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

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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.

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 [$1.20 \leq C_{Hg}$ (mg/kg) ≤ 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 [1,4–9]. 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} 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

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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, $Hg^{2+} = 1.001 \pm 2$ μg/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, Hg = 35.5 mg/kg) and several sediment samples collected from the coastal sites during the investigation spiked of known amounts of the *Analyta* (Inorganic Ventures, $Hg^{2+} = 1.001 \pm 2$ μg/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

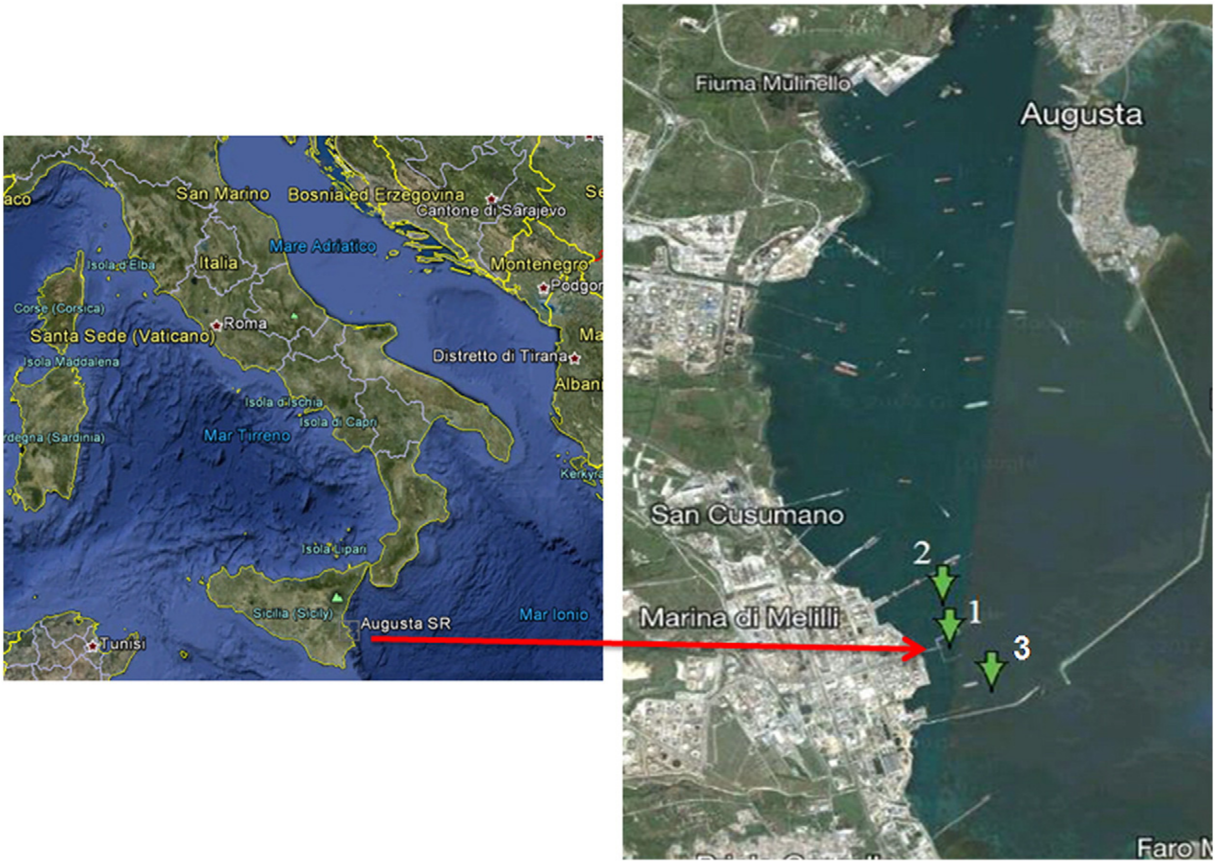

Fig. 1. Position of the sampling stations chosen for the analysis of mercury in sediments of the Augusta coastal area.

(especially Hg) in the environment, as well as their impact on the present organism communities and on the whole coastal ecosystems [25–29]. Studies of ^{210}Pb profiles estimate an average sediment accumulation rate that varies from 1.6 to 5.3 mm/yr moving offshore [5].

