DISTRIBUTION OF THE RARE EARTH METALS CONCENTRATIONS IN THE SEDIMENTS OF ALGIERS BAY AND SURKOUF AREA

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Abstract: Sediments were collected at 33 stations from Algiers Bay to determine potential sources of pollution. The analyses were made with Phillips X-ray fluorescence (XRF) equipment. The results give information about the level of concentrations for La, Ce, Er and Tb. Except for lanthanum and erbium which present a particular distribution (unrelated to the sedimentary facies), the distribution of the different rare earth metals is irregular and depends on the bay morphology. Terbium, erbium and cerium present high concentrations in the vases. The level of pollution by rare earth metals of the botton sediments in Algiers Bay has been shown to be significant compared with that of Surkouf, considered to be a region with low anthropogenic activity.

Keywords: Sediments, rare earths, metals, XRF, Algiers Bay.

1. Introduction

The Algerian littoral, with its 1200 kilometers, is characterized by a great diversity of physical and natural environments, with large plains and littoral plates (Mitidja, hills of the Sahel...) and more or less high reliefs, giving rise to a multitude of bays. With these last, the main portuaives cities and sites of Algeria, are associated.

The zone of study (3°02' E-3°20' E and 36°40' N-36°50' N) belongs to the Algiers coast which extends on 80 kilometers length with a broad bay overhung by the town of Algiers. It leans in the South on the vast plain of Mitidja with a rather regular and not very significant planimetry and opening in North on the Mediterranean.

The area is made up in majority by quaternary alluvia, sands, sandstones and limestones of reef, pliocenes sandy clay and sandy limestones deposits, marls and conglomerates, and miocenes carbonated marls limestones, clays and sandstones. The limits of bay, coinciding with Cap Matifou in the East and the peak of El Kettani in the West, are formed by metamorphic rocks like phyllithes, cristallophylien schist, mica schist and gneiss. The volcanic formations outcroping in the area of Surkouf are represented by basaltic lava, dolerites, diorites, gabbro-diorites and granites [1].

The hydrographic system consists of rivers with reduced flow of which most significant are Oued El Harrach, Oued El Hamiz and Oued Reghaïa in Surkouf area.

In addition to a population of more than two million inhabitants, the area is marked by a significant industrial activity in particular near Algiers harbour and industrial areas of Rouiba and Reghaïa. The population and public infrastructures (hospitals, schools....) are concentrated near the main localities of Algiers such as Algiers center, Bab El Oued, Hussein dey, Kouba, Fort de l'Eau and Aïn Taya.

Algiers bay and the littoral of Algiers in general are prone to many sources of pollution due to significant volume of domestic and industrial worn water rejected directly and without preliminary treatment in the sea, to the derivative of hydrocarbons related to the harbour activity and to the scrubbing residues of the old cement factories and careers.

The vulnerability of the Algiers coast is mainly due to the fact that the Mediterranean sea is almost closed with little exchange with the ocean, thus reducing the circulation and the renewal of its water.

It is known that sediments in Algiers Bay have a high capacity to concentrate and retain toxic trace elements, due mainly to the fine fractions (< 40 µm) present at more than 75% [2-3]. Heavy metals may be natural constituents of the sediments. They come from the rocks and soils via their geochemical mobility. They also can be anthropogenic sources; in which case they are incorporated into the sediments as artificial polluants coming from industrial and urban releases and wastes.

In the environmental sciences, among the many multi-elemental analysis technique, ion beam analysis and X-ray fluorescence have been shown to be the two powerful tools for monitoring the elemental composition and trace element content of soils, sediments, water and air particulates [4-6].

In Algiers Bay, soil comes from the El-Harrach and El-Hamiz rivers. These cross similar rocks. In pelitic sediments found in the bay, clay represents 40 to 50% of deposits in association with kaolinite-illite where illite is predominant. This may represent 60% of the association [7]. However, chlorite may complete this association instead of kaolinite. The Surkouf reference radial is 10 km east of Cap Matifou (east of Algiers Bay). The Surkouf sector is characterized by significant local erosion.

2. Experimental

Samples of sediments were taken by using the oceanographical boat of *the Institute of Sciences of the Sea in Algiers (ISMAL: Institut des Sciences de la Mer d'ALGER)* on 33 stations in Algiers bay, including 5 samples in Surkouf area in order to determine potential sources of pollution by rare earths metals.

Sampling was carried out according to 7 profiles (A, B, C, D, E, F and G) from the shore towards the open sea. The profiles C, D and F were established in order to tally with the mouths of Oued El Harrach and Oued El Hamiz.

