Asian Journal of Chemistry; Vol. 27, No. 7 (2015), 2707-2711

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.18869

Distribution of Inorganic and Total Mercury in Marine Sediments from Two Coastal Areas Delimited by Atlantic Ocean: Galician Rías (NW Spain) and Coast of Dakar (Senegal)

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Received: 20 November 2014; *Accepted*: 9 January 2015; *Published online*: 30 March 2015; AJC-17110

Surface marine sediments proceeding from two Galician Rías (NW Spain) and the coast of Dakar (Senegal) were analyzed by cold vapor atomic absorption spectrometry (CV-AAS) in order to evaluate the distribution of inorganic and total mercury as well as to compare the pollution levels in both aquatic systems. The accumulation of mercury in Galician sediments (values < 0.12 µg/g) was considerably higher than that found in sediments from the Dakar coast (values < 0.025 µg/g). Nevertheless, all the samples studied can be considered unpolluted on mercury according to the quality criteria (values < 0.05 µg/g) used for the classification of sediments. A similar distribution was observed for inorganic and total mercury, with ratios inorganic mercury/total mercury ranging from 97.1 to 99.8 %, indicates that inorganic mercury is the main specie of mercury in all samples studied. Two latent variables, explaining the 99.11 % of the initial variance, were extracted from the data using principal component analysis. This allowed sediments to be grouped in two different subgroups according to their similar behaviour.

Keywords: Inorganic mercury, Total mercury, Marine sediment, Atomic absorption, Galician Rías, Dakar coast.

INTRODUCTION

Mercury is considered as a dangerous contaminant because of its high toxicity and long permanence in the environment[1]. Nowadays, the concentration of total mercury provides poor information about its biogeochemical behaviour and toxicity to organisms, given that various chemical species of mercury behave differently[2]. So, although inorganic mercury is considered the less toxic specie of mercury plays an important role in the environment due to its possible conversion into methylmercury, a potent neurotoxin, through methylation and demethylation processes developed in the aquatic systems[3].

In the last decades, mercury has been widely used in diverse industrial processes (chlorine-alkali industry, manufacture electric devices, paper factories, agrochemical products, *etc.*) and the increase of these and other anthropogenic activities has caused important emissions to the environment[4]. When mercury entering in aquatic systems is usually accumulated in sediments by superficial adsorption or precipitation. In fact, the sedimentary compartment is considered a fundamental component of the biogeochemical cycle of mercury in which it can be transformed and mobilized towards the water column or bioaccumulated in biota[5]. For these reasons, analysis of sediments is an important part of the environmental studies, given that these results can be considered of great relevance to evaluate the impact of diverse anthropogenic activities on marine environments[6].

Galician Rías are located in the Spanish Northwest Atlantic coast and are generally influenced by anthropogenic contamination generated by diverse industrial activities, port facilities, aquaculture, urban settlements, *etc*. In addition, these rías practically behave as estuaries with residual circulation of fresh and salt water, which cause a positive accumulation of metals in the sediments[7]. In any case, the research on mercury in sediments from Galician Rías is scarce[7-9] and the distribution of inorganic mercury was not yet investigated. Nevertheless, this information is relevant because the available inorganic mercury in sediments and the microbial population are considered the most important factors influencing the methylation and demethylation processes developed in the aquatic systems[10]. In fact, the sediment is considered the main production site of methylmercury and, consequently, the fundamental route of bioaccumulation of mercury in biota.

On the other hand, the town of Dakar is an important urban center situated in the Atlantic coast of Senegal (Africa) and, besides the port, account with diverse industrial units largely involved in the manufacture, storage and use of chemicals, petrochemicals, agrochemicals, *etc*. Important discharges both treated and untreated coming from these industrial activities together with other anthropogenic inputs (coastal tourism, fishing activities, *etc*.) dumping to the Dakar coast can threaten the aquatic ecosystem. For these reasons, some scientific studies have been developed in the zone to become aware of the situation[11,12], but any of them have been done about mercury distribution in marine sediments.

