

Classification of Spatial Variation Pattern for Identifying Pollution Sources: A Case Study on Sediment Contamination in Bizerte Lagoon, Tunisia

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Abstract

The concentration of potentially toxic elements (PTEs) was measured for a total of 180 sediment samples collected from the Upper Layer (surface sediments) and the Lower Layer (sediments repository) of lagoon bottom sediments distributed in the Bizerte lagoon, Mediterranean coast, northern Tunisia. The spatial variation pattern of PTEs contamination in the lagoon bottom sediments is classified into three types, Type I, II, and III. (i) Type I: A 'peak'-shaped very high concentration part limitedly appears at several shoreline sites nearby the Menzel Bourguiba industrial zone. The other sites show relatively homogeneous distribution with low concentration values. This variation pattern implies that the contamination is caused by an effluent from the industrial zone, and the contamination has not widely spread toward the lagoon basin. Twelve elements are found in this type: Sb, As, Ba, Cd, Cu, Pb, Mo, Se, Ag, Tl, U, and Zn. Three heavy metals, Ba, Pb, and Zn, and two metalloids, As and Se, show toxic level of values above the regulation. (ii) Type II: A 'plateau'-shaped high concentration zone is present from south western part (Menzel Bourguiba, Tinja, and its north) to the west central part of the lagoon basin. The concentration significantly decreases eastward, southward, and northward. This 'Plateau' type pattern implies that the pollution source is the south western side of the lagoon, and the contamination migrates towards the central part of the lagoon. Seven elements are found in this pattern: Al, Cr, Co, Fe, Mn, Ni, and V. The concentration of five metals, Al, Cr, Co, Mn, and V, indicates above or around the criteria. (iii) Type III: The Hg concentration shows unique spatial variation of which higher values appear only near the south eastern shoreline of the lagoon basin. The Hg contamination is probably due to agricultural chemicals such as pesticides derived from the eastward-southward agricultural zone.

Keywords: sediment contamination, lagoon, potentially toxic elements, spatial variation

1 Introduction

Populated cities and/or industrial zones in northern Tunisia have been mostly developed along Mediterranean coastal lagoons, e.g. Tunis and Bizerte lagoons. It is very common in Tunisia that lagoon basins, depressions, and streams ("Wad") are used as open-dumping solid waste disposal sites. The coastal lagoons are, in consequence, facing the risk of environmental pollution caused by human activities such as industrial effluents, wastewater, and solid waste disposals. The lagoon bottom sediments are, in this context, a sink of pollutants, where the concentration levels of pollutants such as Potentially Toxic Elements (PTEs; Alloway, 1995) become very high in comparison with natural background. Indeed, a significant soil/sediment

contamination of lagoon bottom sediments was known in and around Lake South Tunis (Lac Sud) and Lake Ariana, nearby Tunis urban/industrial zone (Yoshida et al., 2002).

The Bizerte lagoon is one of such coastal lagoons located near the industrial and urban zones, where industrial zones of Menzel Bourguiba, Bizerte, and Menzel Jmil have been developed as urban as well as industrial zones, and three open-dumping type municipal/industrial solid waste landfills have been operated near the Bizerte, Menzel Bourguiba, Menzel Abderahmen, and Menzel Jmil (Figure 1). The south eastern side of the Bizerte lagoon is a widely opened as an agricultural zone where potential pollutants like fertilizer and agro-chemicals (pesticides, herbicides, and insecticides) are disseminated.

In this paper, we report the results of potentially toxic elements (PTEs) analysis of lagoon bottom sediments sampled by the RPP-SEPMCL leg Bizerte2002, and discuss about the spatial variation pattern of PTEs contamination and its relationship with the human activities.