The sediments of the sea-bed were collected, the same day, using Van Veen Snapper according to isobathic profiles with sampling point every 20 meters (in-depth) including six (A, B, C, D, E, F) in Algiers bay and a profile (G) apart from bay in Surkouf area. The sediments were then lyophilised and homogenised in an agate mortar.

Measurments of Rare earth metals are carried out using XRF with a Gazeous Flux detector (FG) and X-Ray tube excitation (Siemens, 70-90 µA, 50-60 kV). The yields of the characteristic X-Ray peaks are measured after background fitting and subtraction.

The concentrations of the metals are determined by use of an external standards. The standards used are: SD-M-2 / TM and SL-3 supplied by IAEA (International Atomic Energy Agency). The attenuation of the emitted X-Rays in the sample matrix is taken into account by use of absorption coefficients [8].

The Algiers bay with a slight slope from the coast towards the open sea and a depth reaching the 100 m contains sediments made up of 40 to 50% of clays (kaolinite, illite and chlorite) with illite dominant up to 60% of association (7). The cartography of the percentage of the fine particle in the deposits of Algiers bay gives the nature and the mode of distribution of the various facies (Fig. 1). A prevalence of the fine particle (> 95%) is observed in an increasing way, from the shore towards the center of Bay [2].

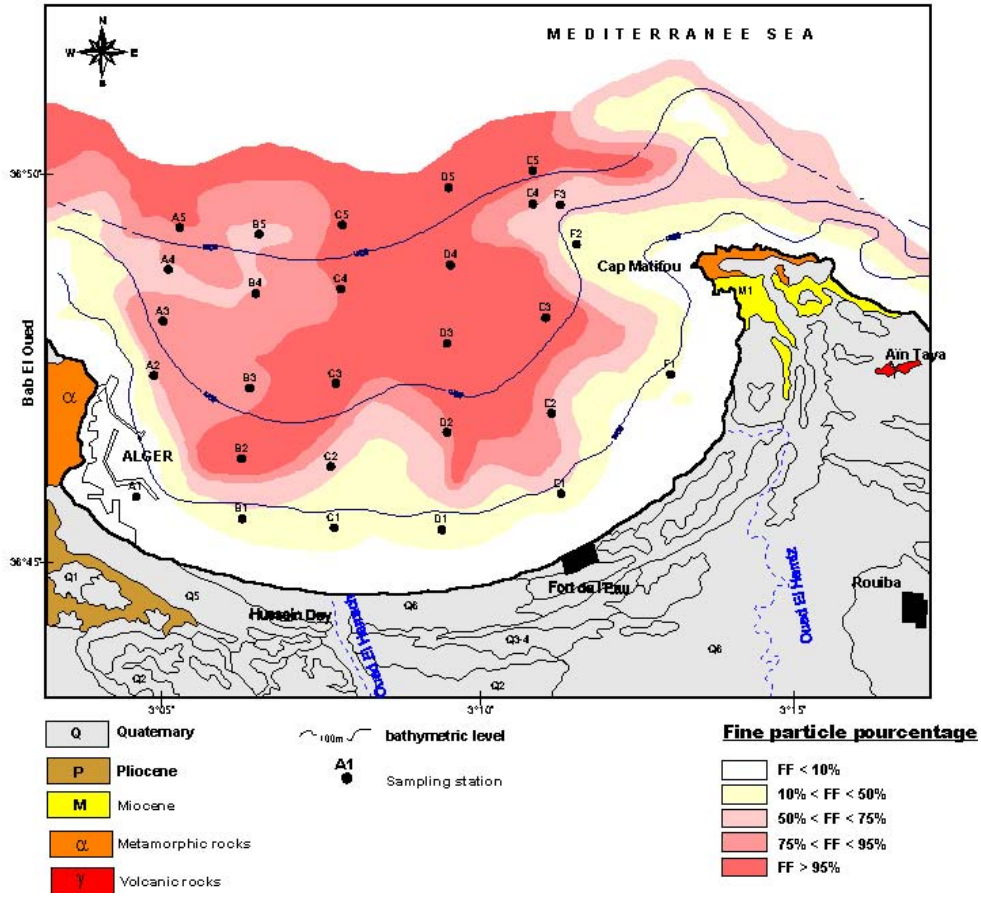

Figure 1: Cartography of sea-bed according to the fine particle percentage in Algiers Bay and Surkouf area (Benamar and al, 1999)

3. Results and discussion

Mono-variable analysis

The cartography of the rare earth metals concentrations in Algiers bay and Surkouf area made it possible to release the distributions of each studied element (Fig. 2, 3, 4, 5 and 6).

