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Contribution to reassess the health of Agadir Bay after the installation of the wastewater treatment plant : evaluation of metallic contamination

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Abstract
Agadir Bay plays a vital role in the socio-economic life of the region Sous Massa Draa (tourism and fishing). However, this ecosystem knows environmental constraints associated with various human activities (wastewater discharges, ports, etc.). Therefore, the ecosystem has been during the past two decades, the subject of much research relating to its health: Physical Chemistry, Hydrocarbons, Eco-toxicology, Biomarkers, Phytoplankton, Phytotoxicology, Microbiology and Zooplankton. The present study concerning the trace metals in the bay of Agadir, consolidates the hypothesis of the role of upwelling in the enrichment of the coastal ecosystem by cadmium, in addition to contributions related to wastewater. However, the relative decline in metal concentrations observed in this study compared to previous studies in the same ecosystem, suggests that the contribution of wastewater from this contamination has decreased. This is probably related to the installation and initial operation of the treatment station wastewater since 2002, whose main consequence is the cessation of discharges of wastewater into the marine environment. It was followed by an improvement in the quality of the coastal environment in the Bay.

Keywords : Sea water, wastewater, Water treatment, metallic contamination, Agadir Bay

1. Introduction

Agadir Bay plays a vital role in the socio-economic life of the region Sous Massa Draa (tourism and fishing). However, this ecosystem knows environmental constraints associated with various human activities (wastewater discharges, ports, etc.). Therefore, the ecosystem has been during the past two decades, the subject of much research relating to its health: Physical Chemistry [1], Hydrocarbons [2], Eco-toxicology [3], Biomarkers [4-6], Phytoplankton [7], Phytotoxicology, Microbiology [8] and Zooplankton.
However, heavy metals do not have the place they deserve in these studies. Besides, first investigations on these pollutants, showed the presence of important concentrations of these metals, including cadmium [9]. These authors attribute these results, in the absence of generating anthropogenic sources of this element, at upwelling phenomenon rife in the region; not discard the hypothesis of an origin related to wastewater discharges.
This work has verified (reassess) the assumptions made in previous work in three trace metals during two annual cycles in three different representative sites of Agadir Bay. This work will also evaluate potential improvements in environmental quality in the Bay as a result of the establishment in the early 2000s, of a treatment plant wastewater in parallel with the development of the Bay and the cessation of discharges.

2. Materials and Methods

2.1. Study Sites

To assess the metal contamination of the Bay of Agadir, three representative ecosystem sites were selected. These sites have large biological resources that are being exploited by the local population. This is (Fig. 1):
- Tamri: Site located 55 km north of the city of Agadir. It is characterized by natural tracts of mollusks (Patella vulgata, Littorina littorea, Murex brandaris, Perna perna and Mytilus galoprovincialis) and an important tourist activity.
- Cap Ghir: Site located about 45 km north of Agadir, it is characterized by malacological tracts similar to the first site and it is known by the ascent of cold water rich in minerals under the effect of upwelling. The site has been the subject of several previous studies on the environmental side [10, 4, 1, 5, 7].

- Tifnit: Site located 52 km south of the city of Agadir, on the limestone cliffs overlooking a large rocky platform housing many molluscan tracts.