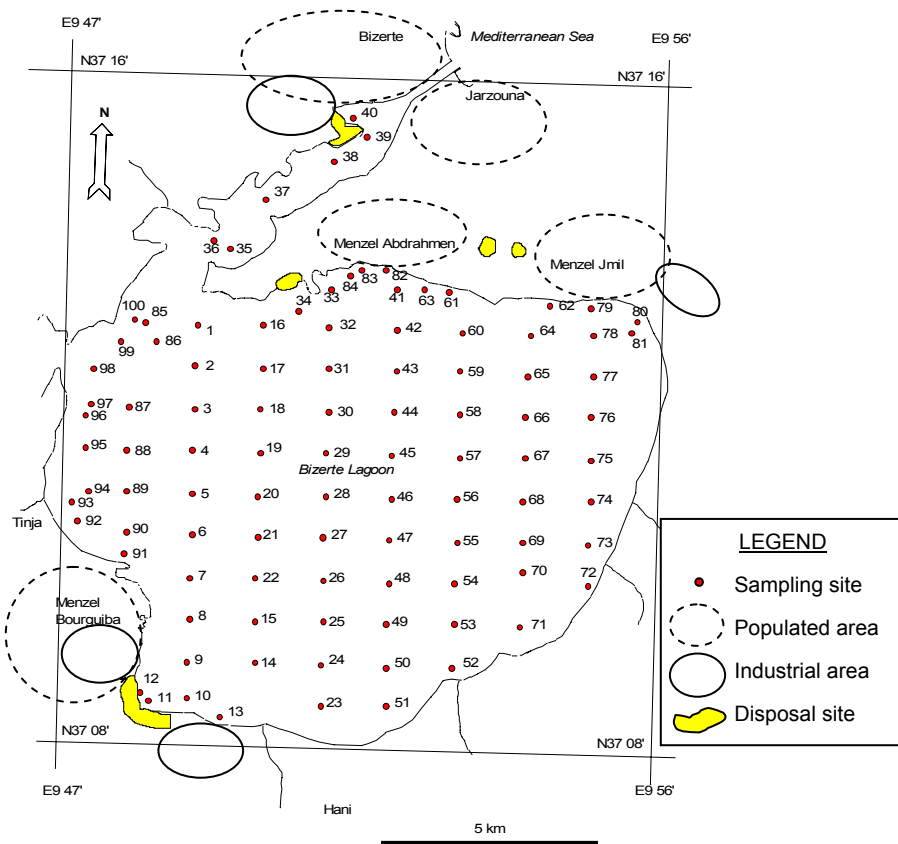


Figure 1. Geographic setting and location of sampling sites. Dashed circles are the areas of populated zones, solid circles are those of industrial zones, and shaded parts are solid waste landfills. The geography is based on the 1/200,000 topographic sheet "Binzart".

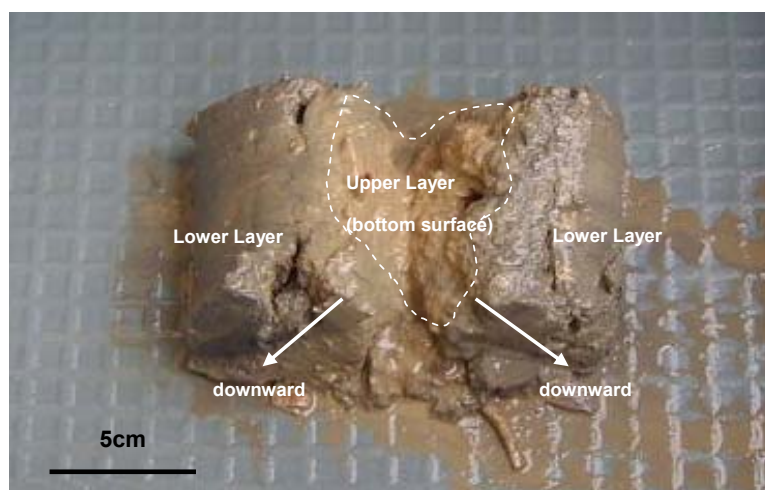


Figure 2. Typical occurrence of the Upper Layer (surface sediment) and the Lower Layer (sediment repository) in a sample of the lagoon bottom sediment dredged by a grab sampler.

