

Bio-monitoring of Trace Mercury Using Seabirds' Dejections from Arzew Gulf: A Potential Risk for Human Health

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Abstract Pollution of the environment can be determined by means of biological methods with the help of bioindicators-organisms which give information on the quality vance of their environment. In the present study the first trace mercury bio-monitoring using seabirds' dejections is investigated in the Arzew gulf. Excrements analysis from ten stations using ICP-MS shows high level (Hg) contamination up to $2.27 \pm 0.05 \mu\text{g}\cdot\text{g}^{-1}$. Dejections' contamination is due to mercury bioaccumulation via web food owing to the presence of this contaminant in coastal area coming from anthropogenic activities. Potential transfer of mercury to human causing health damage is very likely because of population fisheries consumption. Urgent measures must be taken to remedy this pollution aspect and prevent human health.

Keywords: mercury, bio-monitoring, seabirds, fecal matter, chain food, Arzew gulf, coastal pollution

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1. 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 [1,2]. 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 [3,4].

Heavy metals tend to accumulate in advanced organisms through bio-magnification effects in the food chain. Thus they can enter into human body, and accumulate in the human tissues to pose chronic toxicity (Figure 1). Chronic assimilation of heavy metals is known cause of cancer [5] and can damage vital organ functions. Accumulation of heavy metals in the food web can occur either by accumulation from the surrounding medium, such as water or sediment, or by bioaccumulation from the food source [6]. According to Syed Lal Shah and Ahmet Altindag [7] heavy metals may affect organisms directly or indirectly by transferring to the next tropic level of the food chain. The most serious results of their persistence are biological amplification through the food chain. In the aquatic environment, heavy metals in dissolved form are easily taken up by aquatic organisms where they are

strongly bound with sulfhydryl groups of proteins and accumulate in their tissues [8].

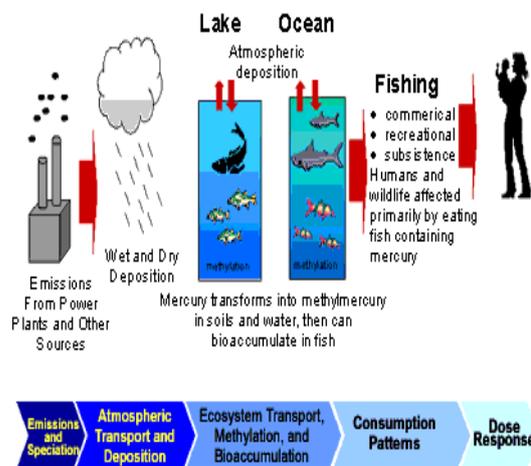


Figure 1. Mercury in the environment (US EPA)

The accumulation of heavy metals in the tissues of organisms can result in chronic illness and cause potential damage to the population. Mercury (Hg) is a highly toxic heavy metal, widely occurring in the Mediterranean environment due to both natural emissions such as volcanoes, fumaroles, solfataras and geological anomalies, and anthropogenic sources from industry and waste incineration. In fact, Hg concentrations in various seabirds, fish and shellfish have been found to be higher in the Mediterranean than in Atlantic areas. In the Mediterranean in particular, Hg deposition is greatly affected by air mass

transportation of particulate and elemental Hg from northern and northeastern Europe. Wet deposition is the most efficient removal pathway for atmospheric Hg, and is predicted to occur in the highest levels over mountainous areas such those in northern Greece, as expected, due to the higher precipitation usually occurring there [9]. Mercury is a special concern in marine ecosystems, where methylation occurs during the process of biotransformation and accumulates in biota [10,11].

Bio-concentration, bioaccumulation and biomagnifications of chemical material in oceanic biota are active processes that depend on chemical characteristics, environmental factors (salinity and temperature), trophic level, concentration of fat, metabolism and bioavailability (entry and transfer of contaminants) [12]. There have been numerous studies dedicated to the study of mercury toxicity. Table 1 shows a few below for the better understanding towards mercury toxicity.