Cerium: The highest concentrations (> 300ppm) are localised in the Western area of the Bay (Bab El Oued and Algiers harbour), on the littoral of share and others of Oued El Harrach (Algiers Town, Hussein Dey, Fort de l'Eau and Oued El Hamiz) and in the side of Aïn Taya in Surkouf area (Fig. 2).

Erbium: The Surkouf area presents weaker concentrations in this element compared to Algiers bay. The strongest contents (> 250ppm) in the latter are localised in front of Cap Matifou, in the area of the Algiers harbour and near the littoral between the mouths of Oued El Harrach and Oued El Hamiz (Fig. 3).

Terbium: This element shows a rather regular distribution with contents higher than 200 ppm in the whole of a Bay with however a zone with stronger concentrations (> 250ppm) located on the littoral at the East of Oued El Harrach (Fig. 4).

Lanthanum: In Algiers bay the Lanthanum contents evolve in a way decreasing from the littoral to the open-sea with stronger concentrations (> 1600ppm) observed share and others of the Algiers harbour and of the zones of discharge of Oued El Harrach and Oued El Hamiz (Fig. 5). Contrary to its distribution in Algiers bay, Lanthanum in Surkouf area moves conversely, its concentration decrease from the littoral towards the open-sea.

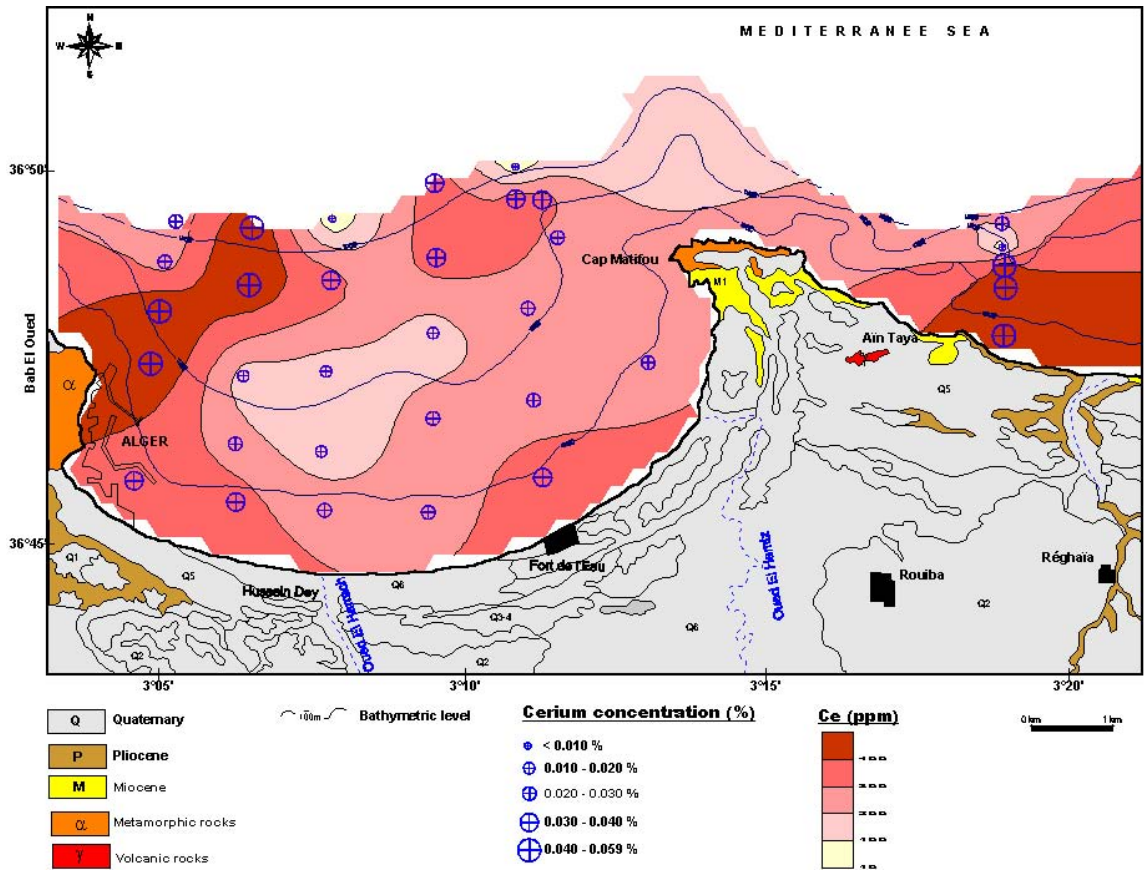

Figure 2: Distribution of the Cerium concentrations in Algiers Bay and Surkouf area

