Mercury pollution in beachrocks from the Arzew gulf (West of Algeria)

Pollution mercurielle des grès formés sur les plages du golf d'Arzew (Ouest Algérien)

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Abstract. The gulf or Arzew extends between the towns of Stidia and Mostaganem on the west coast of Algeria. The gulf receives the discharge of many industries. Mercury contamination level of beachrocks has been assessed through the determination of mercury concentration (Hg) in sandstones formed on the beach. The sandstone samples were collected along the coast, dried, ground and digested in order to be analyzed by atomic fluorescence spectrometry. The analyses showed the presence of mercury in beachrocks with an average geochemical index of 4.1 and high mercury concentrations up to 5.0 $\mu g.g^{-1}$, well above average in the Earth's crust. The geo-accumulation index revealed severe and intense mercury pollution due to anthropogenic activities. The high Hg concentration in beachrocks suggests that mercury accumulated and circulated freely in the gulf before lithification and cementation of beach sediment. This contamination may affect the coastal ecosystem and even human health via the food chain.

Keywords : Pollution, mercury, beachrock, geo-accumulation, Gulf of Arzew, Algeria.

Résumé. Le golfe d'Arzew s'étend entre les villes de Stidia et Mostaganem sur la côte ouest algérienne. Il reçoit la décharge de nombreuses industries. La présente étude démontre la détermination de la concentration en mercure (Hg) dans les grès formés sur la plage. Les échantillons de grès ont été prélevés dans 5 stations échelonnées sur une distance de 25 km environ le long de la côte. Séchés et broyés, ces échantillons sont analysés par spectrométrie de fluorescence atomique. Le mercure est piégé dans ces roches sédimentaires avec un indice géochimique moyen de 4,1 et des concentrations voisines de 5,0 $\mu g.g^{-1}$. Les valeurs dépassent largement la moyenne signalée dans la croûte terrestre. L'indice géo-accumulation révèle une pollution sévère et intense par le mercure due aux activités anthropiques. La forte concentration de mercure dans les "Beachrocks" admet que cet élément toxique s'accumule et circule librement dans le Golfe d'Arzew avant la lithification et la cimentation de sédiments de la plage. Cette contamination pourrait affecter les composantes biologiques de l'écosystème côtier et même la santé humaine via la chaîne alimentaire.

Mots-clés : Pollution, mercure, grès des plages, géo-accumulation, Golfe d'Arzew, Algérie.

INTRODUCTION

Industrial and urban activities in coastal areas introduce significant quantities of pollutants in the marine environment, causing permanent disruption of marine systems and therefore environmental and ecological degradation. Contamination of seawater by heavy metals is due to industrial effluents and land saturation by solid waste (Buccolieri *et al.* 2006; Satpathy *et al.* 2008). These metallic elements are usually found at low concentrations, in the order of ppm, but may pose a potential danger to the health and functioning of the ecosystem. This contamination may occur directly or indirectly by transfer phenomena in the trophic chain (Kannan *et al.* 1998; Benamar *et al.* 2010). The Gulf of Arzew is no exception to this form of pollution, which is a threat to public health.

The problems caused by mercury in both human health and the environment are well known and alarming. Hg presence in the marine environment has many sources, such as direct discharges from industry and individuals in aquatic streams, indirect discharges from the systems of wastewater treatment, mercury previously issued into the atmosphere, or surface runoff and leaching of soil and landfills (UNEP 2002). Coastal and estuarine sediments are considered as reservoirs or wells of many chemical pollutants, particularly heavy metals. Metal contamination of sediments is a danger for water, inhabiting species and human health (Förstner and Wittmann 1981; Boucheseiche *et al.* 2002). The concentrations of heavy metal pollution in coastal sediments are not considered as potential hazards in the coastal zone. The potential availability of heavy metal in the coastal environment is dependent on the metal accumulation and the binding strength with sedimentary phases (Marins *et al.* 1998).

MATERIAL AND METHODS

Brief description of the study area

On the west coast of Algeria, the intertidal zone extends about 20 km between the towns of Mostaganem and Stidia (Fig. 1). Many points of discharge of urban and industrial effluents are found along this coastal area. The gulf of Arzew is the place of discharge of the Cheliff wadi. The river is 795 km long and carries wastewater from many towns. This part of Mediterranean Sea is also characterised by an intense marine traffic and important fishing activities. Several works have demonstrated a high richness of the fishing resources and benthic communities (Kerfouf *et al.* 2007, Dermeche *et al.* 2009, Dermeche 2010, Grimes 2010).

Potential sources of mercury in the Gulf of Arzew

Chlorine production is among the human activities most associated to high mercury use (Sznopek & Goonan 2000). The chlorine industry situated in Mostaganem region is one of the main sources of mercury discharged in the marine environment. This industry uses electrolysis process with mercury cathode. Liquid effluents are directly discharged into the sea without treatment. Petroleum and natural gas processing also contribute significantly to mercury liberation into environment (U.S. EPA 2001). Arzew is the biggest North African oil and gas industry platform.

