



Fractionation of mercury in sediments during draining of Augusta (Italy) coastal area by modified Tessier method



Santino Orecchio ^{a,*}, Giuseppe Polizzotto ^b

^a *Dipartimento di Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche, Italy*

^b *Università di Palermo, Viale delle Scienze, I-90128 Palermo, Italy*

ARTICLE INFO

Article history:

Received 11 April 2013

Received in revised form 28 May 2013

Accepted 29 May 2013

Available online 5 June 2013

Keywords:

Mercury(II) ion

Fractionation

Sediments

Augusta

Remediation

ABSTRACT

A modified Tessier method was applied to sediments dredged from Augusta (Italy) coastal area with the purpose of establishing the amount and the forms in which mercury is present in the different sediment fractions. The mercury fractionation was made by measuring the concentration of the metal ion on the solutions and directly on the sediment fractions obtained by sequential extraction. The measurements on the solutions as well as that on the solid fractions were carried out by using a Direct Mercury Analyser, DMA 80. This new instrument does not require sample preparation, and gives results comparable to those obtained with CV-AAS and ICP-MS and few minutes are necessary for each analysis. The quality of the experimental data together with the applicability of the technique to real samples was checked by analyzing certified reference materials (CRM) and some sediment samples collected from the coastal site during the research. The results of fractionation analysis were used as an assessment tool to establish the best remediation technique for removal of mercury from this polluted area.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Mercury cells of chlor-alkali plants have been identified as one of the major sources of mercury pollution [1] and have been gradually replaced by cleaner technologies.

Augusta is one of the major industrial centers of Italy with heavy chemical plants, oil refineries and several power stations. Since the 50's and until some decades ago, a chlor-alkali plant worked in this area producing chlorine and caustic soda by the mercury cell process. In that period a large amount of Hg finished in the environment causing pollution of soil, groundwater, seawater and sediments. In 2007, Nicotra [2] carried out a systematic study on the total mercury concentration in sediments collected in several points of the area investigated by us. The results published by Nicotra [$1.20 \leq C_{\text{Hg}} \text{ (mg/kg)} \leq 22.5$] evidenced a high mercury pollution of the sediments of Augusta coastal area.

As known, all mercury species are toxic and, in particular, organic mercury compounds show a greater toxicity in respect to the inorganic ones [3]. In general, mercury pollution is a serious and widespread environmental problem due to their persistence and non-biodegradability [4–9]. Moreover, mercury is also responsible for the most fish consumption advisories worldwide and is considered a high priority pollutant by the US EPA [10].

Polluted sediments can be an important source of Hg for aquatic environments and the amount of metal that passes to water depends on the stability and solubility of several possible species formed with

the sediment components (carbonates, oxides, sulfides, organic, etc.). It means that the knowledge of the total mercury concentration in polluted sediments is important but not sufficient if this data is not supported by a correct fractionation study that quantifies the environmental risk and the toxicological consequences [11].

The amount of the different mercury species in sediment also depends on the physical and chemical properties of the substrate, such as the pH, the percent of the organic and inorganic fractions and the redox potential which cause a variety of chemical, photochemical and biological reactions that involve the element; e.g., in anaerobic conditions, most of mercury compounds can be transformed to HgS, one of the less soluble mercury species in water (about $10^{-27} \text{ mol L}^{-1}$) and, as consequence, one of the less dangerous.

This paper represents a part of a greater project on the evaluation of organic and inorganic contaminants [12–15], the sources of pollutants and their chemical fractionation [16–20]. Here we report a fractionation study of mercury in sediments of Augusta coastal area sampled before a probable remediation procedure, for example the dredging.

Since several years the dredging operations used for remediation purposes have captured the attention of public opinion [13]. In fact, in such cases the complex operation of removal of several millions of cubic meters of sediments can cause deterioration and contamination of seawater with consequent short- and long-term ecological, sociological, economic and esthetic problems in the whole area.

The results of fractionation analysis were used as an assessment tool to establish which of the dredging and disposal procedure is the best remediation technique for the removal of mercury polluted sediments from Augusta coastal area. The environmental impact and the risks for

* Corresponding author. Tel.: +39 091 23897968; fax: +39 091 590015.
E-mail address: santino.orecchio@unipa.it (S. Orecchio).

people and other living organisms associated with the remediation procedures were also evaluated.

The determination of Hg in sediments is not easy: the low concentrations and the presence of interfering substances are the main analytical complications [21].

The mercury fractionation was made by using a modified sequential extraction of Tessier [22] which allowed us to recognize metals in seven different fractions classified as follows: a) water soluble mercury; b) exchangeable mercury; c) Hg bound to carbonates; d) Hg bound to iron and manganese oxides and hydroxides; e) elemental and inorganic mercury bound to organic fraction of sediment, and f) mercury as sulfide.

One of the innovations of our extraction method consists of the possibility to estimate the concentration of mercury directly on sediment (before and after extraction step) and in the extract solutions of the various extraction steps by using the same instrument (Direct Mercury Analyser, DMA-80). Indeed, the DMA-80 does not require sample preparation and gives results comparable to those obtained with CV-AAS and ICP-MS. Finally, the analytical concentration of total mercury in seawater was also determined by means of cold vapor atomic fluorescence spectroscopy (CV-AFS) before, during and after a simulated preliminary dredging of the sediments, in order to assess the potential release of mercury to the aqueous phase.