The main objective of this work is to evaluate the distribution of inorganic mercury and total mercury in surface marine sediments from two different geographical areas delimited by the Atlantic Ocean: two Galician Rias (Vigo and Pontevedra) and the coast of Dakar. These results provide essential information to assess the pollution status of both study areas and to evaluate the impact of different human activities on the marine environment. Establishing groups among sediment samples and distribution pattern of inorganic and total mercury was carried out by principal component analysis (PCA).

EXPERIMENTAL

Total mercury and inorganic mercury were determined by cold vapor atomic absorption spectrometry (NIC-RA-3000 System) using $SnCl_2$ as reducing agent. A high intensity ultrasonic processor (Sonopuls, HD 2200) equipped with titanium probes was used for inorganic mercury extraction. A domestic microwave oven (Moulinex, 900 W power) was used for microwave heating. A 45 mL capacity Parr reactor (model 4782) was used for acid digestion. A centrifuge (Kubota 5100) was used for a rapid separation of solid-liquid phases. Statistical analysis was performed with the software SPSS (v 19) for Windows.

All chemicals used were of analytical-reagent grade from Merck (Darmstadt, Germany). Ultrapure water (Millipore Milli-Q System) was used throughout all the work. The calibration standards were prepared from the stock solution of mercury with a concentration of 1000 µg/mL. All glass and plastic containers and materials were soaked in a 1.5 % w/v HNO_3 solution for 24 h and rinsed with ultrapure water three times before use.

Sample collection and preparation: The surface marine sediments analyzed in this work were collected from two different aquatic environments delimited by the Atlantic Ocean: two Galician Rías (Northwest of Spain) and the coast of Dakar (Senegal), during the period of time ranging from December 2010 and January 2012. The maps (Fig. 1) show both study areas as well as the situation of the corresponding sampling points.

Galician sediments were collected in different sampling points of the Vigo and Pontevedra Rías, separated by only 30 Km of distance. In the Vigo Ría is situated the city of Vigo with a population of around 300,000 habitants and is affected by important anthropogenic inputs mainly associated to metal industries (shipyard and dock activities) and an important comercial harbor. On the other hand, the Pontevedra Ría houses the city of Pontevedra, which is considerably smaller. However, this Ría is mainly affected by discharges from an industrial complex (chlorine-alkali industry and paper pulp factory) located there. The sampling points in Vigo and Pontevedra Rías (Fig. 1a) were selected by taking into account the accessibility as well as the punctual pollution sources situated in both zones.

The coast of Dakar has been selected for this study for its relatively high urban and industrial activities. So, the study area contains more than 70 % of Dakar industries and more than 40 % of the population of Senegal. For this research, six representative sites of the Dakar coast (Fig. 1b) were selected by taking into consideration the expected pollution according to the above mentioned items.

All surface sediments (about 5 cm depths) were collected using a plastic spoon-spatula and placed into plastic bags at 4 °C until laboratory processing. Then, all sediments were oven dried at 40 °C, disaggregated and sieved through a 70 µm sieve. Finally, they were stored in glass containers into a silica gel desiccator until analysis.

Chemical analysis: Total mercury in sediment was analyzed following a sample preparation method previously described[13]. A sample of approximately 100 mg of homogenized

