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Pollution by the heavy metals of the superficial marine sediment of Skikda city (Northeastern Algeria)

Doria Gueddah[1,2] and Abdallah Borhane Djebar[2]

[1]Department of Biology, University 20 Août 1955, Route El Hadaïek, Skikda, Algeria
[2]Laboratory of Ecobiology of the Marine and Coastal Surroundings, Department of Sciences of The Sea, University Badji-Mokhtar, Annaba, Algeria

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ABSTRACT

The mineral micropolluants not accumulating in water (receiving) herself is transferred enough quickly in the sediments where they are metabolized in part by the living organisms and is put in circulation in the food chains where their toxicity blooms. The irreversibility of this pollution is especially preoccupying because it is practically impossible to recover these metals comfortably, once inattentive in the nature; their remanence is with difficulty the very reason of an accumulation controllable. The assessment of the content of the superficial sediment of the inshore zone of the region of Skikda in nine (09) heavy metals allowed us to put in evidence of the concentrations raised of pollutants, passing the values limits fixed by the regulation in force as well as (Algerian) the Dutch norms that have been taken like reference and this for some sewages. Virgin zones deprived of all pollution have also been put in evidence.

Keywords: pollution, coastal, Skikda, heavy metals.

INTRODUCTION

A lot of aquatic ecosystems, whose strands urbanized themselves and industrialized, are characterized by sediments rich in metallic elements. In some years, for example, the basin of Arcachon (France) saw to progress his/her/its concentrations made of copper, lead and zinc of 100 to 400% [1]. This growth of micropolluants in the sediments has almost everywhere been observed in the world: in Sicily, in an inshore fairway [2], to Portugal, in the lagoon of Aveiro [3], in Italy, in the lagoon of Venice [4], to Quebec, in the Saint-Laurent's estuary [5], in inshore border of the southwest of the United States [6], in France, on the Mediterranean coast [7], in the pond of Berre [8] and the gulf of Fos [9] and [10], in the bay of Marennes-Oléron[11].

In Algeria, a lot of works concerned the levels of metallic contamination at many marine organisms, notably; the red mullet of rock *Mullus surmuletus* [12], the mussel *Mytillus galloprovencialis* [13, 14, 15], the crustaceans decapods [16] and the bug *Boops boops* [17]. At the time of a work of approach of the pollution problem in the bay of Annaba, non negligible levels of microbial contamination in the superficial waters and metallic contamination in the superficial sediment have been put in evidence [18].

The marine organisms are capable to concentrate several hundreds of metals took in the soluble phase or particular as well as in the sediment. It appears fundamental to put in evidence the origin and to become of these metals if one wants to understand the impact that they can have on the living organisms. The aquatic micro-organisms introduce its micro-pollutants in the biosphere; they are the first links of the food chains the long of which the pollutants remnants are going to accumulate in the tissues of the successive eaters and this by bio-accumulation: The bio-accumulation being a process of assimilation and concentration of the heavy metals in the organism.

The assessment of the pollution by the heavy metals is a part of our work that is inspired of a research project in the setting of the program of surveillance and struggle against the pollution of the coastline. This program of surveillance has for final objective, the protection against the pollution of the coastline of Skikda and this by the setting up of a system of integrated control of the pollutions to the favor of a system of auto control and auto surveillance especially as Skikda city is part of the three hot points of the country.

MATERIALS AND METHODS

1. SITES AND TECHNIQUE OF SAMPLING:

Skikda city is situated to the East of the Algerian coastline, between the latitudes 36°5' N and 36°15'N and the longitudes 7°15' E and 7°30' E, spreading on a surface of 4 137.68 km^2 with 130 km of coasts. It regroups 13 daïras and 38 townships and is limited at the North by the Mediterranean Sea and adjoins Annaba, Constantine, Guelma and Jijel city (Fig.1).

The choice of the maillage of the withdrawal stations was established in order to take in account the different dismissals (industrial essentially) as well as the harbor infrastructure of Skikda. For every site considered the concentration of 9 heavy metals (Zn, Cu, Mn, Ni, Cr, Pb, Cd, Fe, and Hg) is determined. The stations so definite distribute themselves as follows:

N° Station	Nomenclature
10	Ben Mhidi Beach Poste 1
15	New Port (Port hydrocarbons)
16	Saf-saf oued (occupies the Northern part of Skikda)
17	Hot point
18	Former port (port mixed. Hydrocarbons and goods)
21	Port of fishing
23	Miramare beach

The features of every station are indicated in the table 1.