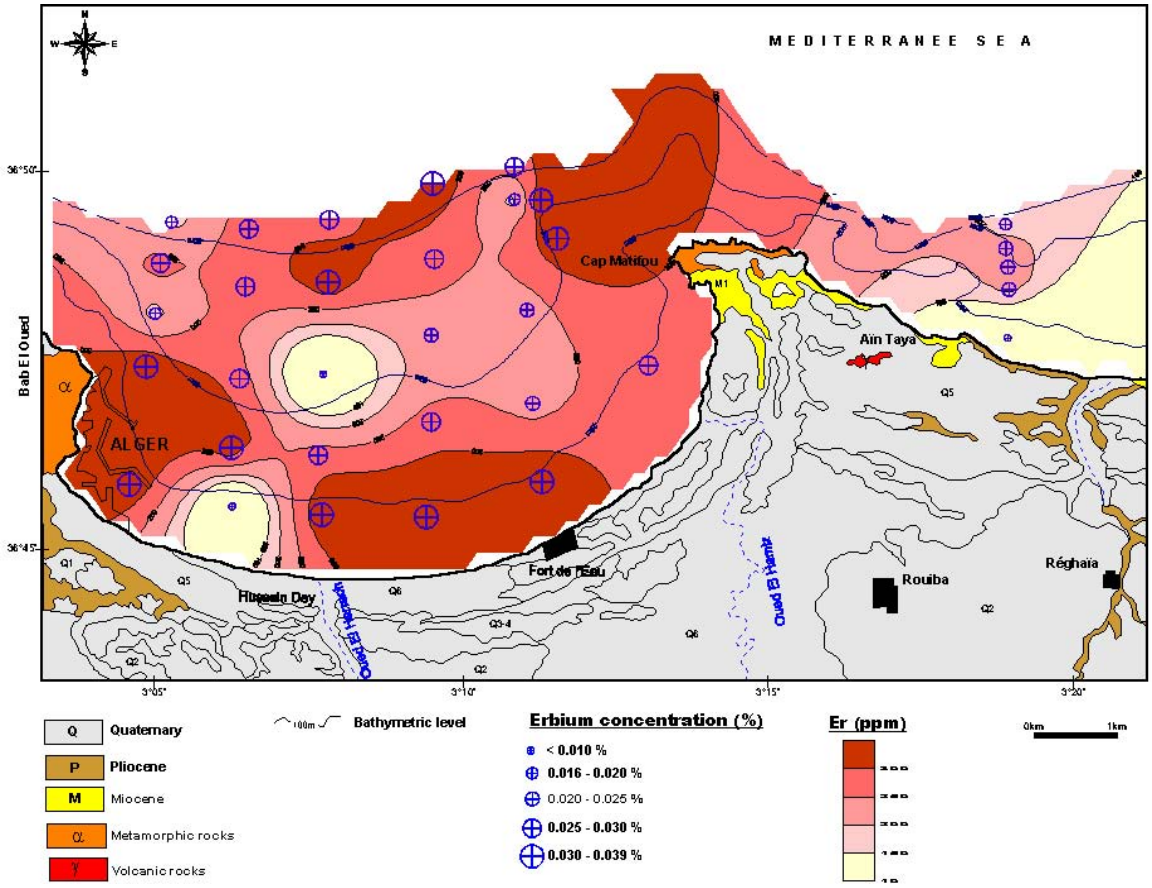

Figure 3: Distribution of the Erbium concentrations in Algiers Bay and Surkouf area

