Full Length Research Paper

Assessment of heavy metals concentrations in coastal sediments in north-western cities of Madagascar

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This study was undertaken to evaluate the heavy metals contamination of copper, zinc, manganese, iron, chromium, nickel, lead and cadmium, to assess the environment quality of the coastal area from town activities. Nickel, lead and cadmium are used in different kind of current accumulators and they are dangerous for sea wild life and for human food resources. The five others metals are usual and at a high concentration they are able to threat environment system. Six samples had been choice at two town of Madagascar north-western coast: Nosy Be and Mahajanga, in February, 2007. These sampling points stand in front of each mean sewage mouths in each locality. Table 1 and 2 give us same descriptions of each sampling points. These two sampling area are among the principal fishing area of Madagascar. Three kinds of analytical method were used for metals determination and quantification: flame spectrophotometer atomic absorption, UV spectrophotometer, and voltammeter method. The flame spectrophotometer atomic absorption gives the best result by testing with certified reference materiel. Our data suggested that Mahajanga's stations have higher values of cadmium (1 mg/kg) and lead (91 mg/kg) than the non-contaminated sediments. However, the concentrations of other metals such as copper, zinc, manganese, iron and chromium in Nosy Be sediments, were twice as higher than in those of Mahajanga. In compiling our data obtained at the same stations in the vertical water column, we would like to confirm the growing order of potential absorption between metals and sediments, nickel, copper, cadmium and lead. According to the results of determinations, we suggested that more determination should have done in open sea to assess metals in a wide scale.

Key words: Marine pollution, heavy metals, coastal sediments, toxicity, Nosy Be, Mahajanga, Madagascar.

INTRODUCTION

Now, Madagascar starts his marine coast pollution control. Before, estimative and qualitative observations have been done to measure the degree of pollution (J. Ranaivoson, 1997). Specially for Mahajanga, the sediments transport had been told as the mean marine environment problem. The results are the logical conti-nuation of the last study and believed to be a reference for the marine coast monitoring work.

Nosy-Be is a small island in the northern part of Madagascar with 74 000 habitants and Mahajanga, the second seaport of Madagascar have 260 000 habitants. These cities occur in the North-western part of Madagascar, in front of Mozambic Channel. Tourism and fishing are the main activities, with the exception of sugar cane in Nosy-Be and same industrial food transformation in Mahajanga. As the same case of all coaster towns, waste water and industrial sewage come directly to the sea (E. Rasoanandrasana, 2006). The usual activities of seaport also cause real effect at the proximity of coastline areas. This study allows us to know at the first time the heavy metal level in the sediment. It means that we want to measure cities activities' effects in coastal area. And it gives background situation because none sediments study had done at Madagascar.

MATERIALS AND METHODS

Samples were extracted such as representative each area by "Van Veen grab" sampler (Villeneuve, 2004; David et al., 2002). 500 g of each individual sample are gathered into plastic container by using

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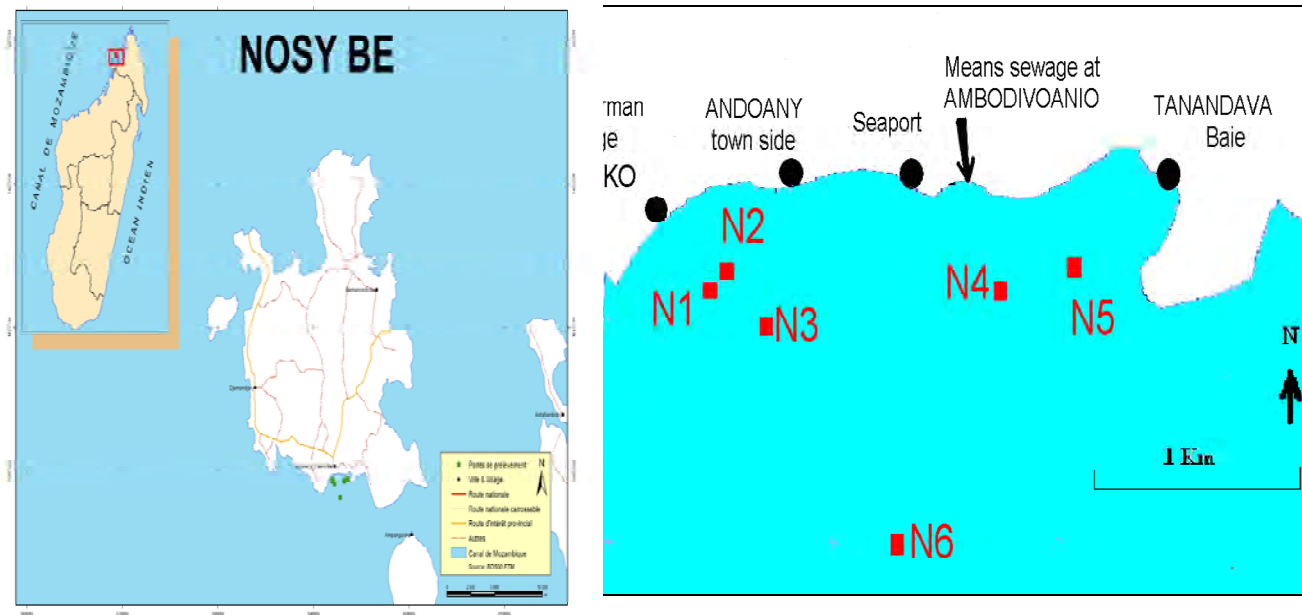
Figure 1. Sampling points location at nosy-be.

plastic spoon and the total metal concentration was determined in the laboratory. Samples were kept at 4°C until processing and analysis (José et al., 2004). Total mineralization was performed by heating 1 g of sediment at 200°C with mixing of 5 ml of nitric acid and 10 ml of chlorhydric acid on Teflon tube (Karageorgis et al., 2003; Khalid et al., 2004). After digestion and filtration, aliquot were analysed according to the availability of material:

- Spectrophotometer atomic absorption flame (SAAF) SOLAR: Fe, Cu, Mn, Cr, and Zn. (KRESS et al. 2004). This SAAF use acetylene and compressed air as flame atomisation and cathode lampe as light sources.
- Spectrophotometer NOVA 60 spectroquant for Ni determination by using 10mm compartment curve width.
- Voltametric kit «trace element analyser»: Pb, Cd using specifics electrodes according to the analysed metals.