2 Sample

Total 180 samples were collected from lagoon bottom sediments of 100 sites using a grab sampler (Figure 1). The location was defined with a receiver of global positioning system (GPS). According to the on-site observation with naked eyes, the collected sediments, which were more or less maintained the original texture, were mostly divided into two layers, the upper thin (thickness < 1 cm) unconsolidated layer ('Upper Layer') and the lower semi-consolidated sediments ('Lower Layer') (Figure 2). The former is normally light brown colour indicating oxidizing conditions but the later is dark gray to black in anoxic conditions. We collected separately for the chemical analysis, named 'U' samples and 'L' samples. The upper layer is discriminated in 80 sites. The latitude and longitude of each site was reported in the Initial Report (RPP-SEPMCL Initial Report 2002 published by INRST-JICA).

3 Chemical Analysis

The dredged sediment samples, Upper and Lower Layers, were disintegrated and dried under 105°C, and powdered by a ceramic mill. Then the powder samples were sieved by a 68 micron, and the finer fraction was used for the analysis.

A 15.0 gm sample split was digested in 90 mL aqua regia (HCl-HNO₃-H₂O) at 95°C for one hour. The solution is diluted to 300 mL with distilled water. Analysis was made by an Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Mass Spectrometry (ICP-MS). Total 37 elements were measured: B, Na, Mg, Al, P, S, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Sr, Mo, Ag, Cd, Sb, Te, Ba, La, W, Au, Hg, Tl, Pb, Bi, Th, and U. The upper detection limit for Ag, Au, Hg, W, Se, Te, Tl, and Ga is 100 ppm, that for Mo, Co, Cd, Sb, Bi, Th, U, and B is 2 %, and that for Cu, Pb, Zn, Ni, Mn, As, V, La, and Cr is 10 %. The aqua regia digestion of sediment extracts only a fraction of the major elements (pseudo-total analysis) because silicates are not completely dissolved with this method. Owing to this limitation, results are total to near total for trace and base metals and possibly partial for rock-forming elements such as Na, Mg, Al, K, Ca, Mn, and Fe. However,

environmentally concerned components like heavy metals or PTEs not bound to silicates are efficiently dissolved (Ure, 1995), which is indicative for the assessment of toxicity.

4 Results of Chemical Analysis

The variation of aqua regia extracted element composition of the sediments from the Upper and Lower Layers is almost similar to each other, while the concentration of several elements such as S, Mo, and U exhibits distinct different range between the Upper and Lower Layers. For clarifying the differences, a 'difference ratio' S is calculated. The ratio is defined by the following equation for the concentration data of given element:

$$D = \frac{(\text{conc. in Upper Layer}) - (\text{conc. in Lower Layer})}{(\text{conc. in Upper Layer})} \times 100 (\%)$$

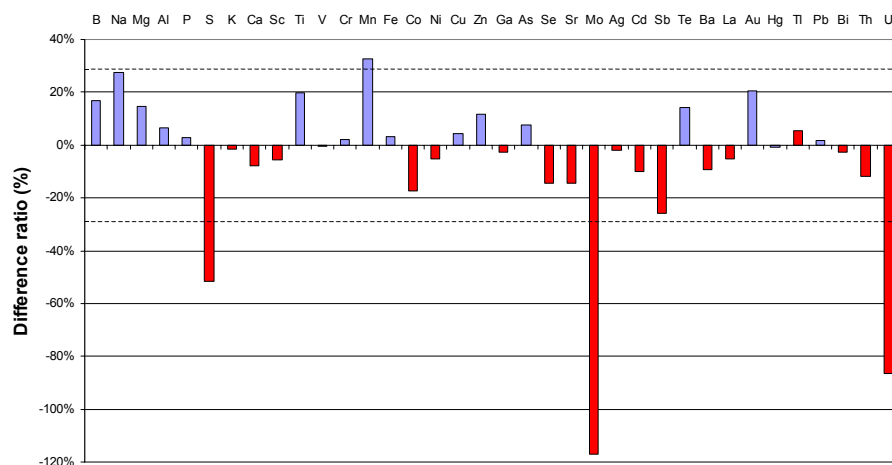


Figure 3. Comparison of the element concentration in sediments between the Upper and Lower Layers using 'difference ratio' D. The ratio for tungsten (W) was excluded because of a lack of sufficient data. The standard deviation of the population of 'difference ratio' is 28% showing dashed lines.