These withdrawals are made with a diver's help while using a rudimentary material. In fact, like a carottier-limps, a bucket of 20 to 30cm diameter is driven by the diver in the sediment and the sample appropriated depends therefore of the penetration of the bucket that essentially depends on the nature of the sediment. A quantity of about 500g is recovered, bet in a sachet in labeled plastic and placed in an icebox to 4°C [19]. Following it, the samples are frozen for ulterior analysis (Fig.1).

Table 1: Characteristic of the stations of withdrawal of the sediments for the assessment of the metallic pollutants

Stations	Temperature (°C)	Depth(m)	Distance of the beach (m)	Nature of the sediment
10	26.50	2.50	200	Gritty
15	26.00	7.50	Port mixte	Gritty
16	27.50	2.00	200	Muddy
17	27.00	2.50	150	Gritty
18	26.05	7.00	Port hydrocarbons	Gritty
21	25.40	4.00	Port of feashing	Muddy
23	25.50	2.00	150	Coarse sand

2. ANALYSIS OF THE SAMPLES

For the determination of the concentrations made of heavy metals, numerous variants exist to all stage of the analytic protocol of sediment [19]. However, it seems necessary to recommend one unique operative fashion, applicable for all laboratories and permitting to value the degree of pollution. Because it agrees for the range of concentrations found in the sediment, the atomic absorption spectrophotometry to flame is used like technique of measure for the present survey. It consists in carrying the elements in their atomic state on the very journey of a luminous ray (cathodic lamp) and to do a measure of the absorption simultaneously to a length of specific wave of the atoms formed.