Special reagent for metal trace analyse was used. The accuracy of the analytical procedures for total metal determinations was checked using the AIEA-405 certified reference material. Replicate analysis of this CRM showed good accuracy, with recovery rates for metals between 70 and 100%. Its depends on the strength and on the kind of links between sediments and particles. In order to check the precision of the analytical processes for target metals, three samples were analysed in triplicate. The average values of the variation coefficients obtained (in general, less than 10%) can be considered satisfactory for environmental analysis.

For metals repartitions in water sediment system, we had proceeded to the determination of metals in deep water at same sampling station as sediment. For water sampling, the "damping-sampling" was used. Sea water was filtered at 0, 45 µm, and was analysed following the same way as the sediment solution.

RESULTS AND DISCUSSION

Spatial metals distributions

The Figure 3 show metals distribution in coastline sedi-

ment of Nosy-Be. Fe, Zn, Mn and Cu had the same type of distribution for sampling points N1 to N6.   Higher values assign to N1 point, while lowers values to N6. N5 was sheltered in Tanandava bay that was the reason why, this point have the lowers metals concentrations after N6.

Sediments gathered at N1 and N2 had high concentration Fe, Zn, Mn and Cu because the sea erodes this side of coastline.

Figures 7 and 8 illustrate this situation. The principal components test is made with STATbox V6 software. The two principal components account for 90% of the total variance. Figure 7 shows the first component F1 (most important), which accounts for 64% of the variance among the metals, is characterised by high positive contributions (loads) for Fe, Zn, Mn and Cu.

Moreover, lead and Nickel which represent 26% of the variance (F2) with the Cd, are linked to the point N4. As shown in Figure 4, Ni and Pb concentrations are maximum in point N4, 38 and 53 mg/kg respectively.

For Mahajanga city, the six stations are located at the Ambombetoka bay, where the river Betsiboka meets Mozambic Channel. The maximum concentrations of Zn and Cu were respectively 122 and 10 mg/kg on M2 point. Those of Mn and Fe were maximum in M6. The Station M3 had the lower value except for Fe, because sediment in this point was constituted mainly by sand. Plots of Principal Components Analyse (PCA) in Figure 9 and 10 shows that Fe, Cr, Mn, Ni are mainly located between M5 and M6. The M6 and M5 samples are away from the others and they come to the Betsiboka river's axe. So, it is not a surprise to find 440 mg/kg of Mn and 64122 mg/kg of Fe. In this area, sea water appeared reddish. This PCA analyse confirms also that the two points (M1 and M2)
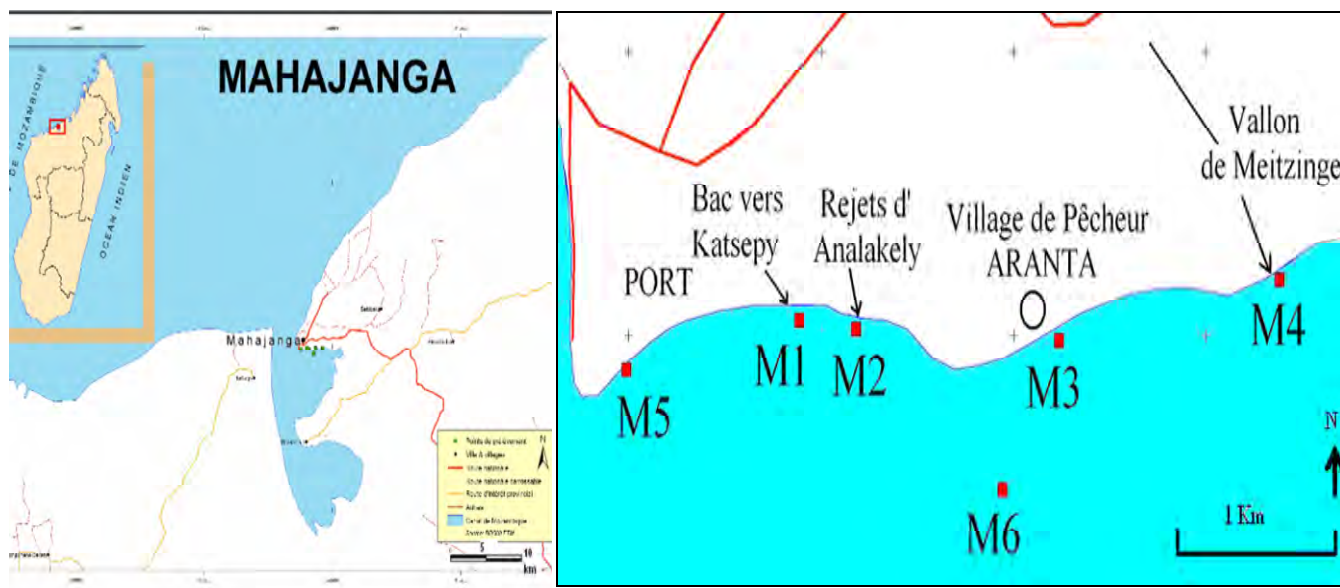
Figure 2. Sampling points location at Mahajanga.

Table 1. Characteristics of sampling station of nosy-be.