Therefore, if the difference ratio is positive then the concentration in the upper layer is relatively larger than that in the Lower Layer for given element, while if it is negative then the concentration in the Upper Layer is smaller than that in the Lower Layer.

The elements showing a negative 'difference ratio' are enriched in the Lower Layer where anoxic conditions are dominant. Indeed, PTEs such as Co, Se, Mo, Sb, and U metals are normally immobilized as sulfides under anoxic conditions. In fact, the concentration of S is very high in the Lower Layer (difference ratio of $S = -52\%$). In contrary, the Upper Layer represents more or less oxidizing materials which are always reworking; the metals are easily released and complexed with chloride ions especially under marine (high salinity) conditions (de Groot, 1995). Thus, the Upper Layer is 'surface sediments' not yet settled completely, and the Lower Layer is the 'sediments repository'.

5 Spatial Variation of the PTEs Concentration

Spatial variation of PTEs; Al, Sb, As, Ba, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Hg, Ni, Se, Ag, Tl, U, V, and Zn, in the Upper Layer (surface sediments) and Lower Layer (sediments repository)

is investigated for assessing sediment contamination of Bizerte lagoon. The spatial data are statistically averaged using a Distance Weighted Least Squares algorithm of which result was expressed by a curved surface (see Figures 4 and 5). The criteria (threshold) for sediment contamination are based on NOAA Screening Quick Reference Tables (SQuiRTs) (NOAA, 1999) and Alloway(1995). The profile on spatial variation of the concentration of each PTE is as follows:

The concentration of aluminum (Al) varies widely but generally the sites of central to central western part of the lagoon basin show very high concentration around the threshold value (1.8 %). The concentration decreases towards the shoreline, which suggests us the granulometry is a controlling factor of the variation (Hamdi et al., 2002).

Antimony (Sb) concentration is rather homogeneous in the lagoon basin except abnormally high values near Menzel Bourguiba landfill (LB-11 and 12), which indicates a strong impact of human activity such as landfilling. However the concentration does not exceed The threshold value for its toxicity (<9.3 ppm).

Arsenic (As) contents is relatively homogeneous but toward Menzel Bourguiba and Bizerte city, the concentration tends to increase, which is more significant in the Lower Layer. The concentration level is rather high in comparing with the threshold value (35 ppm), and it exceeds in the sites near the Menzel Bourguiba.

The concentration of Barium (Ba) is also relatively homogeneous in the lagoon basin but it tends to increase toward Menzel Bourguiba, which is more significant in the Lower Layer. The level of concentration is generally high above and around the threshold value (48 ppm).

Cadmium (Cd) also exhibit similar trend in the cases of Sb, As, and Ba, while even the highest concentration near Menzel Bourguiba does not exceed the threshold value (3 ppm).

Chromium (Cr) concentration is generally high around west central part of the basin to Menzel Bourguiba, and it suddenly decreases eastward and Mediterranean side, which indicates the polluter(s) is possibly found around Menzel Bourguiba – Tinja, and the Cr is migrating central-eastward. It should take note that the concentration level in the west central part (the zone of higher values) does not exceed the threshold value (62 ppm), but very closed to it.

The spatial variation of the concentration of cobalt (Co) is quite similar to that of Cr, which also suggest the polluter is around Menzel Bourguiba –Tinja. The concentration level is also around the threshold values (10 ppm).