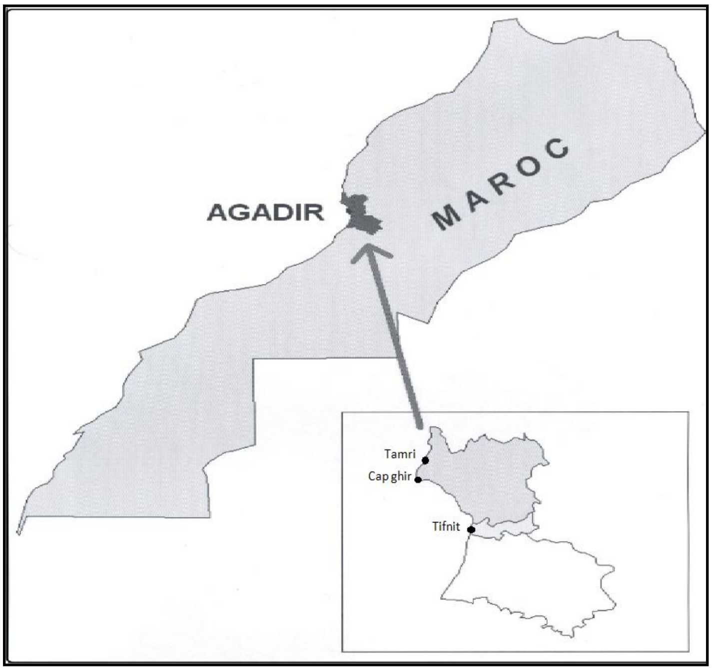

Figure 1: Map locating the Bay and showing the 3 sites

2.2. Biological material

Assessment of metal contamination in the three representative sites of the Bay of Agadir focused on an abundant species along the coast of the Region; it is the Perna perna mussel.

The choice of this mollusk is motivated by the fact that it fully meets the criteria for a good bioindicator; particularly the mold is sedentary, easy to collect and accumulate metals.

Moreover, it is for these reasons that it has often been used as sentinel species in such studies, particularly in the Mussel Watch. In addition, this species is characteristic of the Atlantic coast of southern Morocco.

It is also clear that this species has been the subject of previous eco-toxicological studies in the region, allowing the comparison of our results relatively to these studies as well as those carried out in other regions.

2.3. Dosage of metal elements

2.3.1. Sampling and laboratory processing

Biological samples consist of sampling batches of 50 individuals from the mold (medium size ~40 mm) made at low tide in the intertidal zones of the study sites. The animal samples are cleaned and free of any impurities and then they are placed in cooler containing seawater from sampling site. In the laboratory, the animals are kept in confinement for 48 hours to remove the contents of the digestive tract. Then the animals are frozen at - 30 ° C until they are used for the mineralization step. The thawing is carried out in the open air and then the samples were lyophilized and ground with a porcelain mortar until getting a fine powder.

2.3.2. Molluscs mineralization

Aliquots of 200 mg of solids are placed in polyethylene pipes to which 4 ml of pure nitric acid of analytical grade is added. They are then allowed to stand overnight at room temperature. After that they are placed in a heating block at a temperature of 90 ° C for 3h. After the tubes cooled, freshly deionized water is added (MilliQ water) to get a final volume of 50 ml. The solutions thus obtained are are ready to be analyzed.

2.3.3. Quality Control

To ensure the quality of the mineralization protocol analysis 3 whites containing the same amounts and quality of acid and water are prepared in each analysis series. They undergo the same treatment as the samples. These whites used to detect any contamination during mineralization by controlling the absorbance; they are also used for the dilution of samples and used for the standard range of metal solutions.

To ensure the quality of analysis, standard samples with certified concentration of the element are used. This is a sample of mold which reference is CRM 278R (bcr2) from Brussels Belgium. The results of quality control are shown in table 1.

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Table 1: Performance of the quality control analysis of biota

	CRM 278R		
	Detection limit	**Value measured**	**Value certified**
Cd (µg g^{-1})	0.02	0.36 ± 0.02	0.348 ± 0.007
Pb (µg g^{-1})	0.2	2.0 ± 0.1	2.00 ± 0.04
Hg (µg g^{-1})	-	-	0.196 ± 0.009

2.4. Assays of metallic elements

Analysis of Cd and Pb were performed by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS, Thermo Electron, X series). The Hg was analyzed by atomic absorption spectrometry using hydride system (Varian, AA800 model).

Expression of results

The results of the metal contents in the samples and in the certified standards are expressed in ppm according to the following formula:

$$Ce = \frac{(Cm - Cb) \times FD \times V}{P}$$

Ce: Sample concentration in mg/g fresh weight
Cm: Mineralisate concentration (mg/l)
Cb: Concentration white (mg/l)
FD: Dilution Factor of the mineralisate
V: Final volume (ml)
P: Weight of sample (mg)

3. Results and discussions

Metallic concentrations, expressed as an average value for each season of the two-year study is presented in table 2 as a function of metal, season and site.