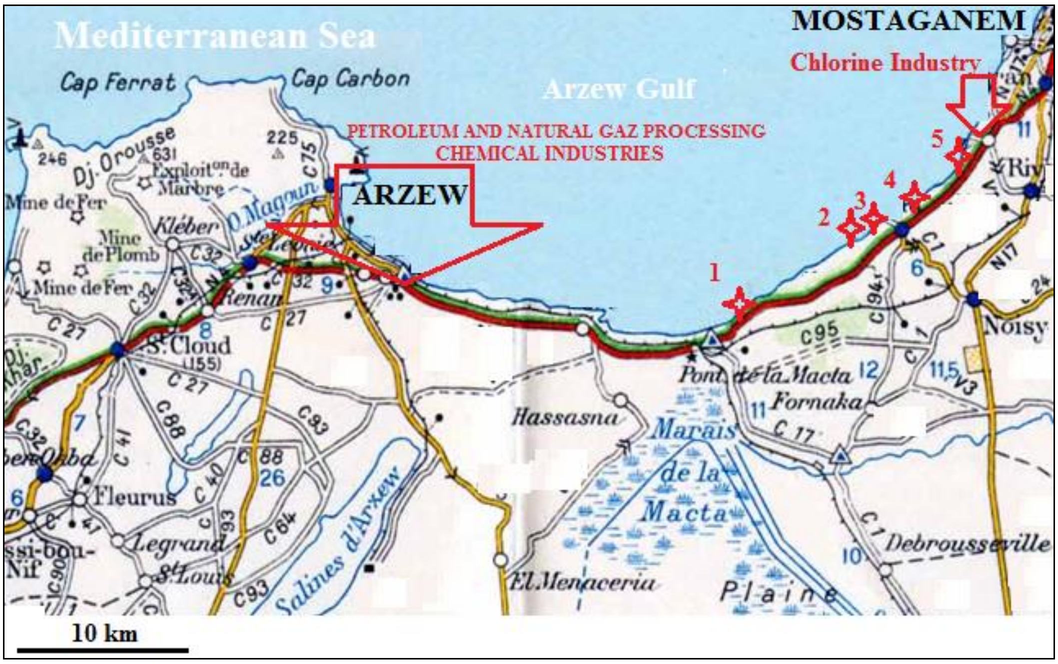

Figure 1. Location of the study area on the west coast of Algeria: Industrial complex and five sampling stations in Arzew Gulf.

Sampling and analyses

Beachrocks are found along the shore at different intervals (Fig. 1). Beachrock formation is infrequent and therefore difficult to find; this is due to the specificity of the intertidal zone in the Mediterranean Sea, which is shallow compared to the Atlantic Ocean intertidal zone. Beachrock samples were collected as available in five different points along the intertidal zone (GPS coordinates of sampling sites are provided in Table 2). The sample number 5 was collected near the discharge of the chlorine industry.

Beachrock samples were dried under sunlight for one day and transferred to the laboratory. They were crushed using agate pestle and mortar before further analytical procedures (Sahyam 2010). According to metal analyses standards, samples were subjected to a pretreatment for determination by ICP-MS. Before analysis, samples were prepared in order to obtain a subsample homogeneous enough to be representative of the main sample. The sample was dried in an oven at 40ºC for 16 hours. The sample was then smashed before being passed through a sieve of 2 mm and the fraction below 2 mm was then ground to a granulation powder smaller than 250 µm. The mineralization was performed on 0.5 g of this powder with 6 ml of hydrochloric acid and 2 ml of nitric acid (aqua regia). This step was done at 950ºC for 75 min on a heating block; the mineral deposit was then adjusted to 50 ml. An appropriate dilution was then performed before analysis. The mercury analysis was made according to the standard ISO 16772-NA. The percentages of SiO_2, Al_2O_3 and $CaCO_3$ were also determined. Concerning the overall analyses, they were performed using five replicates for mercury and duplicates for SiO_2, Al_2O_3 and $CaCO_3$. The detection limit of the analytic method for mercury is at least µg.g^{-1}.

To assess the degree of pollution and measure human impact, the Müller geo-accumulation index (Müller 1981) was used. This index determines the level of metal pollution (Tab. 1) and is quantified from the basic level of metal content in the sediment using the following equation :

$$I\text{geo} = \text{Log}_2\,(C_n/1.5\,B_n)$$

With :$\mathbf{C_n}$: concentration of metal in the sediment sample and $\mathbf{B_n}$: average concentration of the metal in earth crust.