Copper (Cu) content does not vary in the major part of the lagoon basin where it is low around background level (10-25 ppm). However only the sites close to the Menzel Bourguiba landfill show several times higher value as a peak.

The concentration of iron (Fe) is generally high in central to western area of the basin and around Menzel Bourguiba, but the concentration level is lower than the threshold value (22 %).

The concentration of lead (Pb) is again showing Cu-type pattern of variation, and the peak values above the threshold value (400 ppm) can be found in the Lower Layer near the Menzel Bourguiba landfill.

Manganese (Mn) content in the baisn is rather high in comparing the threshold values (260 ppm), where the concentration increases toward Menzel Bourguiba. Central and western parts

of the basin exhibit a plateau of high concentration above the threshold value, which is more significant in the Upper Layer.

The concentration of molybdenum (Mo) is generally low and monotonous, but near the Menzel Bourguiba it suddenly increases several times. The concentration in the Lower Layer also depicts some peaks in the western margin of the lagoon basin. However they do not exceed the threshold value (40 ppm).

The concentration of mercury (Hg) is generally low in the lagoon center, but surrounding areas such as Bizerte, Menzel Bourguiba, and southeastern shore zone show higher values around the threshold value (0.41 ppm). Particularly in the Lower Layer sediments, the concentration suddenly increases near the southeastern part where agricultural area is widely developed.

The variation of nickel (Ni) concentration is again similar to the Cr and Co type behavior, where the central western part toward Menzel Bourguiba shows a plateau of relative high concentration. However the concentration level is low in comparing with the threshold value (110 ppm) even in the sites showing relative higher values ('plateau').

The concentration of selenium (Se) in the Upper Layer sediments is generally low in the major part of the lagoon basin (<1 ppm) while it suddenly increases nearby the Menzel Boulguiba landfill as a peak that exceeds the threshold value (1 ppm). The concentration of Se of the Lower Layer sediments shows an increase not only nearby Menzel Bourguiba landfill but towards Menzel Jmil, which suggests us there are two pollution sources.

The concentration of silver (Ag) is also very low in the major part of the lagoon basin. It only shows a peak value near the Menzel Bourguiba landfill, but it is still less than the threshold value (3.1 ppm).

The concentration of thallium (Tl) little varies in the major part of the lagoon basin but marks peak values only nearby the Menzel Bourguiba landfill which are not above the threshold value (1 ppm). Industrial uses of Tl are varied, but all are, at present, small scale, such as using as a catalyst, semiconductor, and in electric engineering. However, its major use was a pesticide and rodenticide, until banned in many countries in the mid 1970s (Edwards et al., 1995).

The variation of uranium (U) concentration does not vary so much while it increases near Menzel Bourguiba and Bizerte port. There is no reliable criterion for evaluating sediment contamination by U, while the concentration obtained by present study is background level previously reported in other areas (Edwards et al., 1995).

The variation of vanadium (V) concentration is similar to the Cr and Co type 'plateau' behavior, where the central western part toward Menzel Bourguiba shows a plateau of relative high concentration. The higher concentrations in 'plateau' around Benzel Bourguiba are above the threshold vale (57 ppm).

The concentration of zinc (Zn) is rather monotonous in the major part of the lagoon basin. It shows peak values near the Menzel Bourguiba landfill, which marks abnormally high vales above the criteria (410 ppm).

Thus the pattern of spatial variation od PTEs concentration in the lagoon bottom sediments can be classified into three types, Type I, Type II, and Type III. Characteristics of each type are summarized as follows:

Type I: A ‘peak’-type abnormally high concentration site(s) limitedly appears nearby the landfill of Menzel Bourguiba. The other sites show relatively homogeneous distribution with low concentration values. This variation pattern implies that the contamination source is at the Menzel Bourguiba landfill, and the contamination has not widely spread toward the lagoon basin. Twelve elements are found in this type: Sb, As, Ba, Cd, Cu, Pb, Mo, Se, Ag, Tl, U, and Zn. Three heavy metals, Ba, Pb, and Zn, and two metalloids, As and Se, show toxic level of values above the criteria (see Figure 4).

