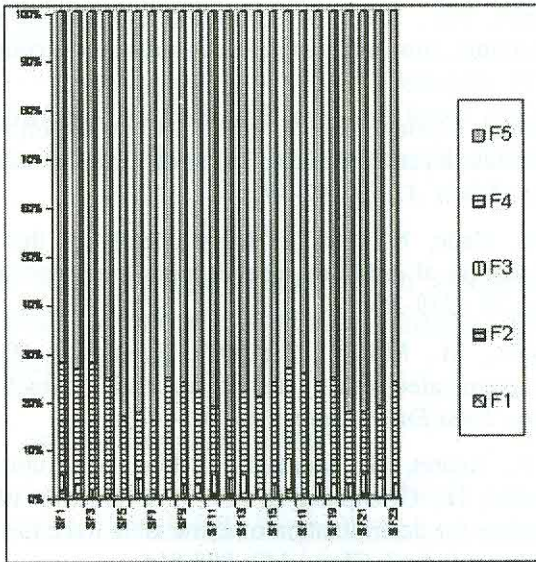


Figure 3g. Results of sequential excavation (% Cr)

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