Table 1. Classification of the pollution degree using the Müller geo-accumulation index

Class	I_{geo}	Pollution degree
0	Igeo ≤ 0	unpolluted
1	0 < Igeo < 1	unpolluted to moderately polluted
2	1 < Igeo < 2	moderately polluted
3	2 < Igeo < 3	moderately to strongly polluted
4	3 < Igeo < 4	strongly polluted
5	4 < Igeo < 5	strongly to very strongly polluted
6	5 < Igeo	very strongly polluted.

RESULTS AND DISCUSSION

Geochemistry

Beachrocks of the Arzew Gulf are a heterogeneous mixture of organic and inorganic matter, mainly composed of quartz sand, heavy minerals, biogenic carbonates such as shell fragments. Table 2 shows the analyses results.

The concentration of SiO_2 ranged from 3.5% to 57.7%, with an average concentration of 22.8%. The high percentage of SiO_2 in the beachrock is due to free quartz and sand rich sediments. The concentration of Al_2O_3 ranged from 1.2% to 17.1% with an average concentration of 7.4%. The high percentage of Al_2O_3 in beachrocks is due to strong diurnal winds and seasonal inflow of rivers. The concentration of $CaCO_3$ ranged from 21.5% to 87.1%, with an average concentration of 61.1%. The low concentration of $CaCO_3$ in these samples is due to high wave energy and low availability of limestone sediments and shell fragments. The concentration of mercury ranged from 1.1 $\mu g.g^{-1}$ to 5.0 $\mu g.g^{-1}$, with an average concentration of 2.4 $\mu g.g^{-1}$. These mercury concentrations in beachrock samples are high compared to the mean value of mercury in the Earth's crust which is 0.08 $\mu g.g^{-1}$ (Taylor 1964). According to Clark (1994), the source of Hg in the beachrock is atmospheric deposition and industrial discharge. The high concentration of Hg (5.0 $\mu g.g^{-1}$) in the sample number 5 is due to its proximity to the discharge point of the chlorine industry.

Table 2. Beachrocks analyses results

Samples	Longitude	Latitude	SiO_2 (%)	Al_2O_3 (%)	$CaCO_3$ (%)	Hg ($\mu g.g^{-1}$)
1	00°01.136' W	35°49.806' N	3.50 $_{\pm 0.02}$	1.15 $_{\pm 0.01}$	83.04 $_{\pm 0.01}$	1.16 $_{\pm 0.03}$
2	00°01.979' E	35°52.195' N	44.98 $_{\pm 0.01}$	17.12 $_{\pm 0.01}$	31.02 $_{\pm 0.01}$	1.13 $_{\pm 0.02}$
3	00°02.072' E	35°52.324' N	57.71 $_{\pm 0.01}$	16.73 $_{\pm 0.01}$	21.53 $_{\pm 0.01}$	2.39 $_{\pm 0.02}$
4	00°02.670' E	35°53.292' N	4.25 $_{\pm 0.01}$	0.96 $_{\pm 0.01}$	82.85 $_{\pm 0.01}$	2.11 $_{\pm 0.01}$
5	00°03.138' E	35°54.415' N	3.42 $_{\pm 0.01}$	1.09 $_{\pm 0.01}$	87.13 $_{\pm 0.01}$	5.01 $_{\pm 0.02}$
Mean ± SD			22.77 $_{\pm 0.01}$	7.41 $_{\pm 0.01}$	61.11 $_{0.01}$	2.36 $_{\pm 0.02}$
Mean $I_{geo \pm SD}$						4.08 $_{\pm 2.70}$

The concentration of this trace element in the analyzed samples is higher than that determined in sediments from other coastal regions in the world and higher than the ecotoxicological assessment criteria proposed by OSPAR (2008) (Tab. 3). It should be noted that sediments analyzed in Taranto gulf came from the sea, whereas the present samples were collected in the intertidal zone. Hard plastic debris were also found among the samples, which explains recent Beachrock formation.

Table 3. Comparison of mercury concentrations in sediments from different regions with lower and upper Ecotoxicological Assessement Criteria (EAC) from OSPAR.

Area	Mean Hg ($\mu g.g^{-1}$)		References
This study	2.36		—
Mean crust	0.08		Taylor (1964)
Southern California Bight	0.05		Schi & Weisberg (1999)
Gulf of Mannar, India	0.17		Sahayam *et al* (2010)
Taranto Gulf	0.12		Buccolieri *et al* (2006)
Background concentrations in sediment	Lower EAC 0.05	Upper EAC 0.5	OSPAR (2008)