Table 1. Effect of low dose mercury toxicity on various organ systems

System	Troubles	Reference
Nervous system Adults	Memory loss, including Alzheimer like dementia, deficit in attention, hypoesthesia, ataxia, dysarthria, subclinical finger tremor impairment of hearing and vision, sensory disturbances, increased fatigue	[13]
Nervous system Children/infants	Deficit in language (late talking) and memory deficit in attention, Autism	[13]
Motor system Adults	Disruption of fine motor function, decreased muscular strength, increased tiredness	[13]
Motor system Children/infants	Late walking	[13]
Renal system	Increases plasma creatinine level	[13]
Cardiovascular system	Alters normal cardiovascular homeostasis	[13]
Immune system	Decreases overall immunity of the body, exacerbates lupus like autoimmunity, multiple sclerosis, autoimmune thyroiditis or atopic eczema	[13]
Reproductive system	Decreases rate of fertility in both males and females, birth of abnormal offsprings	[13]

Monitoring the coastal environment has arisen from the need to protect human health and living marine resources. The simplest solution proposed to date has been to measure and compare the concentration levels of pollutants in space and time and, from the data collected, to identify natural and anthropogenic contamination levels and pinpoint variations. This means of assessing contamination has been widely used for metals in the different compartments of the coastal environment [14].

Bio-monitoring is essential for evaluating the environmental influence of contamination. Several global bio-monitoring programs have been carried out, including United Nations Environment Programme (UNEP) for global monitoring of persistent toxic substances (PTS) and of persistent organic pollutants (POPs). Effective bio-monitors are those with low-cost, ease of sampling, and showing a good correlation with environmental quality change of ecosystems [15].

Various metal-accumulating biomaterials, such as plants, non-parasite organisms (lichens, mosses, algae) and animal tissues and organs (feathers, livers, kidneys, bones) have been used as environmental bio-monitors. Mollusks, especially mussels and oysters, were found promising for monitoring the change of heavy metal contamination in aquatic systems. Using living organism tissues as environmental bio-indicators oftentimes can be limited because of the constraint by different national or international regulations for wildlife protection. In addition, many living organisms are generally difficult to provide a continuous historical record of contamination in an ecosystem. Analysis of trace mercury in fecal matter is a promising way for use of feces as bio-indicator in order to assess contamination and prevent risk that occur human health [15,16].

At present, a significant portion of global diet consists of foods of aquatic origin, either fresh or processed and from fresh or salt water. This consumption has had a positive economic impact on commercial fishing as the

associated food processing industries, and each year a wide variety of manufactured seafood products are launched on the market [17]. Monitoring mercury contamination through the food chain is becoming more and more necessary.

In our study we analyze total mercury (Hg) concentration in dejections of seabirds from *Arzew* gulf to assess level contamination and show potential risk that occur human by consumption of fish from this gulf.

2. Sampling and Analysis Method

2.1. Description of the Study Area

The *Arzew* gulf (Figure 2) is one of the major units of the continental Algerian West shelf. It is between the *Arzew* massif (Carbon cape, 0° 20'W) at the West and the *Cheliff* Delta at the East (Ivi cape, 0° 20'W), which gives a longitudinal development on about 50 km. Two rivers of very unequal importance feed the gulf, the middle *Cheliff* at East and the minor *Macla* at the West [18].

2.2. Sources of Mercury in the Gulf of Arzew

Chlorine production is among the human activities most associated to high mercury use. 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. *Arzew* is the biggest North African oil and gas industry platform [19].

2.3. Sampling

The *Arzew* gulf was chosen to perform this study because of its geographical and demographic importance

(important wetlands for migratory birds, more than 2.5 million habitants). It is the receptacle of pollution from several industries including chlorine industry which rejects mercury in the environment. A previous study showed high mercury in surface sediments [19], the presence of this chemical element in sediments led us to explore its presence in living organisms using seabirds' dejections knowing the lack of studies on mortality of marine birds in Algeria [20].

The number of considered sampling points depends essentially on the result of prospection according to the same species seabirds gathering, it depends also on sampler accessibility to sites allowing a fluent course with reduced carbon footprint knowing that the collection was done each two days during four months from distanced and scattered places along the *Arzew* gulf (50 km).

Ten sampling sites were chosen and birds were recognized generally as Mediterranean gulls during all sampling period. Figure 2 shows also sampling sites. Fresh excrements were collected between March and June 2013 in each sampling site using stainless steel knife removing any strange matter. The collected samples were stored in polythene bags and frozen prior to sample

preparation for chemical analysis. According to Yin [15] "fresh" excrements mean that it's produced by seabirds or in the past couple of days.

2.4. Total Mercury (Hg) Analysis

For each station a homogeneous sample has been constituted in order to be analyzed. Samples were dried under sunlight. They were crushed using agate pestle and mortar before further analytical procedures. According to metal analysis 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 40° C for 16 hours. The sample was then smashed to obtain a fine powder. 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 950° C 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.