Réf. éch	Description	Depth (m)	Latitude	Longitude
N1	Fisherman village	1.15	S13°24.406'	E048°16.171'
N2	Andavako (Fisherman village)	0.32	S13°24.378'	E048°16.203'
N3	Sewage from administrative village	4.9	S13°24.501'	E048°16.315'
N4	Mean sewage of Nosy Be	2	S13°24.408'	E048°16.884'
N5	Tanandava Bay	4.90	S13°24.351'	E048°17.075'
N6	Reference station	11.3	S13°25.030'	E048°16.640'

Table 2. Characteristics of sampling station of Mahajanga.

Ref. ech.	Description	Depth (m)	Latitude	Longitude
M1	Ferry port	2	S15°43.570'	E46°18.913'
M2	Sewage from open Market of Analakely	1.4	S15°43.606'	E46°19.081'
M3	Aranta Village	1	S15°43.593'	E46°19.671'
M4	Mean sewage of Mahajanga from Vallon de Meitzinger	0.8	S15°43.563'	E46°23.311'
M5	Bank	2	S15°43.644'	E46°18.411'
M6	Reference station	2.4	S15°43.963'	E46°18.913'

have positive values for the principal component one (F1:46% of variance) leading us to surmise that the main source of Cd and Pb in sediments come from ferry port activities and from the sewage from Analakely market.

In this study, the comparison between the two cities is interesting. It provides us two different models: Nosy-Be is an isle having a surface area of 300 km^2 whereas Mahajanga is an estuary of less industrialised city (Tables 1 and 2). Figure 11 shows the comparison of average values of each metals between Nosy-Be and Mahajanga. The concentrations of Cu, Mn, Fe, Zn and Cr in Nosy-Be were twice as higher than those of Mahajanga sediments, that is, the opposite case of Pb, Cd and Ni. This is explained by lateritical geology and steep relief of Nosy-Be coastline. Moreover, Mahajanga has more industries and more habitants than Nosy-Be has. Generally, Betsiboka River dilutes and washes sediments that became less absorbent. In addition,
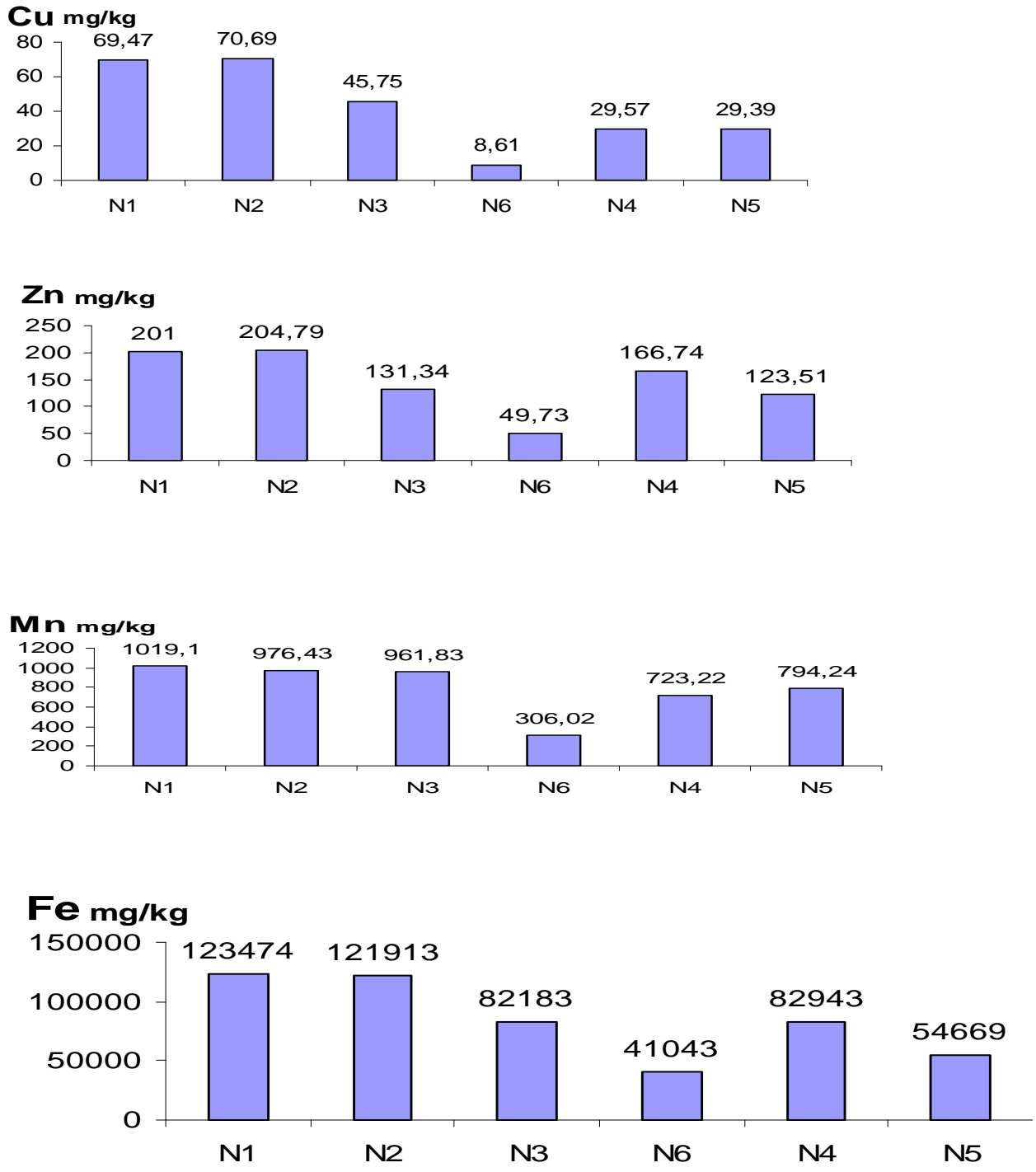
Figure 3. Spatial distribution of Cu, Zn, Mn and Fe in nosy-be sediments.