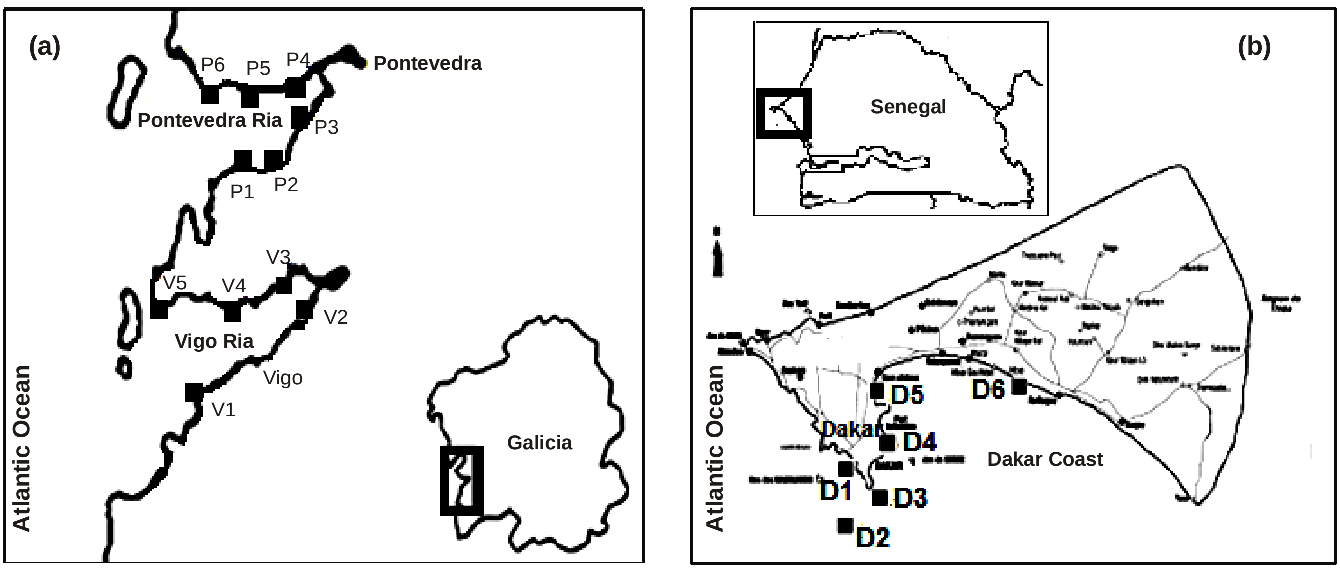

Fig. 1. Maps showing the two coastal areas studied and the selected sampling points in the Galician Rías (a) and the Dakar coast (b)

sediment was mineralized with 4 mL of concentrated nitric acid (65 % w/w) and 2 mL of hydrochloric acid (37 % w/w) in a the PTFE vessel of the Parr reactor. The vessel was closed and heated in the microwave oven during 2 min at 450 W of power. After this, the reactor was allowed to cool in an ice bath, during 15 min, before opening. The resulting solution was filtered and quantitatively transferred into a 25 mL volumetric flask and diluted to volume with ultrapure water.

Inorganic mercury in sediments was analyzed following an ultrasound-assisted extraction procedure, previously used for this purpose[14]. A little portion (100 mg) of prepared sediment was placed into a 50 mL capacity glass tube and 15 mL of a mixture of nitric acid (30 % w/v) and hydrochloric acid (2.5 % w/v) were added. Then, the mixture was sonicated at room temperature during 2 min at 25 % of amplitude. After sonication, the supernatant liquid was separated from the solid phase by centrifugation during 6 min a 1200 rpm. This solution was quantitatively transferred into a 25 mL volumetric flask and diluted to volume with ultrapure water.

RESULTS AND DISCUSSION

The results obtained in marine sediments from Galician Rías (Vigo and Pontevedra) and the Dakar coast are shown in Tables 1 and 2, respectively. All the values are expressed in µg/g (dry weight) and they are given as mean of four separated determinations and their standard deviation.

TABLE-1
CONCENTRATIONS OF INORGANIC AND TOTAL MERCURY IN MARINE SEDIMENTS FROM THE GALICIA RÍAS (NW SPAIN)

Sampling points (Sampling date)	Total Hg (µg/g)	Hg(II) (µg/g)	Ratio Hg(II)/ Total Hg
Vigo Ría (October 2011)			
V1	0.0434 ± 0.0041	0.0433 ± 0.0026	99.8
V2	0.1143 ± 0.0075	0.1126 ± 0.0026	98.5
V3	0.0107 ± 0.0007	0.0106 ± 0.0004	99.1
V4	0.0103 ± 0.0005	0.0100 ± 0.0007	97.1
V5	0.0097 ± 0.0006	0.0096 ± 0.0008	99.0
Pontevedra Ría (January 2012)			
P1	0.0104 ± 0.0006	0.0101 ± 0.0007	97.1
P2	0.0105 ± 0.0007	0.0103 ± 0.0003	98.1
P3	0.1075 ± 0.0050	0.1070 ± 0.0061	99.5
P4	0.0360 ± 0.0039	0.0356 ± 0.0021	98.9
P5	0.0116 ± 0.0006	0.0114 ± 0.0007	98.3
P6	0.0114 ± 0.0007	0.0112 ± 0.0009	98.2

These results displayed in the graphics of Fig. 2(a,b) in order to better compare the distribution of inorganic and total mercury in all samples studied. According to the results, it was observed in all sediments, a great similarity between the contents of inorganic and total mercury, with ratios always ranging from 97.1-99.8 %. It means that inorganic mercury is the most abundant chemical form of mercury available in sediments, which was not previously evaluated in neither of the two studied areas. In addition, these results are in good agreement with those obtained in marine sediments from the south Arabian Sea[15] with ratios inorganic mercury/total mercury between 90 and 96 %.