Table 2: Concentration standardized, expressed as medium value with standard deviation (SD) for each season of the two years of study, in the mold Perna perna collected seasonally in three sites in the Bay of Agadir (Tamri, Cap-Ghir and Tifnit)

Metal/Season		*Site*					
		Tamri		*Cap Ghir*		*Tifnit*	
		2006	*2007*	*2006*	*2007*	*2006*	*2007*
Cd	Summer	0,31	0,22	0,41	0,42	0,27	0,28
	Autumn	0,39	0,22	0,46	0,17	0,38	0,30
	Winter	0,20	0,31	0,13	0,37	0,15	0,29
	Spring	0,25	0,39	0,36	1,00	0,13	0,85
	Medium±SD	***0,288±0,082***	***0,285±0,082***	***0,34±0,146***	***0,49±0,357***	***0,2325±0,112***	***0,43±0,28***
Hg	Summer	0.01	0,03	0.01	0,04	0.01	0,02
	Autumn	0,02	0,115	0,02	0,078	0,02	0,092
	Winter	0.02	0,02	0.02	0,02	0.02	0,02
	Spring	0,01	0,03	0,02	0,03	0,01	0,02
	Medium±SD	***0.015±0,006***	***0,049±0,044***	***0,018±0,005***	***0,042±0,025***	***0.015±0,006***	***0,038±0,036***
Pb	Summer	0,62	0,28	0,36	0,21	0,24	0,18
	Autumn	0,27	0,32	0,54	0,37	0,22	0,24
	Winter	0,15	1,28	0,16	0,28	0,09	0,23
	Spring	0,49	0,01	0,64	0,03	0,42	0,04
	Medium±SD	***0,383±0,212***	***0,473±0,556***	***0,425±0,211***	***0,223±0,144***	***0,283±0,136***	***0,173±0,092***

Reading results, shows variations between sites, seasons and the metals studied. generally metals (Cd, Pb, and Hg) have similar tendencies, as regards seasonal variations. Moreover, for all three elements, winter and spring concentrations seem higher than those observed in summer and autumn.

In the case of Cd, it seems clear that these levels are higher in Cap-Ghir, especially during the spring. Indeed, in spring of 2007, the contents of this metal are high (max 1.28 ppm) and exceed the accepted standard (consumption) which is 1ppm since 2006. The results for Cd in the shellfish from this site may be explained by the high levels of mercury in seawater. Enrichment of the latter by certain metals, including Cd resulting from upwelling (Upwelling-related phenomenon), which is intense in Cap-Ghir. The same explanation was also suggested by other study, which showed high levels of Cd, Cu and Zn in the coastal waters off California. They attributed these levels to lift deepwater rich in nutrients in this area also known by the upwelling. The same trend concerning Cd, Fe and Zn was also reported by Romeo and Gnassia-Barelli [11] on the Mauritanian coast, area of the same phenomenon.

Moukrim and al. [12], conducting a study on the contamination of two sites in the Bay of Agadir, recorded, against all odds , the reference site (Cap Ghir, away from any source of contamination) denotes concentrations of Cd, larger than those found on the site-industrial Anza (receiving discharges). They also concluded that there is the possibility of the influence of upwelling at Cap-Ghir as the Anza site is relatively sheltered. It should also be noted that the values revealed by these authors seem similar than those we obtained. Otherwise, comparison of metal levels between the three study sites also shows that the levels of Pb recorded higher values in Tamri. This result is probably related to the availability of the metal in this site, located just south of an estuary that receives large amounts of wastewater, in addition to the significant effect of road traffic noted in the site.