Ambobetoka bay is shallow than Nosy-Be coast (1.6 m towards 4.1 m).

By comparing metals concentrations (expressed in mg/kg) in differents area of Africa (Biney et al. 1995) with those of Mahajanga and Nosy-Be. We conclude that:

- The maximum values of Cd 1, 089 mg/kg at Mahajanga and 0,489 mg/kg at Nosy-Be seemed to be the normal

Pb mg/kg

Ni mg/kg

Cd µg/kg

Cr mg/kg
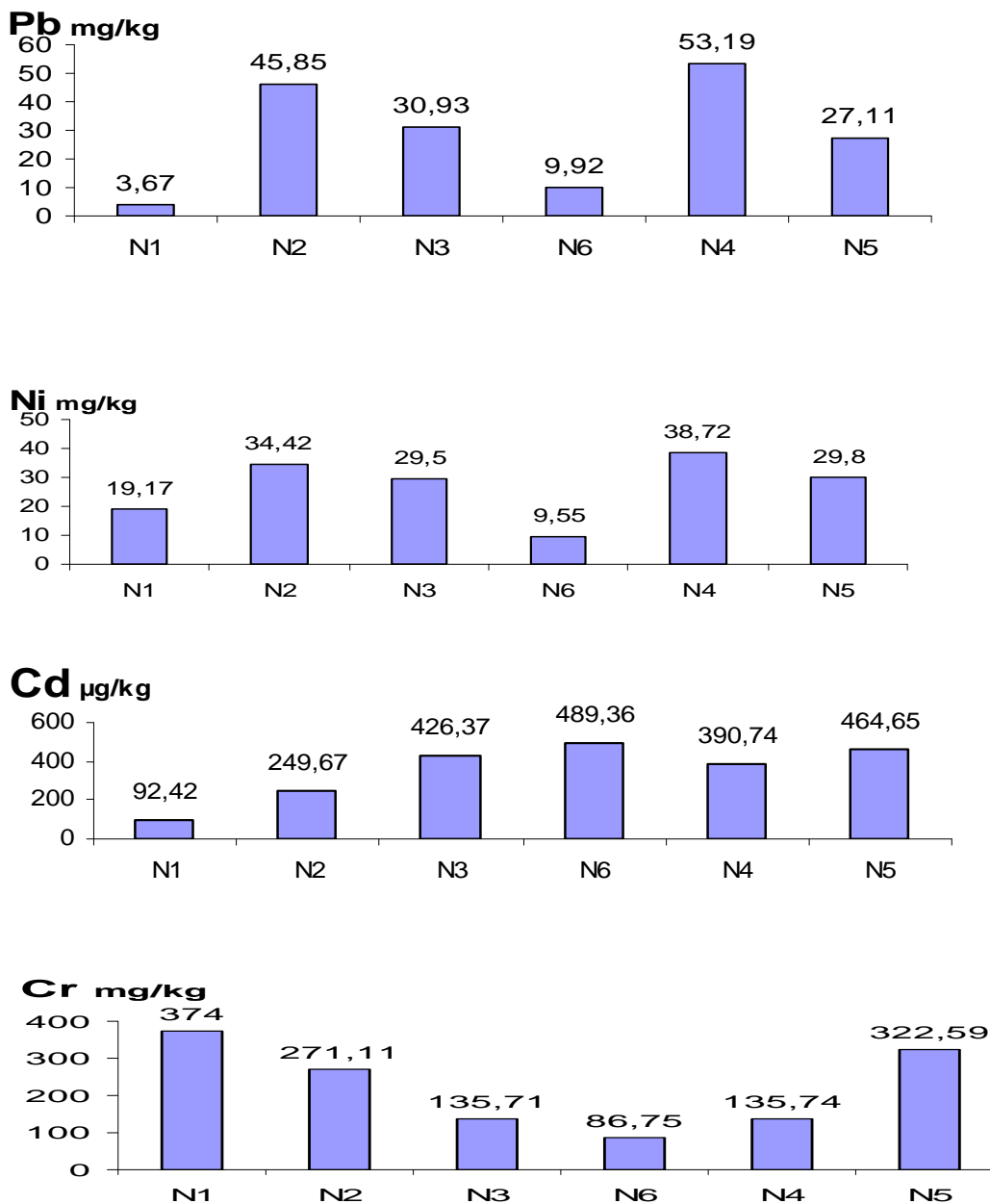
Station point at Nosy Be

Figure 4. Spatial distribution of Pb, Ni, Cd, and Cr in nosy-be sediments.

values compared with non-polluted sediment (0.2 - 5 mg/kg of Cd: natural mean value for Africa) Two sample stations of Mahajanga (M1 and M2) had concentration higher than 60 mg/kg of Pb and another point (M5) had 54 mg/kg. This means that Mahajanga is threatened by lead pollution. For Nosy-Be, two points such as N2 and N4 had values closer to 60 mg/kg. The mean sewage which is in front of point M1 brings at less 4.7 ug of Pb per litter (A. Nirilalaina, 2007). The point N4 which stands