Type II: A ‘plateau’-type very high concentration zone is present from southwestern part (Menzel Bourguiba, Tinja, and its north) to the west central part of the lagoon basin. The concentration significantly decreases eastward, southward, and northward. This ‘Plateau’ type pattern implies that the pollution source is the southwestern side (Menzel Bourguiba, Tinja, and its north) of the lagoon, and the contamination migrates towards the central of the lagoon. Seven elements are found in this pattern: Al, Cr, Co, Fe, Mn, Ni, and V. The concentration of five metals, Al, Cr, Co, Mn, and V, indicates above or around the threshold value in the ‘plateau’ zone. The ‘plateau’ zone corresponds to the area of clay and organic matters distribution zone (Ouakad, 2000) which shows high cation exchange capacity (Hamdi et al., 2002). It means these metal elements have been adsorbed by the clay mineral and/or complexed with organic matters (see Figure 4).

Type III: The others patter. The variation of Hg concentration basically shows ‘peak’ pattern but it also enhances near the southeastern part of the lagoon basin. The peak values exceed the threshold value. One of the pollution sources can attribute to the Menzel Bourguiba landfill, but the other is probably due to a non-point pollution of Hg contained agro-medicals such as pesticides in the eastward-southward agricultural zone (see Figure 5).

Consequently, sediment contamination by 11 PTEs, Ba, Pb, Zn, As, Se, Al, Cr, Co, Mn, V, and Hg, can be recognized in the Bizerte lagoon, of which concentrations indicate hazardous (toxic) level of contamination (Table 1).

Table 1. Summary of spatial variations of PTEs contamination in Bizerte lagoon sediments.

	Constituting PTEs	Toxic level of concentration	Possible source(s)	Migration in the basin
Type I (‘peak’ type)	Sb, As, Ba, Cd, Cu, Pb, Mo, Se, Ag, Tl, U, and Zn	Ba, Pb, Zn, As, Se	Menzel Bourguiba landfill	Local pollution, not widely spread
Type II (‘plateau’ type)	Al, Cr, Co, Fe, Mn, Ni, and V	Al, Cr, Co, Mn, and V	Menzel Bourguiba, Tinja, and its north	Widely spread into lagoon basin, adsorption by clay and organic matters
Type III	Hg	Hg	Menzel Bourguiba landfill and souther and eastern agricultural zone	Local pollution, Not widely spread

6 Contaminant Inflows Model

There are five potential polluters caused by human activities around the Bizerte lagoon basin, Menzel Bourguiba industrial zone, Bizerte urban zone, Menzel Abderahmen town, Menzel Jmil town & factories, and south to east agricultural area. Based on the spatial variation of each PTE, inflow of contaminants and potential polluters are estimated.