2. Experimental part

2.1. Reagents and standards

All reagents were of analytical-reagent grade. The solutions were prepared using ultra-pure water Milli-Q. The calibration standards of Hg(II) were prepared by making appropriate dilutions of concentrated solution (Inorganic Ventures, $\text{Hg}^{2+} = 1.001 \pm 2 \mu\text{g/mL}$ in 5%

HNO_3 (v/v)). A blank calibration solution was also used for a zero calibration. All diluted standard solutions containing Hg were stabilized by adding HNO_3 .

The analysis using DMA-80 requires about 5 min and the quality of the results and the applicability to the real samples were checked by analyzing a certified reference material (CRM) (Quality Consult Material QC2009 09SS1, $\text{Hg} = 35.5 \text{ mg/kg}$) and several sediment samples collected from the coastal sites during the investigation spiked of known amounts of the *Analyta* (Inorganic Ventures, $\text{Hg}^{2+} = 1.001 \pm 2 \mu\text{g/mL}$).

All the chemicals used for the extraction procedure were purified by re-crystallization or by treatment with Chelex 100 resin (Fluka).

To prevent contamination of tools, instruments and other materials, only clean glassware and high purity reactants were used. To avoid the contamination of the solutions, different glasswares were used for standard and sample solutions.

2.2. Site and sampling stations

The Augusta bay extends about 30 km in South East Sicily and is a wide gulf facing the Ionian Sea (Fig. 1). The Augusta coastal area hosts harbors and several chemical and petrochemical industries. In general, the pollution in this area is due to chemical and petrochemical activities, heavy traffic of tankers and commercial cargo boats, medium agriculture runoff, and sewage from the nearest urban areas. Moreover, the coastal area is also affected by a mercury contamination mainly attributable to the activity of the chlor-alkali industry that was operating in the bay until some decades ago.

This area has been recognized as a site at high environmental risk, both by the World Health Organization [23] and the Italian Government [24]. Some researchers published offshore works in Augusta Bay mostly focused on the effects of industrial activity and related contaminants

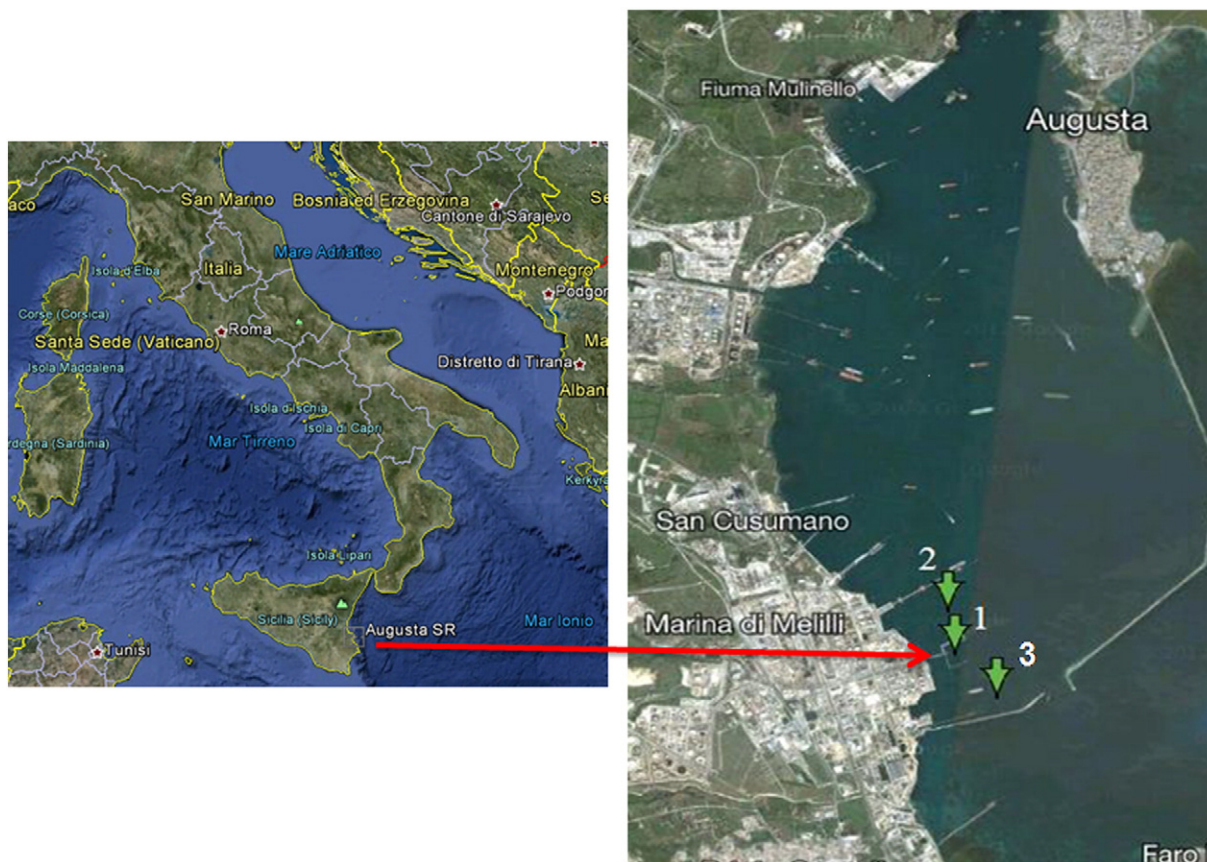


Fig. 1. Position of the sampling stations chosen for the analysis of mercury in sediments of the Augusta coastal area.

Download English Version:

<https://daneshyari.com/en/article/7643928>

Download Persian Version:

<https://daneshyari.com/article/7643928>

[Daneshyari.com](https://daneshyari.com)