A possible strategy in the remediation of the Augusta coastal area could be the dredging of the contaminated sediments but the environmental impact of dredging operations had to be previously evaluated. Indeed, depending on the stability and solubility of mercury species in sediments, the sediment dredging could cause an increase of the metal concentration in seawater.

The environmental impact of the dredging operations was evaluated in this work by a mercury fractionation study carried out on the sediments of Augusta Bay in May 2011. Sediment samples (0.1–15 cm depth) were collected in three different points of Augusta coastal area (Fig. 1) by using a 18 L Van Veen grab and the samples were stored in plastic bag at −4 °C. The position of the three sampling stations was chosen in order to be representative of the whole area (Table 1).

Moreover, samples of surface seawater were manually collected before, during and after (24 h) the dredging simulation of sediments and were stored into 1 L acid-cleaned borosilicate glass containers. Collected samples were frozen and transferred to the laboratory for the analysis. Special precautions were taken to avoid sample contamination during sampling, transportation, preservation and laboratory analysis.

2.3. Sample treatment

The same protocol was adopted to treat the sediments collected from the three sampling stations. Approximately 10–20 g was centrifuged for 10 min at 4000 rpm and overlying water was pipetted off. Then the samples were dried in an oven at 35 °C for 48 h and were weighed in triplicate.

2.4. Metal sequential extraction procedure

The classical procedure used by Tessier was modified by adding a first extraction step with water at 100 °C in order to separate the soluble fraction of mercury in the sediments. Another extraction step was added at the end of the procedure to quantify the mercury sulfide. Water soluble mercury easily passes in the aquatic system and accumulates in organisms and can be considered the most hazardous Hg fraction. On the contrary, the mercury sulfide has a very low solubility and, as a consequence, is the lowest toxic and mobile mercury fraction.

In order to optimize the procedure, in a previous paper [16] particular attention was paid in determining the reaction times of each extraction step. The following fractions were separated:

- *Fraction 1* (*soluble Hg*): 5 g (dry weight) of <2 mm sieved sediment sample was treated with 40 mL of water at 100 °C and stirred for 1 h. The residue was separated from the solution by centrifugation and a portion of 0.5 g was dried and analyzed by Direct Mercury Analyzer.
- *Fraction 2* (*exchangeable Hg*): the sediment from step 1 was treated with 40 mL of 1 M sodium acetate solution for 1 h under continuous stirring. The residue was separated from solution by centrifugation and a portion (0.5 g) was dried and analyzed.
- *Fraction 3* (*mercury bound to carbonates*): sediment from step 2 was treated with CH_3COONa/CH_3COOH solution at pH ~ 5 and the suspension was stirred for 4 h. A new residue was obtained after centrifugation and a portion (0.5 g) was dried and analyzed.
- *Fraction 4* (*Hg bound to Fe and Mn oxides*): sediment from step 3 was treated with a solution of $NH_3(OH)Cl$ 0.04 mol L^{-1} in 25% CH_3COOH (v/v) under stirring at 96 °C for 6 h, until the free iron–manganese oxides were completely dissolved. A portion of residue (0.5 g) was dried and analyzed.
- *Fraction 5/6* (*elemental Hg and Hg bound to organic matter*): two portions of the sediment from step 4 were collected. The first portion was heated at 180 °C in order to eliminate the elemental mercury and then analyzed (*Hg bound to organic matter*). The second portion of the residue was mineralized in a high performance microwave digestion unit (Milestone, mod. mls 1200 M) by adding 6 mL of HNO_3 and 1 mL of 30% hydrogen peroxide. A new residue was obtained after centrifugation and solution removal. A portion of residue (0.5 g) was dried and analyzed (*elemental Hg and Hg bound to organic matter*).
- *Fraction 7* (*Hg bound to sulfides*): the last residue was digested with 6 mL of HCl and HNO_3 mixture (3:1) and dissolved in a microwave digestion unit. A portion of residue (0.5 g) was dried and analyzed.

A good agreement (±10%) between the sum of the Hg concentrations of each fraction and the total metal concentration in sediments was found.

Table 1
Coordinates of sampling sites.