In addition to the intervention of upwelling, intense spring, seasonal variations of metal levels may also be related to other factors such as metal speciation in water and sediments, characteristic hydro-chemical fluctuations of ecosystem (pH, salinity, suspended solids, ...), variations of the biological activity associated with an increase in phytoplankton food availability resulting from higher temperatures and longer days in spring and changes of the biological status (fluctuation of the fabric weight , metabolism, sexual maturity...). Thus, the development period of the sexual maturity of gonads leads to increased weight, which causes dilution of the metal in the body. According to Id-halla and al. (1997), gonad maturity Moulds P. perna occurs in summer. This may explain the low values found during this season. However, the release of genital products (containing little metal) leads to a reduction of weight and as result a reconcentration of metal in the body.

Moreover, comparing the results of this study with those obtained in other region of Morocco shows that our results are in agreement with those of A. Banaoui [9] and Cheggour M. [13], which show, in general, that the Bay of Agadir is little contaminated area compared to Northern Ecosystem Centre (between El Jadida and Essaouira), which is influenced by the wastewater discharges from phosphate processing industries located there, and the concentration of Cd, for example, may be about 17.39 mg/g. Kaïmoussi and al. [14] reported similar results in Mytilus galloprovincialis in the same geographical area. However, everywhere else the results are similar to those obtained in this study, with the exception of Cd, the high levels would be attributable to the phenomenon Upwelling.

According to Cheggour M. [13], analysis of metal concentrations in the tissues of the Mediterranean mussel M. galloprovincialis, along the Atlantic coast of Morocco, shows a clear contamination of this species, especially along the coast stations in major urban and industrial centers, including Mohammedia-Casablanca and Kenitra-Mehdiya. Molds of Jorf Lasfar and Safi, where an industrial chemical pollution is chronic , due to complex processing phophates predominates, are much more loaded Cu and Cd. In the relatively remote locations of pollution sources are fortunately "little influenced" by the flow of pollutants.

Concerning the bioaccumulation of Pb, our results remain low compared to those of the Region of Casablanca, in the North of Morocco. Indeed, as reported by Banaoui [9], who noted a sharp contamination by metal, in raison of the several industrial and domestic releases espace of this city which is the most industrialized and it has the largest fleet of cars in Morocco. Pb contamination is linked to the increased use of fuel, where the metal is used as an anti explosive additive. The same explanation was announced by Cheggour and al. [15, 16]. We recall that the use of this element in fuels has been banned in the U.S. since the 70s and in Europe since the late 80s, which explains the relatively low rates of bioaccumulation for this metal, as described in these countries.

Concerning the mercury, it has ben reported that concentrations element at three areas: two in the Atlantic, Casablanca/Mohammedia and El Jadida/Jorf Lasfar, and in the Mediterranean at the site of Martil. Maximum bioaccumulation in molluscs collected was recorded in the latter site (2.6 mg/g). The authors attributed this contamination to important and diversified industrial activities in the site of Martil.
Concerning the comparison of metal levels recorded in the Bay of Agadir relatively to other neighboring regions, it's appropriate to cite the works on the Mauritanian coast (West Africa) by Romeo and Gnassia-Barelli M. [11]. These authors recorded values of heavy metals rather than those we obtained (0.6 Cd in the Donax trunculus collected in the beach of Nouakchott).
In the study by Mzoughi and Shuba in 2012 [17] on heavy metals in north coast of Tunisia (Mediterranean Sea), concentrations of contaminants which are obtained in this study were compared to those obtained in the framework of the Network of harmful contaminants (RECNO) performed at different sites along the Mediterranean coast of Tunisia between 1996 and 2010 and they noted the same results.
It is deduced out of this study that recorded concentrations of heavy metals in these sites are generally higher compared to the averages for the Bay of Agadir and more particularly Cd. These authors explained these results by the effect of wastewater discharges.

Conclusion

The present study concerning the trace metals in the bay of Agadir, consolidates the hypothesis of the role of upwelling in the enrichment of the coastal ecosystem by cadmium, in addition to contributions related to wastewater. However, the relative decline in metal concentrations observed in this study compared to previous studies in the same ecosystem, suggests that the contribution of wastewater from this contamination has decreased. This is probably related to the installation and initial operation of the treatment station wastewater since 2002, whose main consequence is the cessation of discharges of wastewater into the marine environment. It was followed by an improvement in the quality of the coastal environment in the Bay.

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