in front of the sewage of Ambodivoanio has the higher value of lead because it brings 5ug per litter of sewage (A. Nirilalaina, 2007).
- About others metals content in sediment at same area of Africa x found 147 mg/kg of Zn at Atlantic coast of Nigeria; 15 mg/kg of Cu and 36 380 mg/kg of Fe at Lagos Lagoon. The metals concentrations in Nosy-Be sediment reached 201 mg/kg for Zn, 123 474 mg/kg for Fe and 70 mg/kg for Cu.
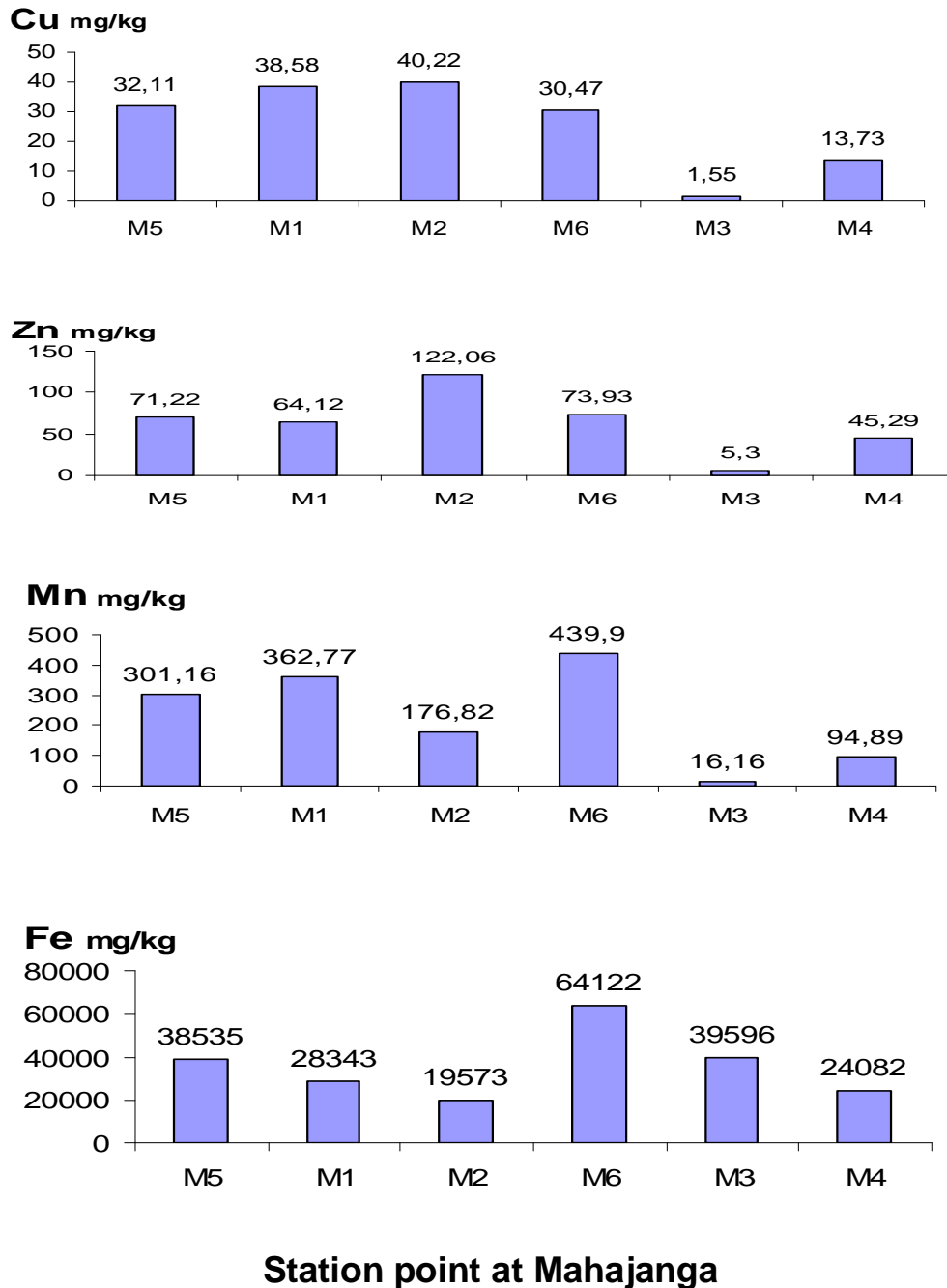
Cu mg/kg

Zn mg/kg

Mn mg/kg

Fe mg/kg

Station point at Mahajanga

Figure 5. Spatial distribution of Cu, Zn, Mn and Fe in Mahajanga sediments.

By comparing our results with industrialised areas as Djakarta bay in Indonesia and at Liverpool in England, concentration of total metal found at Mahajanga and Nosy-be are still relatively low.

Metals distribution in sea water – sediment system

Metal concentration in column water (Nirilalaina , 2007) at the same station point allow us to establish metals distri- bution in sea water-sediment system. These values show the metals affinity to be fixed in sedimentary particles. Fe and Mn are the less diffused metals and they form real components of sediment. Table 1 show that Pb is the easily-absorbed metal by sediment among these eight metals. This study confirms the metal classification accor- ding to their potential absorption draw by Serpaud et al. (1994) as Pb > Zn > Cd >Cu.