Station	Coordinate
1	Lat: 37° 10′ 42.542″ N – long: 15° 12′ 13.972″ E
2	Lat: 37° 10′ 57.835″ N – long: 15° 12′ 10.220″ E
3	Lat: 37° 10′ 28.283″ N – long: 15° 12′ 31.284″ E

2.5. Instrumentation

The mercury concentration on seawater, solutions and directly on the residue samples obtained from sequential fractionation procedure was measured by using the Direct Mercury Analyser (DMA-80, Milestone). The amount of mercury in seawater and in the solutions was also checked by the cold vapor atomic fluorescence spectrophotometer (CV-AFS) (Mercur, Analytikjena).

In the measurements carried out with the DMA-80, 100–500 mg of the sediment samples or 1.5 mL of solution samples were weighed in a quartz boat and then introduced into the instrument's combustion tube. The instrument self-seals and oxygen begins flowing over the sample at a rate of ~200 mL min^{-1}. The solid sample is dried and then thermally decomposed by controlled heating. Gaseous combustion products are moved by an oxygen flow through a Mn_3O_4/CaO-based catalyst (T = 750 °C). Then sample oxidation is completed and halogens, nitrogen and sulfur oxides are trapped. Elemental mercury and other decomposition products are moved to a tube containing gold-coated sand. Here the Hg^0 is selectively trapped (by an amalgam with gold) whilst other products are flushed out of the system. The Hg concentration is then calculated by the software on the basis of the absorbance measured at 253.7 nm and the weight of the sample.

The instrumental parameters (settings) are reported in Table 2.

Instrument calibration was made by using a certificate standard solution of mercury and a second order equation was used to fit experimental points. Instrumentation has dual measuring cells for an extended analysis range of 0–600 ng mercury. The analytical range of the method was from 50 to 5000 μg/kg when samples of 100 mg were analyzed. Using a 100–500 mg sample, as in our case, a quantification limit, estimated as the blank plus 10σ (IUPAC criterion) of 8 μg/kg was obtained with a detection limit of 2.6 μg/kg estimated as the blank plus 3σ (IUPAC criterion). Maximum sample size is 500 mg.

The accuracy of the instrument was tested by three replicate analyses of a certified reference material (Quality Consult Material QC2009 09SS1, Hg = 35.5 mg/kg). The accuracy of the analysis on the certified sewage sludge sample was of 97%. Relative standard deviations of the three Hg analyses are about 10%.

Reproducibility of analyses was tested by three replicate analyses of sediments; it ranged from 3.2% to 20% of the relative standard

Table 2
Parameters for the DMA-80 instrumental setting.

Period	T/°C	Cleaning time	Amalgamator heating time	Signal recording time
2′00″	From 0 to 200	60″	12″	30″
2′30″	From 250 to 650			
3′00″	650 (constant)			

deviation. A blank was run up every 5 samples. All the reported data were blank corrected.

3. Results and discussion

The sediment sampling carried out in the three stations chosen for this investigation can be considered a dredging simulation. For this reason, the first part of the investigation regarded the measure of the total mercury in seawater collected in correspondence to the three sampling stations before, during and after the dredging simulation in order to evaluate the correspondent release of mercury to seawater.

As can see from the data shown in Table 3, in all the three stations, the concentration of mercury in seawater collected before and after the dredging simulation is almost the same, whilst an increase of mercury concentration was registered in seawater collected during dredging simulation (e.g., for seawater samples of station 1 $C_{Hg} = 0.9 \pm 0.09$, 2.0 ± 0.15 and 1.2 ± 0.10 ppb was found before, during and after dredging simulation, respectively). Only for station n°1 the three samples of seawater collected were filtered before mercury determination and the total Hg concentration found in the samples was always 0.2 ± 0.10 ppb. It means that the great part of the mercury found in marine water before dredging simulation, as well as that found during and after the dredging simulation is contained in the particulate phase suspended in the water column.

The concentrations of total mercury measured in the marine water collected at three sampling stations of the Augusta bay were significantly lower than that found in sediments and were also lower than the average concentrations of the element in marine environments not subject to particular sources of pollution [26].