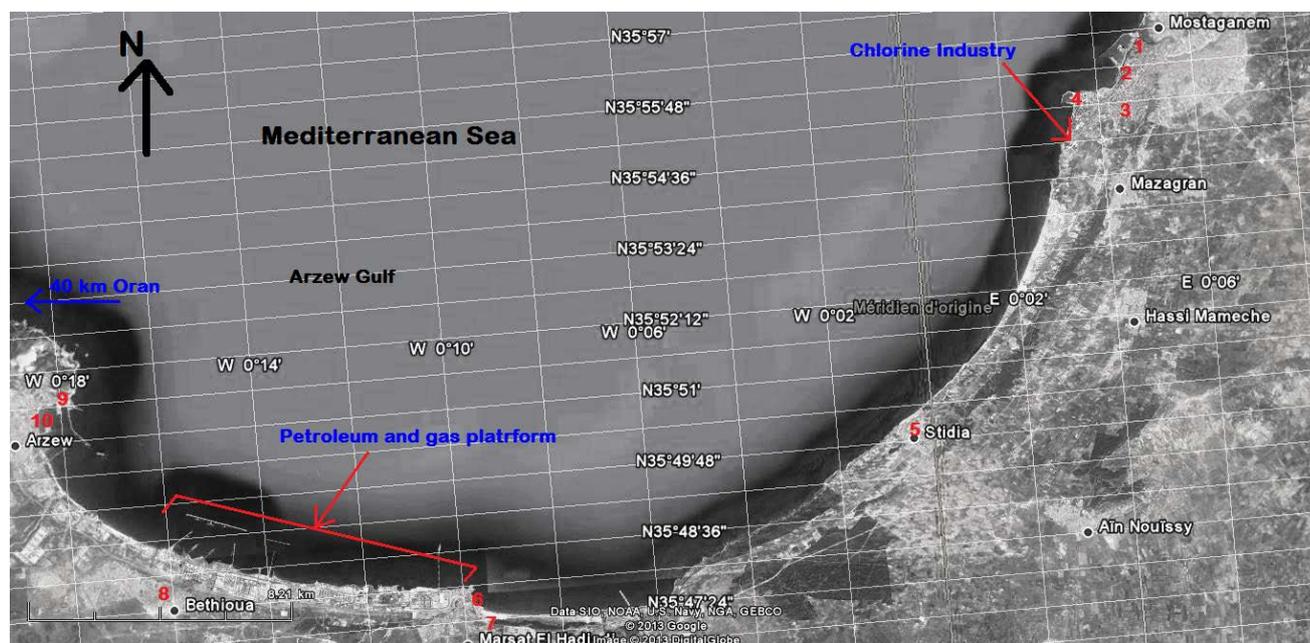


Figure 2. Geographic position of sampling sites and important mercury sources in Arzew gulf

Table 2. Total mercury concentration in seabirds' excrements from Arzew gulf

Position sampling	01	02	03	04	05	06	07	08	09	10
Total mercury concentration (Hg) ($\mu\text{g}\cdot\text{g}^{-1}$)	1.14 ± 0.04	2.01 ± 0.04	1.88 ± 0.04	2.27 ± 0.05	1.92 ± 0.05	0.87 ± 0.7	0.08 ± 0.02	1.01 ± 0.03	1.61 ± 0.03	1.43 ± 0.03

3. Results and Discussion

Fecal analysis shows presence of mercury in seabirds' dejections. Figure 3 and Table 2 show total mercury concentration in samples collected from chosen sites in Arzew gulf. The highest concentration was found in station number 04 (2.27 ± 0.05) and the lowest one in station number 07 (0.08 ± 0.02). Relying on previous study [16], mercury exists and freely circulates in coastal water of Arzew gulf. Presence of mercury in seabirds'

dejections can be due to two factors; first one is chain web; seabirds are omnivorous and their diet is based mostly on fish which can accumulate mercury. The second factor is inhalation via air because chlorine industry presence in Mostaganem region which uses electrolysis process and releases mercury in atmosphere. Sample number 07 gives the lowest mercury concentration; this is can be due to seabirds' difference diet compared to other sampling sites, and also presence of other migrant seabirds. Table 3 shows mercury concentrations in excrement and seabirds from other regions over the world. It is important to mention that studies on mercury presence in fecal matter

are uncommon. Even if mercury concentrations in seabirds' excrement from *Arzew* gulf are lower than mean mercury presence in penguins dejections from Antarctic,

our results are preoccupant because of economic and demographic context of the region.