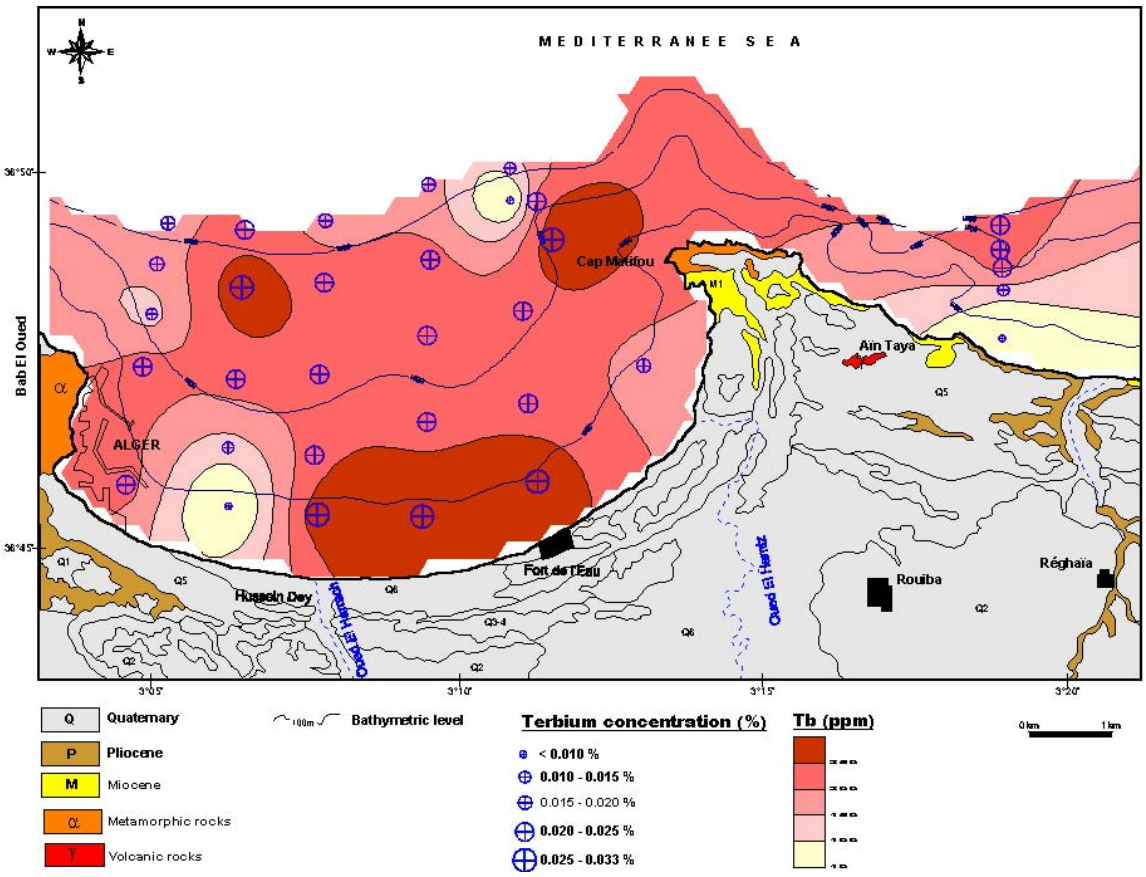

Figure 4: Distribution of the Terbium concentrations in Algiers Bay and Surkouf area