TABLE-2
CONCENTRATIONS OF INORGANIC AND TOTAL MERCURY IN MARINE SEDIMENTS FROM THE COAST OF DAKAR (SENEGAL)

Sampling points (Sampling date)	Total Hg (µg/g)	Hg(II) (µg/g)	Ratio Hg(II)/ Total Hg
December 2010			
D1	0.0148 ± 0.0012	0.0144 ± 0.0016	97.3
D4	0.0224 ± 0.0020	0.0218 ± 0.0016	97.3
D5	0.0182 ± 0.0014	0.0178 ± 0.0011	97.8
D6	0.0131 ± 0.0009	0.0128 ± 0.0014	97.7
February 2011			
D1	0.0140 ± 0.0013	0.0139 ± 0.0006	99.3
D2	0.0120 ± 0.0006	0.0119 ± 0.0007	98.5
D3	0.0133 ± 0.0011	0.0131 ± 0.0014	98.4
D4	0.0184 ± 0.0014	0.0180 ± 0.0012	97.8
D5	0.0181 ± 0.0013	0.0178 ± 0.0008	98.3
D6	0.0136 ± 0.0012	0.0135 ± 0.0012	98.3
June 2011			
D1	0.0143 ± 0.0007	0.0141 ± 0.0013	98.6
D2	0.0129 ± 0.0010	0.0127 ± 0.0009	98.4
D4	0.0184 ± 0.0014	0.0180 ± 0.0012	97.8
D5	0.0181± 0.0013	0.0180 ± 0.0008	98.4
D6	0.0138 ± 0.0011	0.0136 ± 0.0011	98.6

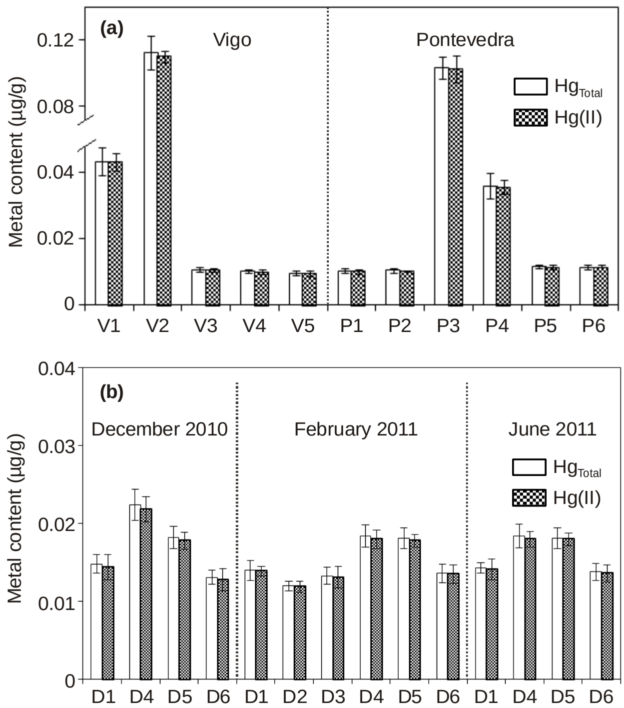

Fig. 2. Distribution of inorganic and total mercury in marine sediments from the Galician Rías (Vigo and Pontevedra) (a) and the coast of Dakar (b)