With the exception of Mn and Cd, Mahajanga's sedi- ment fixed more strongly metals than Nosy-Be's sediment.
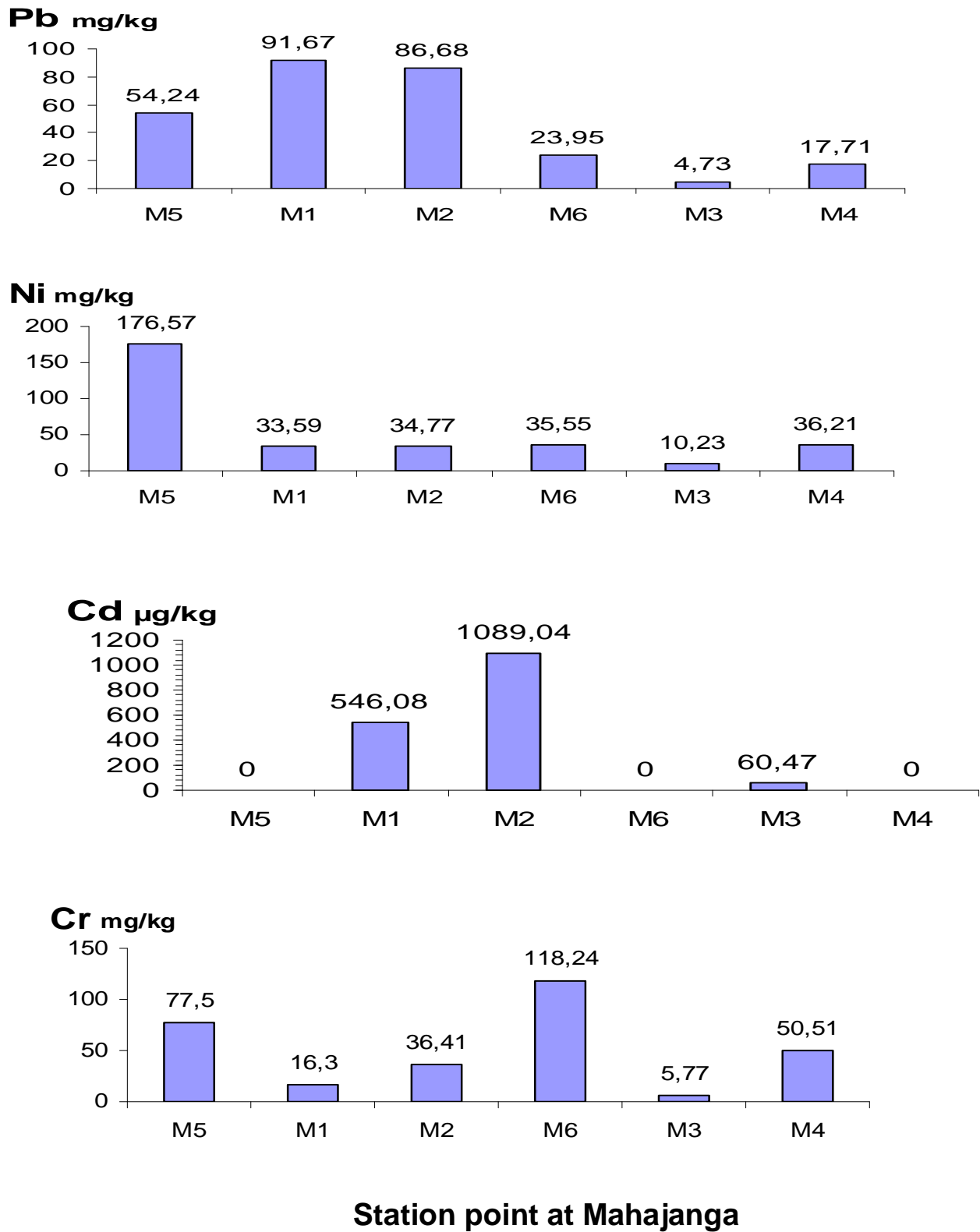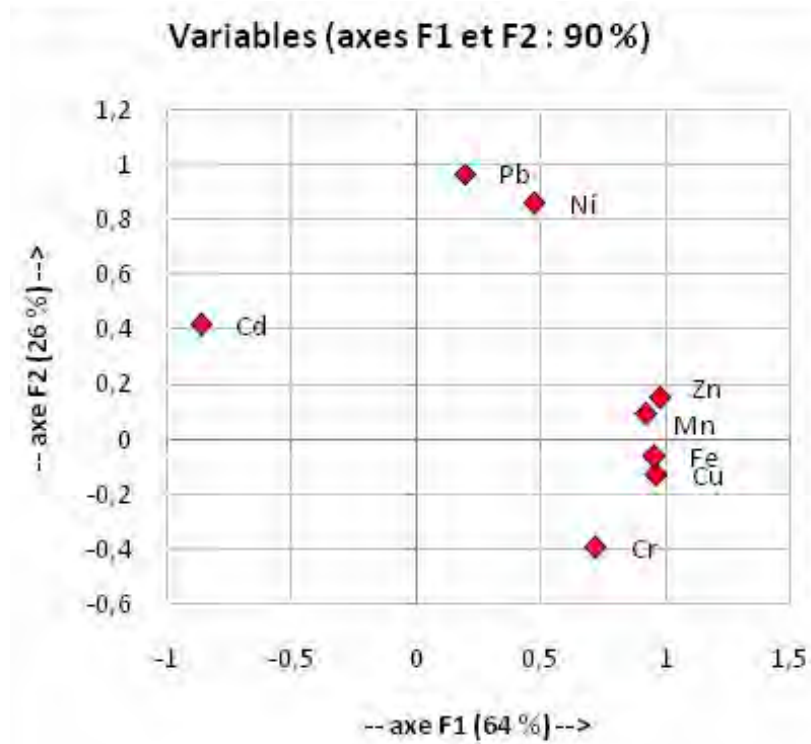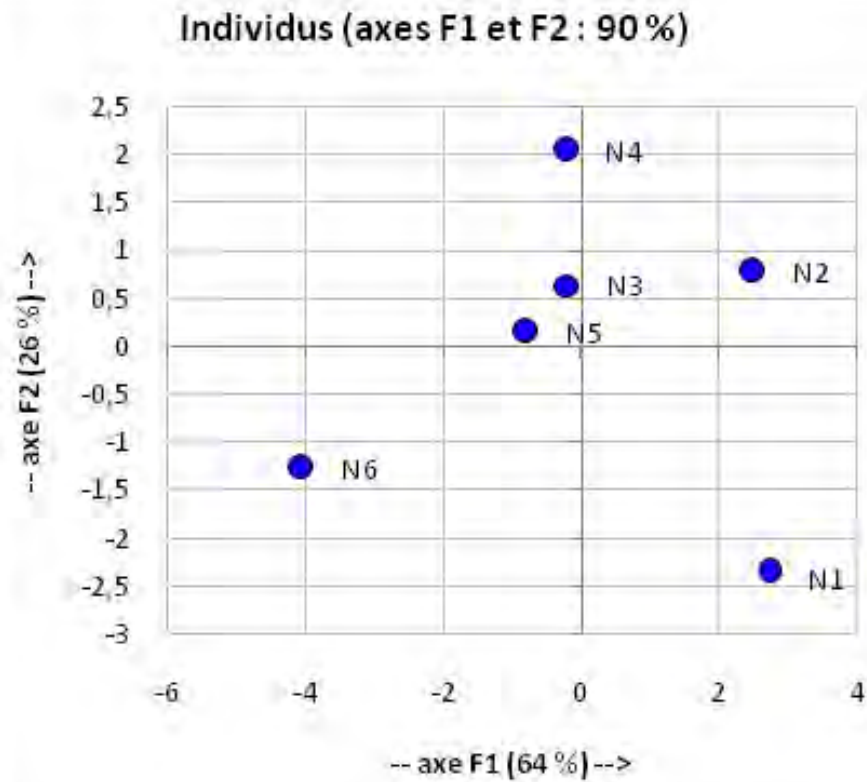
Figure 6. Spatial distribution of Pb, Ni, Cd, and Cr in Mahajanga sediments.