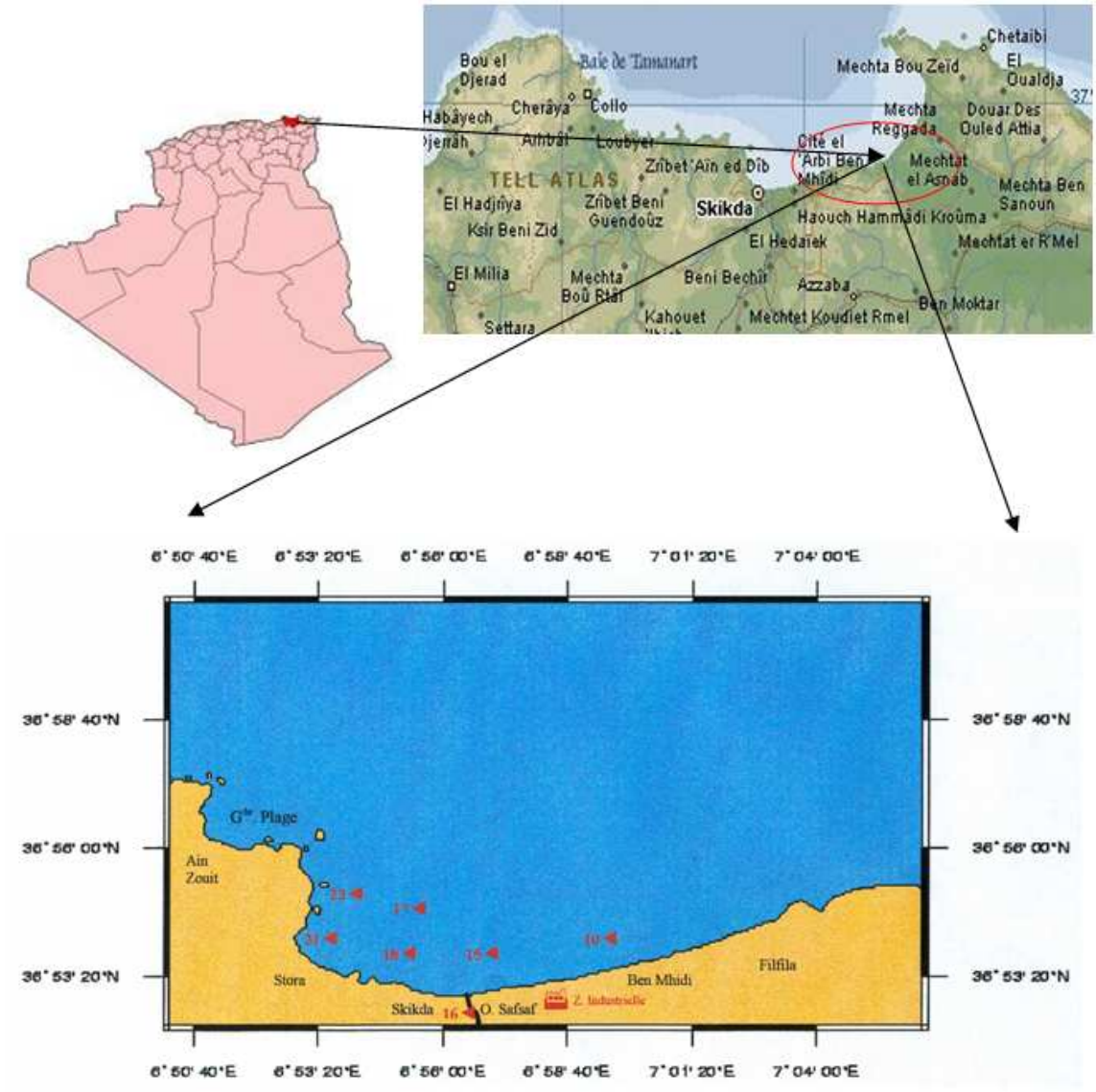

Figure 1: Study area and sampling locations (◄Sampling point)

3. EXPRESSION OF RESULTS :

The concentration (CMe) of the metallic element in the sediment is gotten by the following formula [20] in [19]:

$$CMe\ (mg/kg) = \frac{CE \times V}{M}$$

With :
CE: Read concentration on the curve of standardization (mg / kg)
V: Volume of the final solution after digestion (ml)
M: Mass of the sediment mineralized (g)
The results are expressed in milligram of metal by dry sediment kilogram.

The state of the pollution can also be appreciated by the calculation of the contamination indication (IC) whose expression is specified by the agency of the Basin Rhone Mediterranean Corsica [21] :

$$IC = \frac{\text{Concentration observed}}{\text{Concentration considered like normal}}$$

For the normal concentrations, we referred to the French norms for the calculation of the IC.

RESULTS AND DISCUSSION

Of one point of global view, we can note what follows:
The maximal values of mercury and the cadmium are observed to the level of the site 15 (mixed Port); the presence of mercury can be bound to a contamination by the hydrocarbons [22]. Following the physic-chemical conditions of the middle, the mineral mercury, that arrives in the marine ecosystem, is converted by the benthiques bacteria in different mercurial compounds of which the methyl-mercury (the most dangerous) that can accumulate very well along the food chains [23]. When to the cadmium, the agents of contamination are essentially the mines and the refineries, the industrial dismissals and the urban worn-out waters, manures phosphates and insecticides. In the aquatic surroundings, this element is transferred quickly to the sediments and absorbed by the organisms that there evolves. More toxic again that mercury for the navy life, it essentially concentrates in the liver, the kidneys but also in the flesh of fish, these there being especially sensitive. For lead the maximal value is observed to the level of the site 21 (port of fishing), its artificial broadcasts essentially have for origin the foundries of metallurgy and the incinerators of garbage, the gainages of cables in alloy of lead that guarantees the tightness and the armor electric or certain insecticides. The maximal values of every remaining micropolluant are recorded to the level of the site 18 (port hydrocarbons). Among the considered micropolluants, iron is the predominant element. The presence of iron is bound to its natural presence in the water of sea [22]. It clearly appears through the table 2 that iron is metal the more represented of one point of quantitative and spatial view with a predominance of 96.11%, consistent of the manganese with 1.35%.