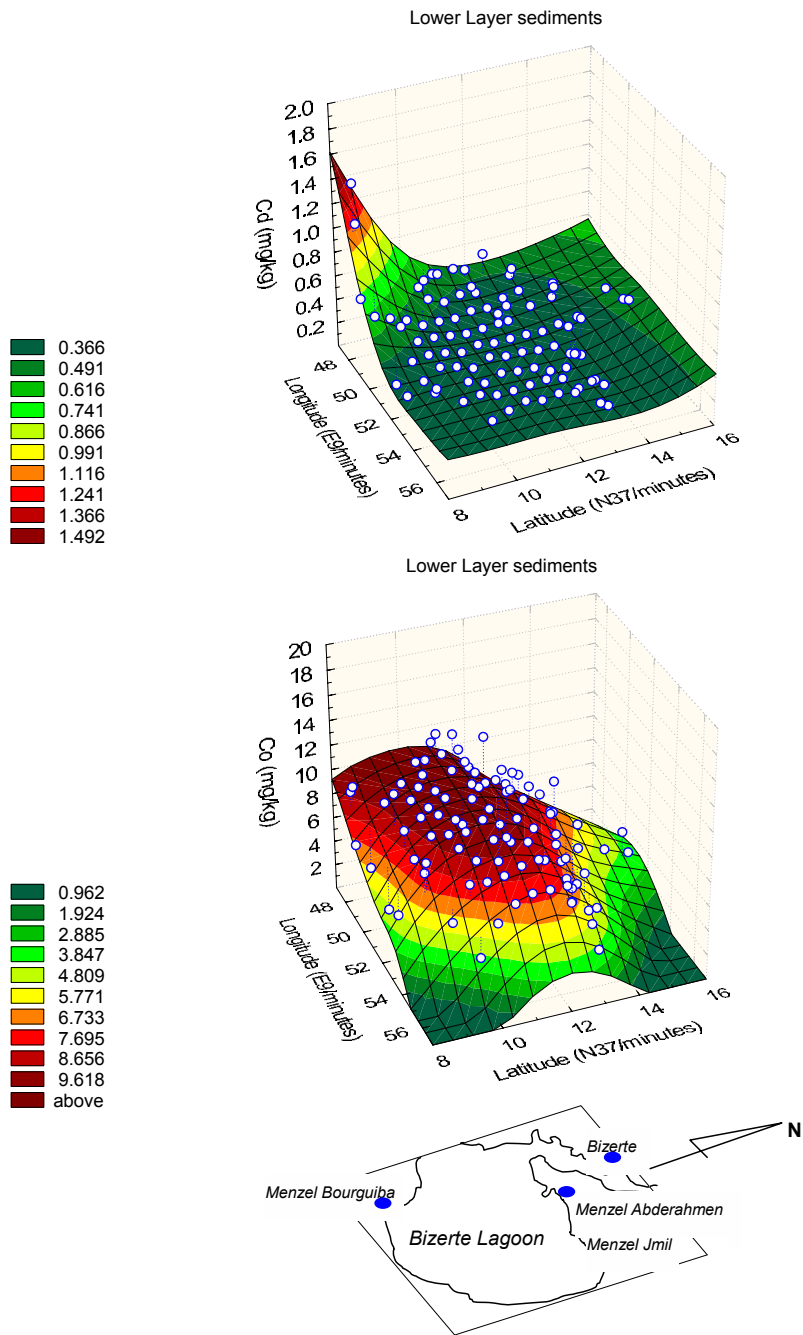


Figure 4. Spatial variation of Cd contamination (above; example of Type I) and Cr contamination (below; example of Type II) Vertical axis shows the concentration of each element in the Lower Layer of lagoon bottom sediments.