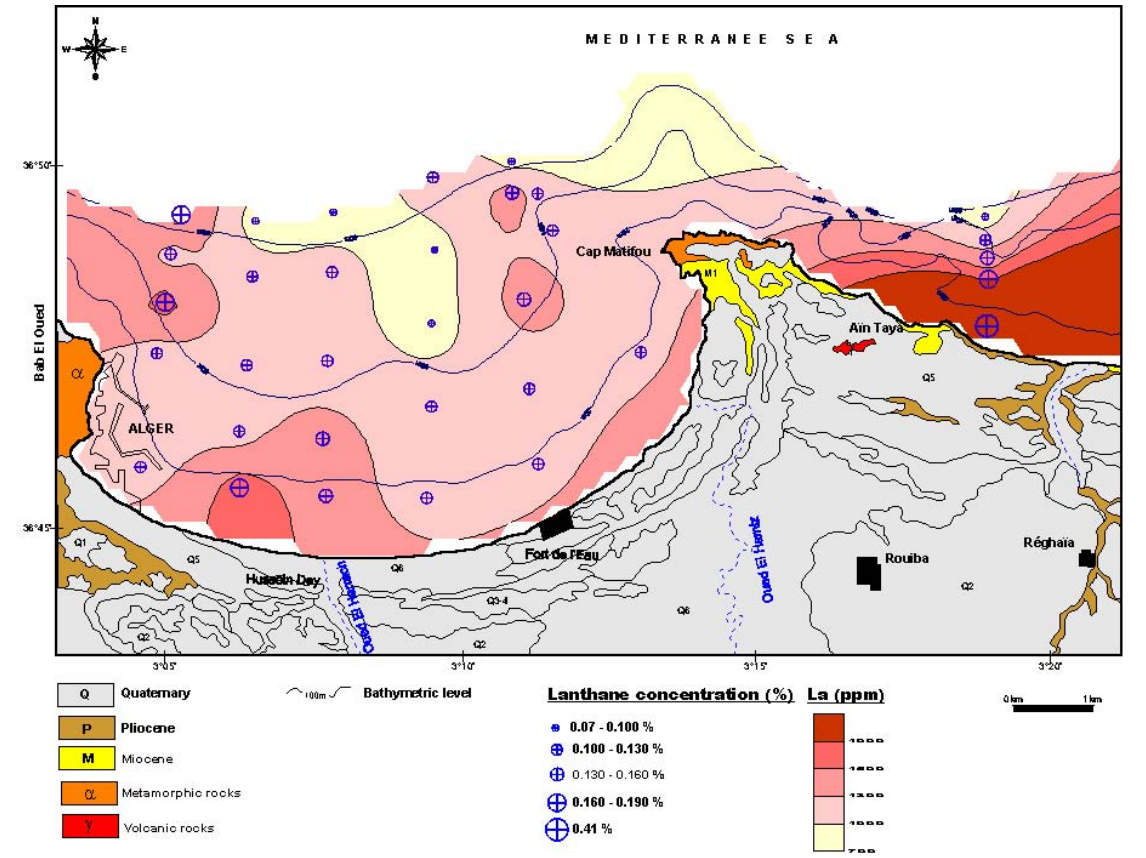

Figure 5: Distribution of the Lanthane concentrations in Algiers Bay and Surkouf area

The cartography of the distribution of rare earths metals in Algiers bay emphasizes three (03) zones with strong concentrations in Ce (> 400ppm), Er (> 300ppm), Tb (> 250ppm) and La (> 1600ppm). The first zone with a prolongation SO-NE is localised in the area of Algiers harbour (Ce, Er, Tb and La), the second is spread out shore towards the open-sea between the two mouths of oued El Harrach and oued El Hamiz (Er, Tb and La) and the third is in front of Cap Matifou (Er and Tb). We note the strong Lanthanum concentrations on the side of Hussein Dey and Aïn Taya localities (Fig. 6).

The interdependence of the distribution of rare earths metals with the percentage of the fine particles and the depth of sea-bed in Algiers bay is not announced.