The analysis on the solutions obtained from the first step of sequential extraction (treatment with water at 100 °C) gave evidence that the amount of mercury released from the sediments was lower than the LOD value. For further confirmation, the solid phase remaining after this extraction step was also analyzed and no differences were found with the mercury concentrations of the samples not treated, within the range of the experimental errors.

As can see from the histogram reported in Fig. 2, total mercury concentration in the sediments of Augusta bay ranged between 40 ± 3 ppm (station n°3) to 214 ± 6 ppm (station n°1) and is higher than the Mediterranean background value [30].

To establish the Hg background concentration of Sicilian sediments, the method of maximum likelihood of log-normal distribution parameter was applied to the sediments older than 1920, separated from the more recent ones by using the calculated sedimentation rates [5]. Based on this approach, the background concentration of mercury in Sicilian sediments is 0.038 mg/kg. Our data indicate that the lithogenic component is not a controlling factor of mercury in the sediments and Hg concentrations are affected by hard discharges from anthropogenic sources.

Table 3
Total mercury concentration (ppb) in the seawater samples.

Sampling phase	Total mercury (ppb)		
	Station 1	Station 2	Station 3
Before dredging simulation	0.9 ± 0.1	2.3 ± 0.1	1.4 ± 0.2
During dredging simulation	2.0 ± 0.2	5.2 ± 0.1	3.1 ± 0.3
After dredging simulation	1.2 ± 0.1	1.8 ± 0.2	1.7 ± 0.2
Filtrate samples	0.20 ± 0.02	–	–

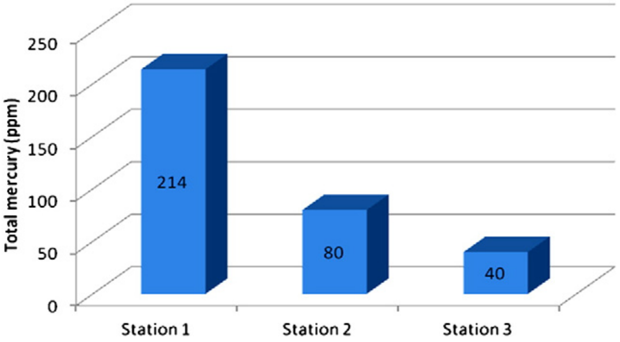

Fig. 2. Total mercury concentrations (ppm) in the sediments of Augusta Bay.

In Table 4 are reported the results of the mercury analysis (ppm) carried out on the solutions and residues of the fractions obtained by the sequential extraction of the sediments of the three sampling stations. These data were calculated as average of three determinations and the histograms of the data (in % of mercury species) were also reported in Fig. 3 in order to have a quick overview of the mercury distribution in the sediments of the three stations.

As can be seen, the total mercury concentration in the sediments of the three sampling stations is above the recommended limit [31]. As shown in Fig. 3, the mercury fractionation of sediments of stations n°1 and n°2 is similar whilst considerable differences were found in the mercury distribution of samples of station n°3.

The heat treatment at 180 °C carried out on fraction 5 of the sequential extraction has not caused any elementary mercury loss in the sediments of the three sampling stations. In fact the concentrations of total mercury before and after the thermal treatment were practically equal, considering the experimental error range. Therefore the sediments of Augusta coastal area do not contain elemental mercury and the fifth fraction only consists of mercury bound to organic matter.

The distribution of mercury species in the sediments of station n°1 is: carbonate (36%), labile (27%). The remaining amount is distributed almost equally in the organic, sulfide and iron and manganese oxides fractions.

In station n°2, the concentration of labile Hg and of mercury bound to iron and manganese oxides was negligible. As for sediments of the station n°1 the metal is more concentrated in the carbonate phase (49%). In this station also the organic fraction contains a relevant percentage of mercury (35%).

The mercury distribution in Station n°3 is completely different with respect to that of the other two stations. In fact, in this case the mercury is mainly present as sulfide (58%).

The fractionation study carried out on mercury of sediments of Augusta bay can be very useful when a remediation strategy of this coastal area has to be planned.

Dredging and disposal or ex situ treatment are the most commonly applied remediation methods for contaminated sediments but are very

Table 4
Mercury concentration (ppm) in each fraction of the sequential extraction of the sediments of Augusta coastal area.