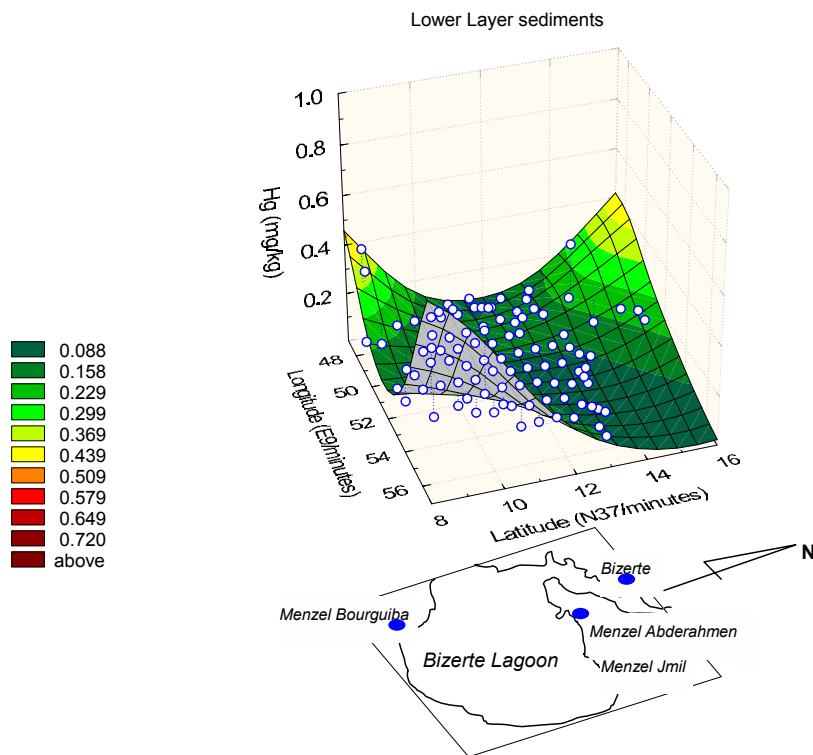


Figure 5. Spatial variation of Hg contamination (example of Type III). Vertical axis shows the concentration of each element in the Lower Layer of lagoon bottom sediments.

According to the spatial variation patterns of PTEs contamination, the largest polluter can be identified at Menzel Bourguiba industrial zone. The Type I pattern of spatial variation clearly indicates a single polluter for the PTE contamination (hotspot), where major contaminants are Cr, Mn, Ni, Cu, Zn, As, Se, Cd, Ba, Hg, and Pb. The peaked high-level concentration near the landfill indicates that the contaminants are transported directly from the landfill through runoff, leachate or airborne deposition. The Type II pattern of spatial variation is also derived from the Menzel Bourguiba industrial zone, however the contaminants are transported by water (wastewater) because of relatively wider distribution in the lagoon basin.

The Hg contamination presenting the Type III pattern of spatial distribution shows strong influence from south eastern side, agricultural zone.

The influence of other potential polluters, Bizerte urban zone, Menzel Abderahmen, and Menzel Jmil, is rather weak in comparison with that of Menzel Bourguiba industrial zone.

The model of contaminant Inflows into the Bizerte lagoon basin is illustrated in the Figure 6.

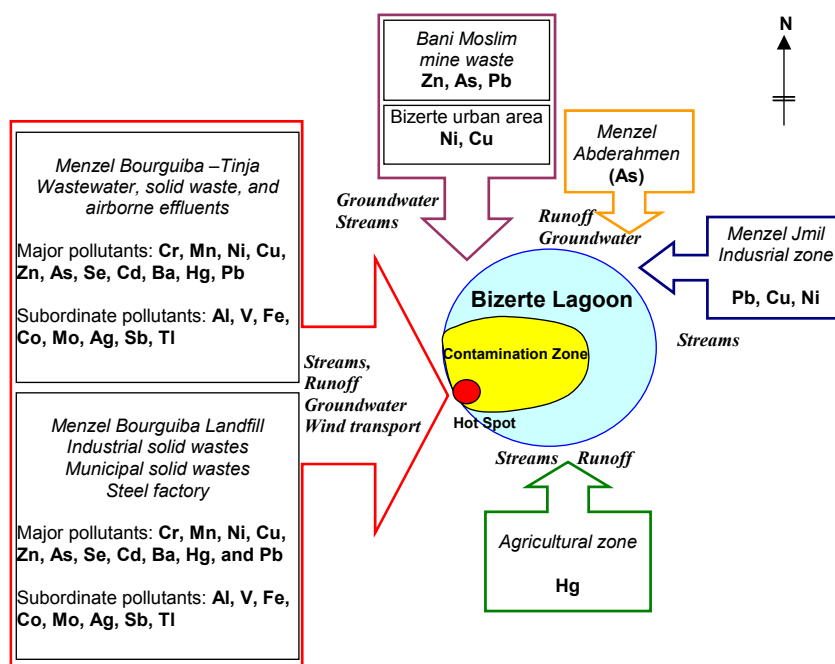


Figure 6. Contaminant inflows model estimated from the spatial variation of PTEs concentration of the lagoon bottom sediments, Bizerte lagoon.

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