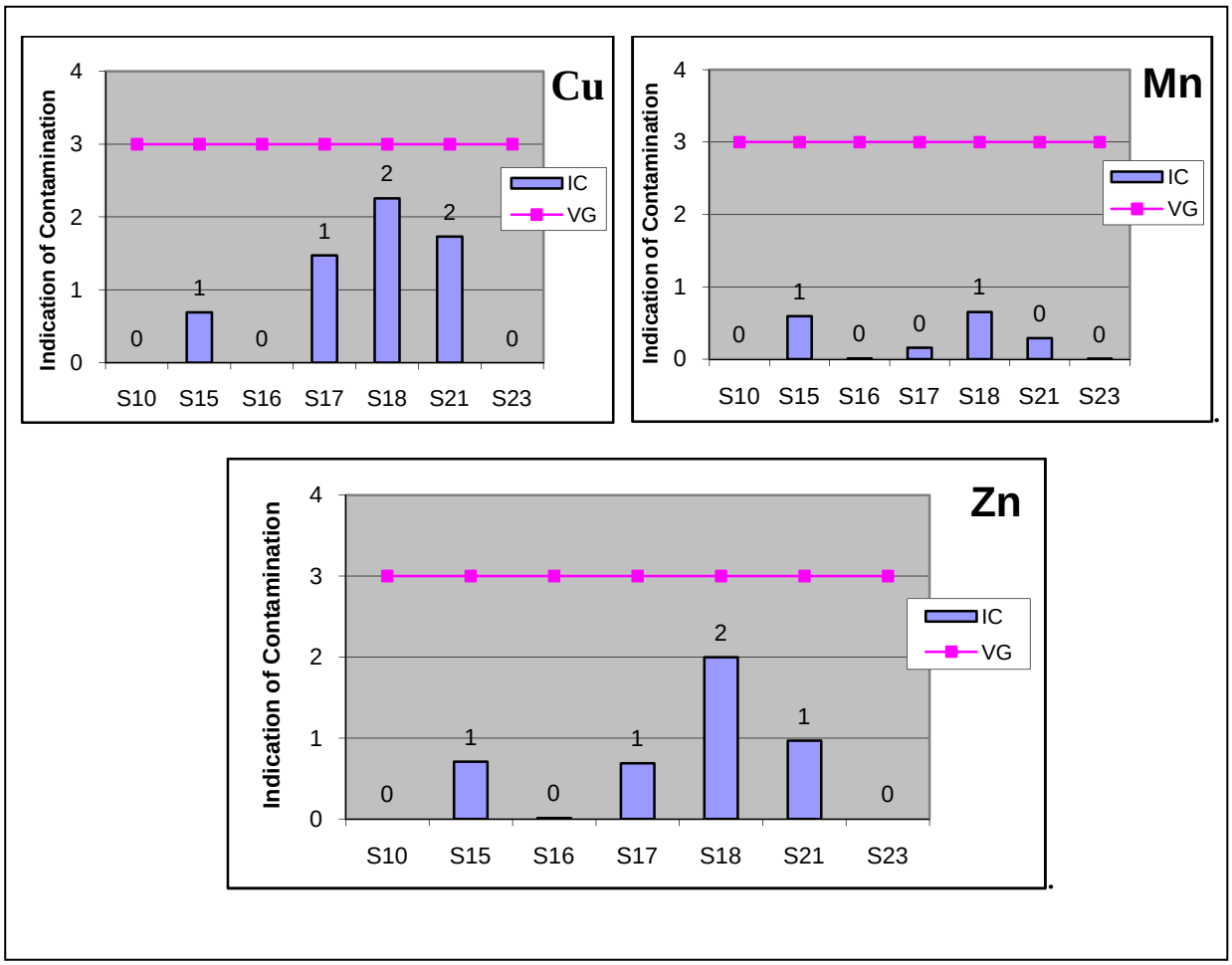

Figure 2: Graphic representation of the indication of contamination
(IC: Indication of contamination, VG: Value guides)

The calculated contamination indication for the copper, the manganese and zinc is variable of a metal to another and a site to another. However the values of this indication for the 3 considered metals and for every site are on this side of the value 3 (Fig. 2). The presence of the copper is bound to the corrosion of some facilities (hoses) and the materials manufactured in copper [24]. Zinc is a crystalline, water insoluble metal. Its artificial origin can be only

industrial. For the manganese, the industry is a potential source especially as the city of Skikda is a zone greatly industrialized.