Assessment of the pollution level by the Müller index

The average geo-accumulation index calculated for Beachrocks analyzed (Tab. 1) indicates that the pollution of the samples belongs to the class 5 (severely polluted) according to the classification of Müller. This pollution degree shows that mercury was abundant in the intertidal zone during the formation of these Beachrocks and therefore also abundant in coastal waters. This high accumulation of mercury in Beachrocks is a direct consequence of local events, such as industrial and municipal discharges and riverine inputs, but is also due to the conditions of Beachrock formation and climatic conditions. The movement of surface waters is among of the reasons for coastal water pollution in the study area. The water recirculation in the Mediterranean can carry mercury released in other coasts. Oceanic waters may also contain mercury due to the transcontinental and global transport of mercury (Fig. 2). The water circulation in the Mediterranean basin also allows regional and even global dispersion of pollution (Millot & Taupier-Letag 2005). The gulf of Arzew is less than 300 nautical miles far from the Strait of Gibraltar and the Atlantic Ocean. The Algerian marine current is one of the most energetic flows in the Mediterranean basin. One branch of this current reaches the coast and return to the west direction (Fig. 2). According to Salas *et al* (2001), this marine current is formed by a series of mesoscale eddies at different scales. Statistical analyses of 15 surface buoys tracks provided a complete Lagrangian view of the Algerian current. The buoys, released upstream and across a coastal meander between 0°E and 1°E longitude, were followed for three months. They travelled eastward at an average speed of 14 cm.s-1 and showed high energetic fluctuations related to several mesoscale eddies. For the zonal component, these are about four days and 66 km, and for the meridional component, about two days and 26 km (Sals *et al*. 2001). This marine surface current is the main factor of dispersion of pollutants to other coastal areas in western Algeria.

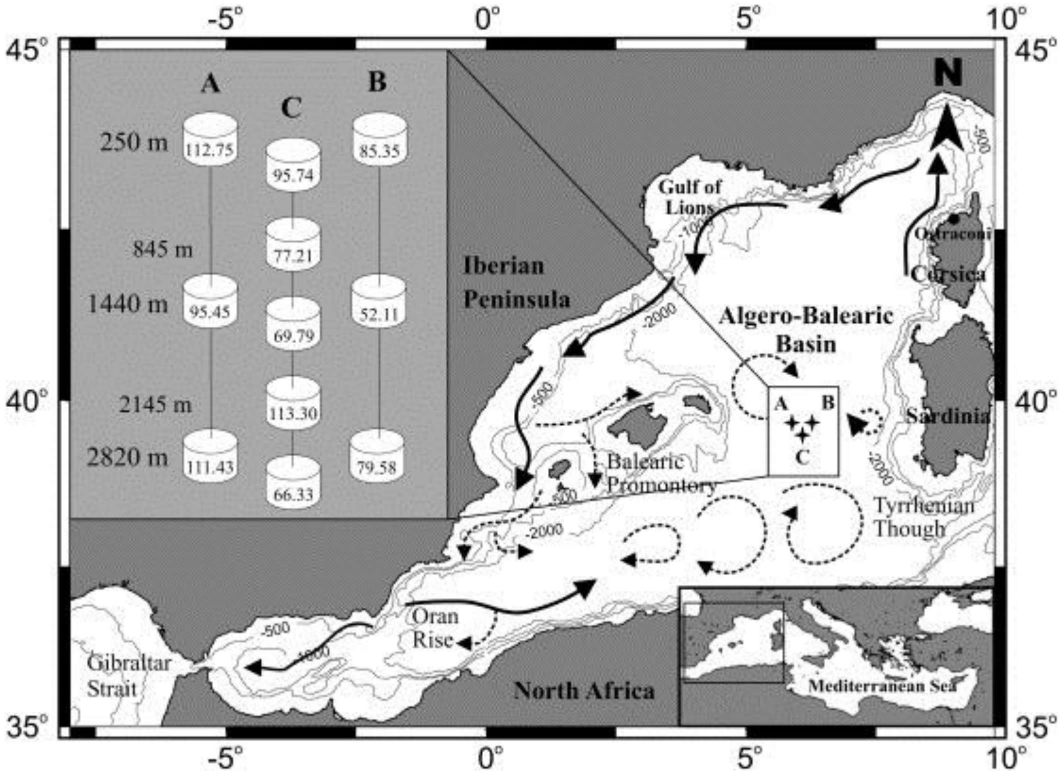

Figure 2. Surface water circulation in the western Mediterranean Sea (Zúñiga *et al.* 2007)

CONCLUSION

This study highlighted mercury Beachrock pollution. The concentration of mercury in Beachrocks is much higher compared to that in the Earth's crust or to that found in Beachrocks in other parts of the world. The geo-accumulation index revealed severe mercury pollution due to anthropogenic activities. The high concentration of mercury accumulated in Beachrocks suggests that seawater was strongly and continuously polluted during lithification and cementation.

A significant health threat and environmental risk was revealed in this study. A proper treatment of industrial efluents and urban waste before rejection in the rivers and sea is required, in order to preserve the environment and protect human health.

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