In the case of Galicia, the contents of total mercury obtained in sediments from Vigo and Pontevedra Rías were relatively similar (between 0.0097 and 0.1143 µg/g) when both zones are affected by a moderate industrial activity. The most polluted sites in the Vigo Ría (sampling points V1 and V2) are located next to the Vigo town [Figs. 1(a) and 2(a)]. The point V2 (0.1143 µg/g) shows the higher values of total mercury and is mostly affected by shipyard activities and also by an active recreational harbor. In addition, the point V1 (0.0434 µg/g) is mainly influenced by discharges from a municipal wastewater treatment plant close to the sampling zone. In the Pontevedra Ría, the higher values of mercury corresponds to the inner zone of the Ría (sampling points P3 and P4), with values of 0.1075 and 0.0360 µg/g, respectively [Figs. 1(a) and 2(a)]. In general, these results can be attributed to the combined effect of two important industries, a chlorine-alkali and a paper pulp factory, located in this zone. In addition, other anthropogenic emissions can be considered such as urban discharges and little harbor facilities placed there. Nevertheless, in the scarce bibliography focused on mercury determination in Galician Rías were found higher contents of total mercury in marine sediments from Vigo and Pontevedra Rías, with values ranging from 0.076-2.73 µg/g[8] and between 0.02 and 1.79 µg/g in surface sediments from the Vigo Ría[9]. This significant decreasing trend could be attributed to diverse measures taken to reduce mercury dumping to the aquatic environment, what was previously disclosed by other authors[16].

On the other hand, total mercury contents obtained in sediments from the Dakar coast were considerably lower than those found in Galician Rias, with values always lower than 0.025 µg/g. Moreover, these values were rather similar in all sampling points and with an insignificant seasonal variation. The most polluted sites are situated near the Dakar city (sampling points D4 and D5), with values ranging from 0.0181-0.0224 µg/g [Figs. 1(b) and 2(b)]. These higher values can be attributed to diverse anthropogenic activities developed in this zone (port facilities, chemical and agrochemical industries, seafood factories, oil refining, *etc.*) as well as untreated municipal discharges from the surrounding urban centers. Higher total mercury contents were found in marine sediments from the coast of Algeria[17] with values varying between 0.01-2.01 µg/g. In contrast, considerably lower values (about 0.0001 µg/g) were obtained in estuarine sediments proceeding from the Republic of Guinea[18]. Finally, it's important to indicate that the accumulation of mercury in all sediments analyzed was below the Lower Chemical Exceedance Level (LCEL, 0.5 µg/g) used in the quality criteria for the classification of sediments[19] and consequently, all of them can be considered unpolluted on mercury.

The analytical methodology employed to determine inorganic and total mercury in the unknown samples was evaluated by analyzing two certified reference materials (sediment CC-580 and soil CC-135a) prepared in the Institute for Reference Materials and Measurements (IRMM) of the European Commission. The results obtained are shown in Table-3 and the statistical comparison of the experimental and certified values (t-test, confidence level 95 %), indicates that no significant differences were found between them, which permit to verify the quality of the results reported in this work.

Statistical analysis: In order to get a better interpretation of the results obtained in the two studied aquatic systems (Galician Rías and Dakar coast), principal component analysis was applied. The analysis of the matrix data, containing all the result obtained, allows to extract only two variables (principal components or factors) explaining the 99.11 % of the initial variance of the data. The highest variance (62.44 %) corresponds to the fist factor (component 1), whereas factor 2 achieved a variance of only 36.67 %. The factor loadings obtained by principal component analysis are listed in Table-4.

TABLE-3
CONCENTRATIONS OF INORGANIC AND TOTAL MERCURY IN CERTIFIED REFERENCE MATERIALS

Reference materials	Certified Hg_{Total} (µg/g)	Certified Hg(II) (µg/g)	Hg_{Total} (µg/g)	Hg(II) (µg/g)
CC-580	132 ± 3	131.9 ± 3*	131 ± 9	129.2 ± 4.4
CC-135a	2.9 ± 0.6	–	2.86 ± 0.12	3.01 ± 0.13

*Calculated by difference between the certified values of total mercury and methyl mercury.