Sediment fractions	Mercury concentration (ppm)		
	Station 1	Station 2	Station 3
Labile	58 ± 3	2.1 ± 0.2	1.0 ± 0.2
Carbonate	77 ± 5	38 ± 3	–
Fe/Mn oxides	22 ± 1	1.0 ± 0.2	–
Organic/metallic	31 ± 2	28 ± 3	15 ± 1
Sulfide	25 ± 2	9.4 ± 0.8	23 ± 2

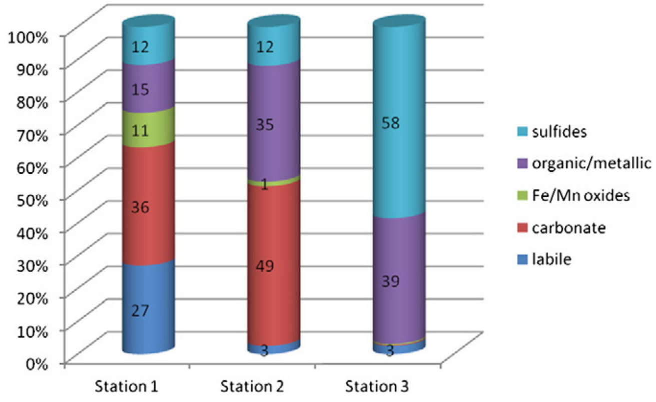

Fig. 3. Percentages of mercury in each fraction of the sequential extraction of sediments of Augusta Bay.

expensive, considering the amount of sediments (about one million cubic meters).

Some authors [32] suggested dredging and/or capping as suitable remediation approaches for sediments polluted by Hg. Moreover, they affirmed that in situ capping is a relatively low-cost remediation process but leaves the contaminant in the same area, with possible risks regarding long-term environmental effects, such as the remobilization of buried Hg, the possible transformation of inorganic to organic Hg and the migration through the capping layer into the water column. Nevertheless, in the case of heavily polluted systems, as those of Augusta Coastal area, dredging and confinement may be the only effective solution. This has been successfully applied in Minamata Bay, where approximately 1.5 millions of m^3 of sediments were removed from an area of about 2 km^2 and were contained in a reclaimed area of the bay; in that case, the sediments were capped with clean soil after stabilization with volcanic ash [32].

In the case of Augusta bay, in particular for sediments of stations n°1 and n°2, in which mercury is mainly bound to carbonates, the best remediation strategy can be the dredging and capping. In fact, an ex situ treatment would be very expensive and could cause a release of mercury in the environment if the sediments come in contact with acid rain, whilst, dredging and capping would be a safer remediation strategy. In fact, during this procedure the sediments would be transferred to another part of Augusta bay which is always in contact with seawater. The pH of seawater (7.7 ÷ 8.4) does not cause dissolution of the carbonate fraction with the consequent release of mercury in the environment. The dredging treatment of sediments of station n°3 is not so problematic like that of the other two stations because in this case mercury is present in a very stable form. In this case also an ex situ treatment can be done without particular consequence for the environment.

4. Conclusions

The following conclusions can be done on the basis of the obtained results:

1) The knowledge of the amount of mercury in sediments of a polluted site like the Augusta coastal area is important but not sufficient for the evaluation of the environmental risk related to its presence and to a possible remediation treatment. Indeed, only an accurate fractionation study can furnish the information necessary to assess the possible release of mercury to the aquatic environment;
2) an efficient, rapid and inexpensive methodology for the mercury fractionation in sediments was developed by making some modifications to the classical Tessier procedure;
3) the mercury concentration was measured directly on the residues obtained by sequential extraction by using the DMA-80. This new instrumental technique does not require sample preparation, gives results comparable to those obtained with CV-AAS and ICP-MS and few minutes are necessary for each analysis;
4) the results obtained indicate that the proposed method for the mercury fractionation in sediments is reproducible;
5) during and after the simulation of dredging operations the sediments did not release soluble mercury to the overlying water column. In fact, the amount of mercury found in seawater samples collected during the sampling operations was contained in particulate material which, however, quickly precipitates;
6) the results obtained in the fractionation study of mercury of sediments collected in the three stations of Augusta coastal area suggested that the dredging and capping is the best remediation procedure to be adopted.

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