Table 2: Spatial evolution of the heavy metals in the superficial sediment

Elements (mg/kg) / Sites	Zn	Cu	Mn	Ni	Cr	Pb	Cd	Fe	Hg
S10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.04	0.01
S15	62.25	18.00	236.50	38.00	44.25	36.50	1.50	16457.5	02.01
S16	01.05	0.00	03.55	0.00	0.00	0.00	0.00	03.52	0.00
S17	60.50	38.33	62.15	15.00	53.86	83.05	0.00	0.37	0.00
S18	175.87	58.66	260.50	40.00	63.47	129.60	0.00	16846.50	0.91
S21	85.00	45.00	115.00	35.00	38.33	145.00	0.00	14935.50	01.07
S23	0.00	0.00	01.03	0.00	0.00	0.00	0.00	05.33	0.00

The table 3 allows us to establish a comparison between the results gotten during our survey to the level of the ports of Skikda with those of various Algerian ports, it takes of it out again that for mercury, the most elevated value is recorded to the level of the port hydrocarbons of Skikda (Present survey) and the minimal value to the level of the mixed port of Skikda. These results being in conformity with the results gotten for the same port during previous studies [25], idem for the chromium, while noting the results lower to the Dutch norms and Algerian recommendations compared to the results gotten for the port of Annaba [18] that are extensively in overtaking. In the same way for the copper where all results are comparable with the exception of those gotten for the port of Annaba [21, 18] that are characterized by relatively elevated and superior values to the Dutch norms and no in conformity with the Algerian recommendations. We can note that the concentration of lead increased to the level of the former port (mixed port) and the port of fishing of Skikda compared to the concentrations observed during previous studies [25] what confirms the presence of a potential source. These values remain lower to the Algerian recommendations; however, they pass the Dutch norms extensively. In the same way for zinc, we note an increase of the concentrations and while being lower to the Algerian recommendations, those observed for the former port of Skikda are in overtaking of the Dutch norms. This being, the values observed to the port of Annaba [21 et18] remain extensively superior to those observed to the ports of Skikda. We also mark a light overtaking (of the Dutch norms) of the zinc concentration observed to the port of Mostaganem [21]. For the manganese, the results gotten to the level of the different ports are comparable with the exception of those of the port of fishing of Skikda where the concentration is well lower compared at the other Algerian ports. For the nickel, not having results that can allow us to establish a comparison, we can only note that the observed values remain lower to the Algerian recommendations. For iron, he/it is given us to note that the concentrations observed to the ports of Skikda are raised compared considerably to those observed for the port of Annaba [18].

Table 3: Comparative table of the results gotten with those of various Algerian ports

Metals (mg/kg) / Ports	Hg	Cr	Cu	Pb	Zn	Cd	Mn	Ni	Fe	References
Skikda (Mixed port)	0.92	67.89	59.64	118.73	166.51	<10	-	-	-	[25]
Skikda (Port of fishing)	1.23	48.31	40.62	125.59	73.51	<10	-	-	-	
Mostaganem port	-	-	47.66	-	142.96	-	219.43	-	-	[21]
Annaba port	-	-	116.77	-	427.60	-	279.38	-	-	
Annaba port	-	295.00	208.00	-	401.00	-	203,78	-	1548.0	[18]
Skikda (Mixed port)	0.91	63.47	58.66	129.60	175.87	0	260.50	40	16846.5	[26]
Skikda (New port)	2.01	44.25	18.00	36.50	62.25	1.5	236.50	38	16457.5	
Skikda (Port of fishing)	1.07	38.33	45.00	145.00	85.00	0	115.00	35	14935.5	
Dutch norms (Limite A)	**0.3**	**100**	**36**	**85**	**140**	**0.8**	-	-	-	[27et 28]
Algerian Recommandations	**1.5**	**250**	**150**	**250**	**500**	**3**	-	**75**	-	[29]

CONCLUSION

The assessment of the pollution of the inshore zone of the region of Skikda; with the help of spatial withdrawals of marine sediment samples; Notably, by the analysis of the contents made of heavy metals of the superficial sediment permitted us to establish a preliminary diagnosis of the state of health of the inshore ecosystem. Thus, the sites the more contaminated by the heavy metals are the three ports of Skikda and the indication of contamination for the copper, zinc and the manganese indicates an absence of pollution by these metals (according to the French norms). Struggle against the risks of pollutions is of a fundamental importance in order to minimize the negative impacts already on an economy fragile and on the inshore and marine ecosystems. Considered as the key space of the totality of the national territory, the coastline summarizes the problematic of environment, the planning and the lasting development; the civilization lives a race of speed henceforth with its marine environment. What is in game, it is

notably; to preserve a coastline and an ecosystem fragile and that, by the constant research of a just balance and the man's deep rehabilitation as actor and recipient of the effects who are waited for some.

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