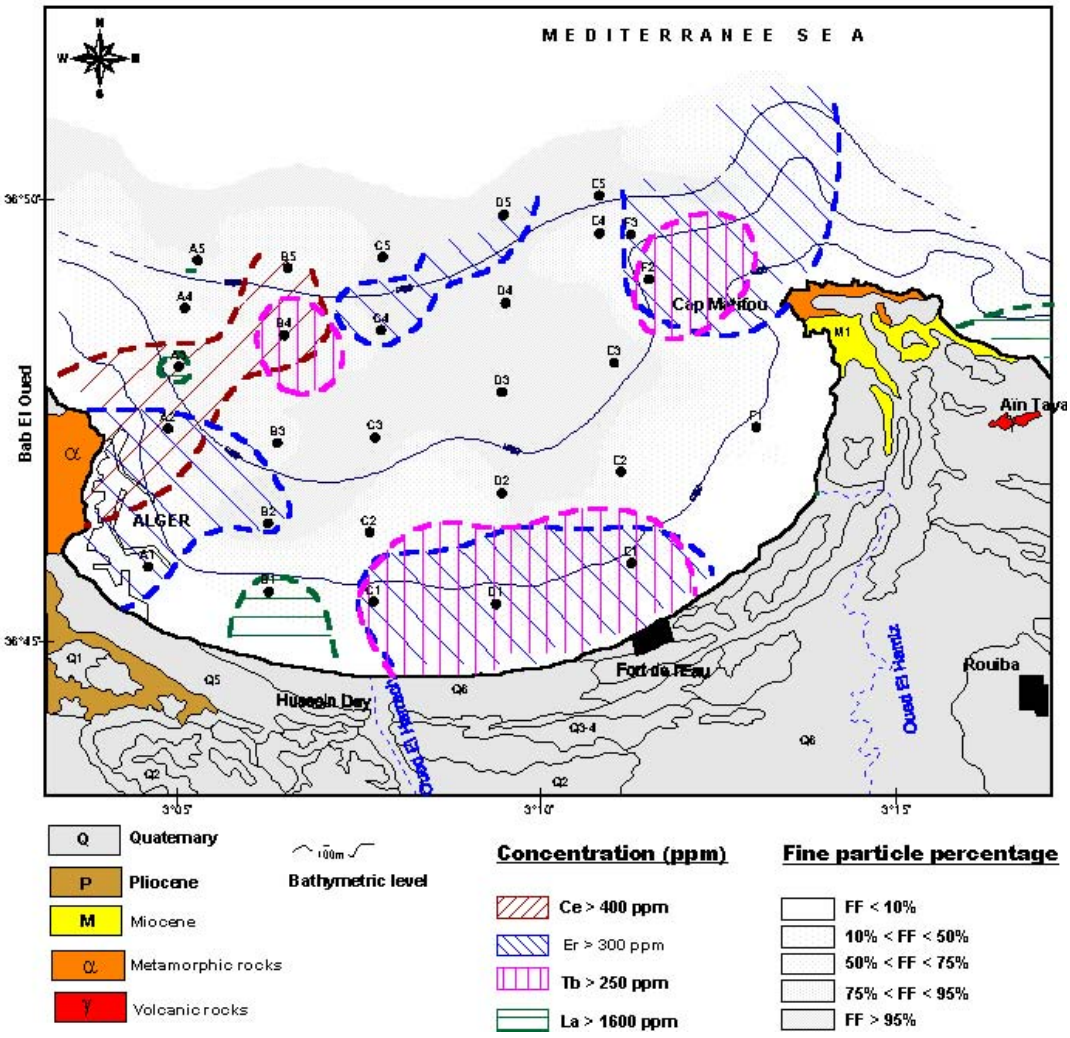

Figure 6: Distribution of the rare earth metals concentrations and the percentage of fines particle in Algiers Bay sediments

Multivariable analysis

The application of the multivariable statistics to the data collected in Algiers bay - Analysis in Principal Components (ACP) - makes possible correlations and associations between the chemical elements (rare earths metals), the depth of sampling and the percentage of the fine particle in the sampled sediments.

Table 1 shows that only Erbium and Terbium present a significant correlation (0.53).

Table 1: Correlation matrix - Algiers bay Data.

	Er	**Ce**	**La**	**Tb**	**Z**	**Fr**
Er	1,00					
Ce	0,12	1,00				
La	-0,42	0,25	1,00			
Tb	0,53	0,03	-0,37	1,00		
Depth (z)	0,07	0,08	0,27	0,18	1,00	
% Fine particle (%FF)	-0,22	-0,23	-0,20	-0,21	-0,70	1,00
Minimum (ppm)	9,00	9,00	850,00	9,00	-99,00	5,00
Maximum (ppm)	345,00	495,00	1750,00	290,00	-12,00	99,00
Average (ppm)	265,46	282,07	1203,57	201,54	-54,64	70,84
Standard deviation	88,79	124,83	249,99	69,99	27,92	28,34

Correlations between loadings factors and rare earths metals, where each factor can represent an interpretable phenomenon which associates chemical elements and/or samples parameters, show following associations (see Table 2):

Table 2: Correlation factors loadings/Data in Algiers bay.

Eigenvalues	L1 = 2.03	**L2 = 1.84**	**L3 = 0.98**	**L4 = 0.49**	**L5 = 0.40**
Loadings factors	**F1 = 33,79%**	**F2 = 64,43%**	**F3 = 80,83%**	**F4 = 88,99%**	**F5 = 95,63%**
Er	0,60	0,59	-0,21	0,28	-0,40
Ce	0,31	-0,30	-0,87	0,00	0,21
La	-0,06	-0,86	-0,11	-0,25	-0,42
Tb	0,63	0,54	0,00	-0,55	0,03
Z	0,71	-0,47	0,37	0,00	0,10
% Fine particle	-0,81	0,39	-0,16	-0,21	-0,08

- Factor 1 positively associates Er, Tb and the depth, and negatively the percentage of the fine particle.
- Factor 2 positively gathers Er and Tb, while expressing a negative correlation with La.
- Factor 3 is negatively correlated with Ce.

The cartography of the correlations between the factors loadings and rare earths metals in Algiers bay emphasizes what follows (Fig. 7):

- A zone with high concentrations of Er and Tb is observed throughout littoral of Algiers bay on low depths while joining facies with small percentage of fine particles.
- Cerium with significant concentrations appears in a zone of orientation SO-NE in front of Algiers harbour while joining at least the great depths and the facies with strong percentage in fine particles.
- The strong Lanthanum concentrations appear in the center and in the western part of Algiers bay: From Bab El Oued and Algiers harbour until Fort de l'Eau while passing by the mouth of Oued El Harrach. Another zone is localised in front of and in the West of Cap Matifou. The distribution of the Lanthanum concentrations is done independently of the depth and of the percentage of the fine particles in the sampled facies.

Figure 7 shows also other zones presenting rare earth metals associations with their most significant concentrations:

- Ce and La are present in front of Algiers bay and in the West of Cap Matifou.
- La, Er and Tb appear together near to the littoral, in the central and western parts of Algiers bay.
- The association of Ce, Er and Tb is localised in front of Algiers harbour.