TABLE-4
FACTOR LOADINGS OBTAINED BY PRINCIPAL COMPONENT ANALYSIS (PCA)

	PC1	PC2
Hg Vigo	0.991	-0.074
Hg(II) Vigo	0.991	-0.075
Hg Dakar	0.864	0.496
Hg(II) Dakar	0.860	0.497
Hg(II) Pontevedra	-0.384	0.921
Hg Pontevedra	-0.385	0.921

The graphic representation of the two principal components extracted is shown in Fig. 3. It is observed that both total mercury (Hg) and inorganic mercury [Hg(II)] present a similar behaviour in all sediments studied (Vigo, Pontevedra and Dakar) and consequently, are positioned together. It indicates a positive relationship between the inorganic and total mercury contents in all analyzed sediments.

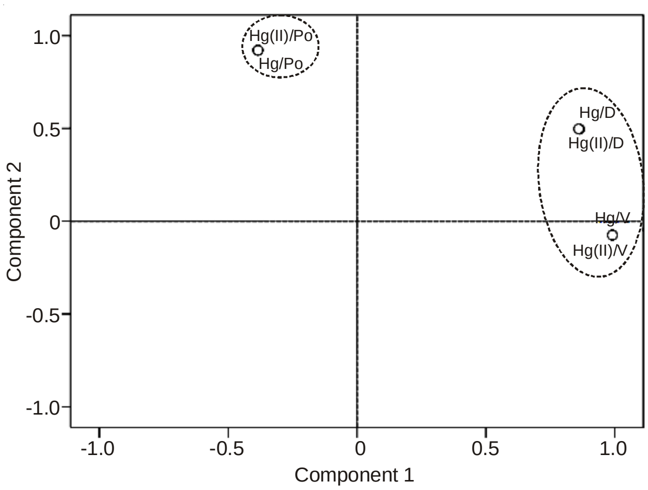

Fig. 3. Principal component analysis (PCA) for total mercury (Hg) and inorganic mercury Hg(II) in marine sediments from the Galician Rías and the coast of Dakar. Symbols: V = Vigo; Po = Pontevedra; D = Dakar

On the other hand, two different subgroups could be separated according to a similar behaviour. The first group includes the sediments from Vigo Ría and Dakar coast, given that they are mainly associated to positive side of the component 1 (coefficients between 0.860-0.991). The second group corresponds to the sediments from Pontevedra Ría because they are mainly influenced by the positive part of component 2 (coefficients of 0.921). Therefore, the distribution of variables in the graphic of principal component analysis (Fig. 3) indicates a great similarity between the sediments from the Vigo Ría and the Dakar coast. This fact could be attributed to similar sources of mercury contamination, probably related to the anthropogenic activities developed in the two studied areas. So, in both cases, it must be taken into consideration the port facilities, urban discharges and diverse effluents from industrial activities placed in the Vigo Ría (shipyard, canning factories, aquiculture, *etc.*) and the Dakar coast (chemical and agro-chemical industries, seafood factories, oil refining, *etc.*). In contrast, in the Pontevedra Ría, the main sources of mercury contamination are discharges from a chlorine-alkali industry and a paper pulp factory, situated in this zone.

Conclusion

The results of this work allow us to compare the pollution status and the environmental impact caused by anthropogenic inputs in two coastal areas delimited by the Atlantic Ocean: two Galician Rías (NW Spain) and the coast of Dakar (Senegal). In this way, it's possible to conclude that surface marine sediments from Galician Rías (values between 0.0097-0.1143 µg/g) were more contaminated than those found in the coast of Dakar, with values always lower than 0.025 µg/g. However, all the results obtained were below the Lower Chemical Exceedance Level (LCEL, 0.5 µg/g) used for the classification of sediments. On the other hand, inorganic mercury is the most abundant specie of mercury found in all sediments analyzed, with ratios inorganic mercury/total mercury between 97.1 and 99.8 %. Data analysis by principal component analysis permits separate two different subgroups of sediments according to their similar behaviour: on the one hand, are grouped the sediments from Vigo Ría and Dakar coast; on the other hand, the sediments from the Pontevedra Ría. This fact could be attributed to similar pollution sources, probably related to the anthropogenic activities developed in the corresponding zones.

ACKNOWLEDGEMENTS

This work has been financially supported by Vigo University in support of research (09VIB08). One of the authors, Birame Ndiaye thanks Agencia Española de Cooperación Internacional para el Desarrollo (AECID) for a grant.

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