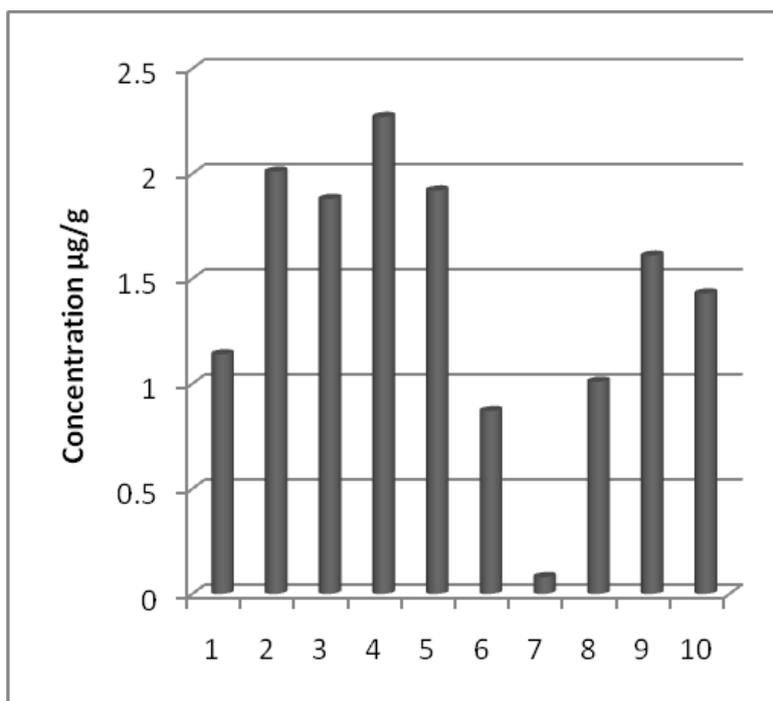


Figure 3. (Hg) concentration in seabirds' dejections

Table 3. Mercury concentration in seabirds excrements

Mercury presence	Region	Concentration	References
Penguins excrements	Antartic Peninsula (O'Higgins)	7.55 ± 1.28 ($\mu\text{g}\cdot\text{g}^{-1}$)	[21]
Penguins excrements	Antartic Peninsula (Videla)	0.75 ± 0.84 ($\mu\text{g}\cdot\text{g}^{-1}$)	[21]
King penguins excrements	Antartic (Zhongshan station)	$200 < \text{Hg} < 400$ ($\text{ng}\cdot\text{g}^{-1}$)	[15]
Adelie penguins excrements	Antartic (Zhongshan station)	$100 < \text{Hg} < 200$ ($\text{ng}\cdot\text{g}^{-1}$)	[15]
Arctic gulls excrements	Arctic	$\text{Hg} < 100$ ($\text{ng}\cdot\text{g}^{-1}$)	[15]
Mediterranean gull larus chicks	Greece	$229 < \text{Hg} < 2845$ ($\text{ng}\cdot\text{g}^{-1}$)	[9]
Seabirds' excrements	Arzew gulf (Algeria)	$0.08 < \text{Hg} < 2.27$ ($\mu\text{g}\cdot\text{g}^{-1}$)	This study

As shown above, contamination of excrements is due to Hg bioaccumulation in seabirds and transfer via chain food. This contamination let us understand that sea products are contaminated too by mercury. The *Arzew* gulf is containing two big towns (*Oran* and *Mostaganem*) which have a population around 2 500 000 habitants (ANOS; Algerian National Office of Statics). A Fish consumption ratio in this region exceeds 10 kg/habitant/year (ANOS). The given data show that human health may directly and seriously be affected by this kind of contamination via chain food. It's important to note that no studies on fish contamination in this region have been done. It's well known that fisheries production of *Arzew* gulf is not consummated only by costal population but also distributed to other towns and even exported this fact may have local and international impact.

Our study on seabirds' dejection contamination by mercury is unique in the South West part of the Mediterranean basin and contributes significantly to the enrichment of the international data base on this kind of contamination. Comparison to other contamination levels around the world can give an overview of the results found elsewhere even if it is not the same bird species

used but let's say that the high contamination level found in *Arzew* gulf is alarmist.

4. Conclusion

Results reported in this study constitute the first mercury contamination bio-monitoring using seabirds' dejections. Important contamination levels founded which have food web and inhalation as origins are alarmist and may affect both human health and marine ecosystems via chain food. Presence of mercury in the coastal environment is due to anthropogenic activities. Urgent measures must be taken in order to prevent human health. Further studies are in perspective to evaluate development mercury pollution aspects.

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