It should be noted that the zones gathering the four elements (Ce, La, Er and Tb) with high concentrations are very reduced.

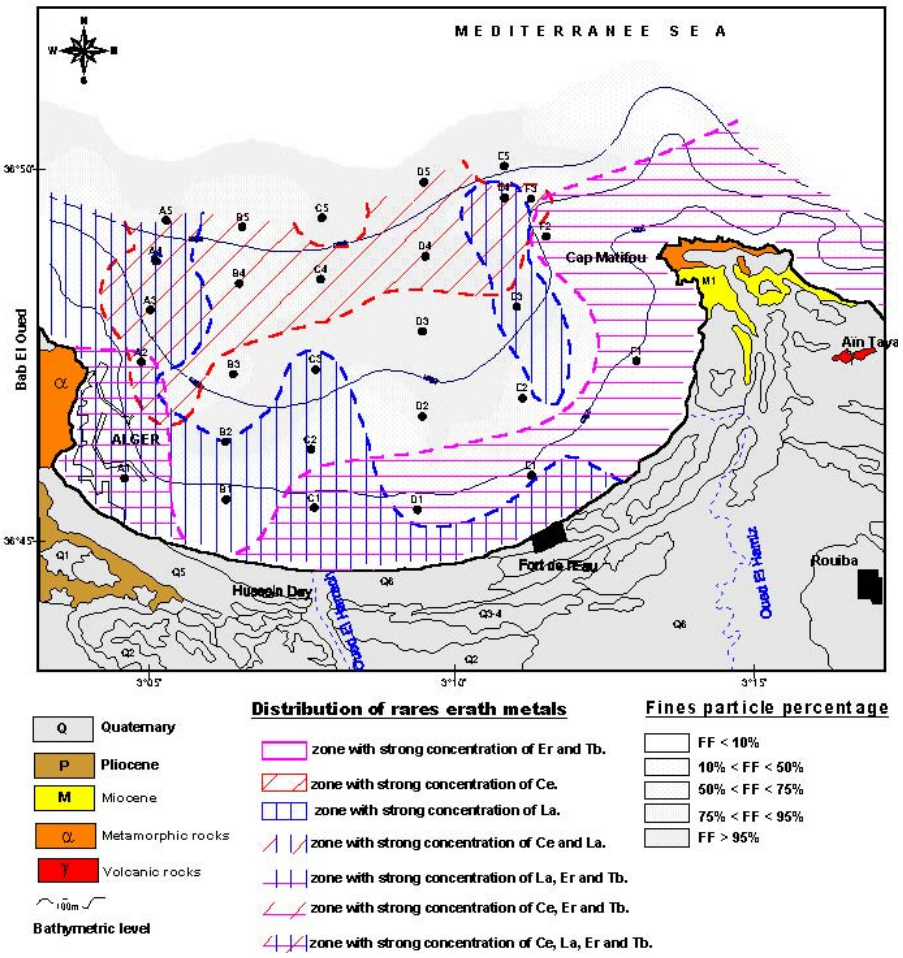

Figure 7: Distribution of rare earth metals according to the PCA cartography in Algiers Bay

4. Conclusion

In conclusion, the statistical analysis emphasized that a rather significant correlation between Erbium and Terbium can be observed, no other correlation is announced.

The monovariable cartography of the rare earth metals in Algiers bay and Surkouf area highlighted the mode of distribution of these elements concentrations and the zones of their high concentrations.

Projections of the results of the multivariable analysis emphasized zones distinct with some rare earth metals associations on the one hand and allow observing the independence of the distribution of these elements with respect to the depth of sea-bed and the percentage of the fine particles in the sediments of Algiers bay.

The most significant observations are those related to the distribution of Cerium, Erbium, Terbium and Lanthanum in Algiers bay:

- the high values in Cerium are located in the open sea of Algiers harbour and Bab El Oued.
- the significant Lanthanum concentrations are observed throughout the coast in front of Bab El Oued localitie, Algiers harbour until the town of Fort de L'eau.
- Erbium and Terbium are present with high contents throughout littoral of Algiers bay (from Bab El Oued to Cap Matifou).

In the distribution of the rare earth metals concentrations in Algiers bay the influence of industrial, domestic and hospital activities is manifest. This influence is observed in the immediate surroundings of Algiers harbour, of Bab El Oued, Hussein Dey and Fort de l'Eau localities and the zone of discharge of Oued El Harrach and Oued El Hamiz whose direct implication in the problem of contamination is obvious.

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