This means that at Mahajanga, metals outstay one's   sediment. They are old and resist to dilution and
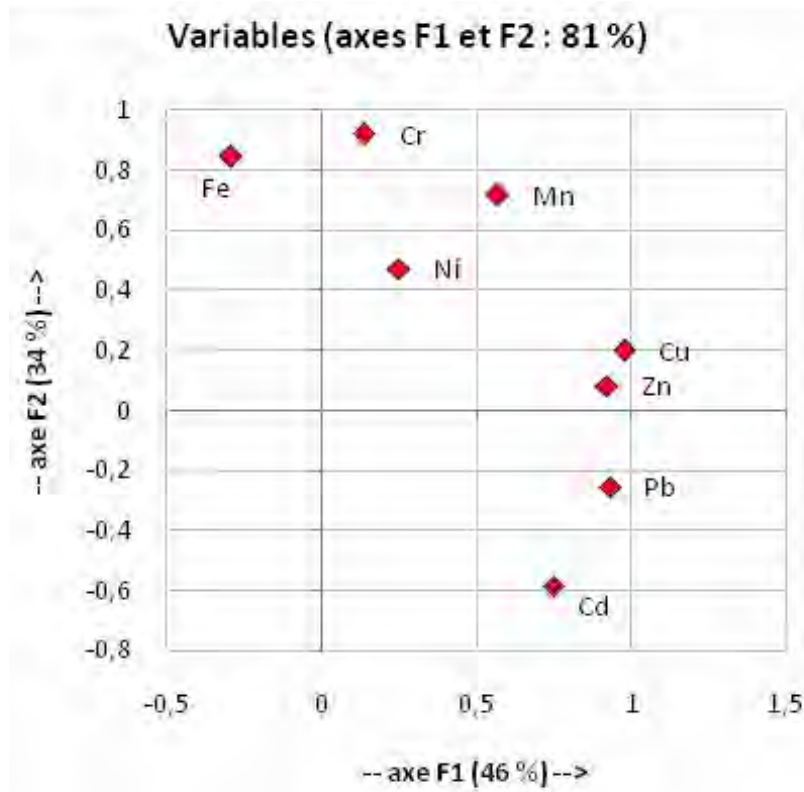
Variables (axes F1 et F2 : 90 %)

Figure 7. Plot of principal component loads for Nosy Be metals concentrations.
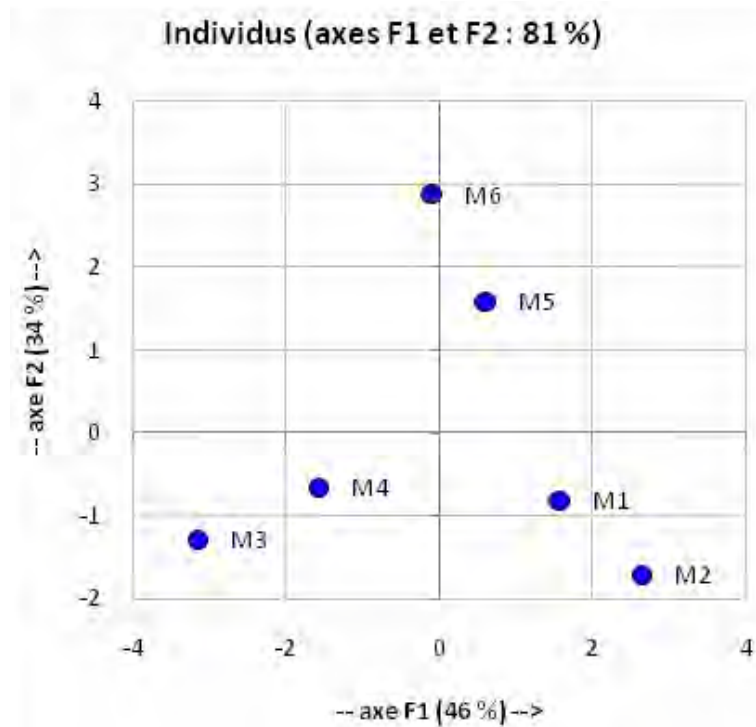
Individus (axes F1 et F2 : 90 %)

Figure 8. Plots of Nosy Be's object sample scores in space spanned by principal component one and principal component two (F1 and F2).

Figure 9. Plots of principal component loads for Mahajanga metals concentrations.

Figure 10. Plots of Mahajanga's object sample scores in space spanned by principal component one and principal component two.
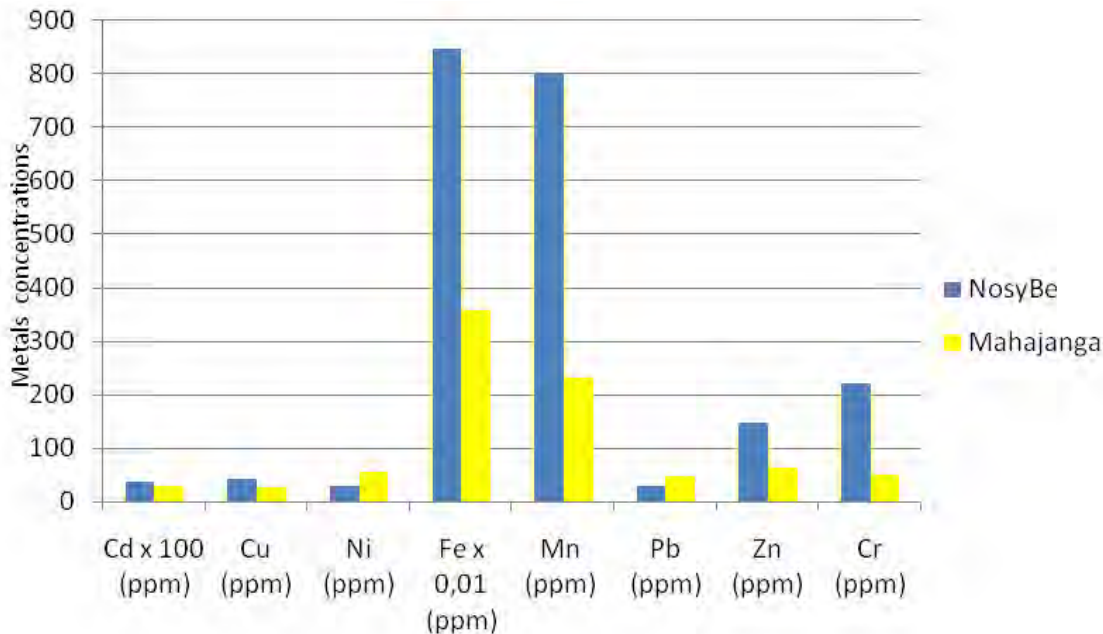
Figure 11. Comparative diagram between Mahajanga and Nosy-Be metals concentration.

Betsiboka washing courant.

Conclusion

Level of metals from soil erosion in coastal sediments such as Fe, Mn, Zn and Cu are higher in Nosy-Be and Mahajanga sediments than that of other areas in Africa. Higher concentration of these elements in sediment can threaten marine organisms. Concentrations of Pb and Cd found closer to Mahajanga Seaport were higher than their natural concentrations. They are known by their toxicity (M. MORLOT 1990) (FAO, 1995).

Metals in sedimentary coastline are caused either by seaport activities or by non-treated sewage of different sources such as industrial and dustbin. So it is proportional on number of industries and habitants as the case of this study. At Nosy-Be at Mahajanga metals absorption in sediments can be ordered in this decreasing range: Pb, Zn, Cd, Cu and Ni. It is true that efforts have been done, and these need to be encouraged to improve environment quality. But, rapid development of urban plan and economic activities push us to make more work on the preservation of sea area. It is important to assess a pollution control in a national scale.

REFERENCES

Nirilalaina A (2007). Evaluation de la qualité de l'eau sur l'environnement marin et côtier de la ville de Nosy-Be et de Mahajanga ; Université d'Antananarivo ; Faculté des sciences ; DEA option chimie minérale.

Karageorgis AP, Nikolaidis NP, Karamanos H, Sloukilidis N (2003). Water and sediment quality assessment of the Axios River and its coastal environment. Continental Shelf Res. 23: 1929–1944.

Biney C, Amuzu AT, Calamari D, Kaba N, Mbome IL, Naeve H, Ochumba O, Osibanjo O, Radegonde V, Saad MAH (1995). Revue de la pollution dans l'environnement aquatique Africain: étude des métaux lourds ; FAO Département des pêches.

David H, Donna K (2002). Traces metals in sediments from Torres Strait and the Gulf of Papua: concentrations, distribution and water circulation patterns. Marine Pollution Bull. 44 : 1296 – 1313.

Rasoanandrasana E (2006). Contribution à l'étude des déchets domestiques et industriels de Mahajanga: Application à la gestion et méthanisation simultanés des effluents de distillerie de l'industrie sucrière et d'abattoir ; Thèse de Doctorat de troisième Cycle, option Energétique Faculté des Sciences Université d'Antananarivo.

FAO (1995). Effects of riverine inputs on costal ecosystems and fisheries resources

José M, José U, Ignacio G (2004). Heavy metal distribution in marine sediments from the southwest coast of Spain. Dept. Chemical and Environ. Eng., Univ. Seville Spain. Chemosphere 55: 431–442.

Villeneuve JP (2004). Training manual on the measurement of organochlorine and petroleum hydrocarbons in environmental samples; Int. Atomic Energy Agency; Marine Environ. Laboratory Monaco.

Ranaivoson J (1997). Strategic Action Plan for Land-Based Sources and Activities Affecting the Marine, Coastal and Associated Fresh Water Environment in the Eastern African Region. FAO report.

Khalid M, Mahmond N (2004). Trace metal in water, sediments and marine organisms from the Northern part of the Gulf of Suez, Red Sea. J. Marine Syst. 46 : 39– 46.

Morlot M (1990). (coordonnateur de l'Association Générale des Hygiénistes et Techniciens Municipaux), Aspect analytique du plomb dans l'environnement ; Lavoisier TEC DOC.

Kress N, Herut B, Galil Bs (2004). Sewage sludge impacts in sediment quality and benthic assemblages off the Mediterranean coast of Israel _ a long-term study. Marine Environ. Res. 57 : 213–233.

Serpaud R, Al-Shukry M, Casteicnau M, Matejka G (1994). Revue des sciences de l'eau ; Adsorption des métaux lourds (Cu, Zn, Cd, et Pb) par les sédiments superficiels d'un cours d'eau : rôle du pH, de la température et de la composition du sédiment 7: 343 – 365.