

## **Remediation of Hg-contaminated marine sediments by simultaneous application of enhancing agents and microwave heating (MWH)**

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### **Abstract**

The aim of this work was to investigate Hg removal ability of a novel microwave heating (MWH) treatment for marine sediment remediation enhanced by the application of several agents, biodegradable complexing agent (methylglycinediacetic acid, MGDA), surfactant (Tween<sup>®</sup> 80), and citric acid. Main results revealed that MWH allowed a very rapid heating (~450 °C in 7 min) of the irradiated medium. However, without the addition of enhancing agents, a maximum Hg removal of ~72% can be achieved. The application of MGDA led to a higher contaminant removal of ~87% (residual concentration = 5.4 mg kg<sup>-1</sup>). For the treatment including the simultaneous addition of both chelating agent and surfactant, their synergetic action and stripping processes resulted in a very high Hg removal of ~99% for an irradiation time of 7 min, corresponding to a residual concentration of 0.56 mg kg<sup>-1</sup>, which is lower than the Italian regulatory limit of 1 mg kg<sup>-1</sup>. The use of citric acid resulted in a shortening of the removal kinetics, which allowed the successful application of a shorter remediation time of 5 min. The observed strong passive ability of sediments to convert a microwave irradiation energy into a rapid and large temperature increase undoubtedly represents a key factor in the whole remediation process, making the studied treatment an excellent choice. Kinetic data are suitable for a preliminary assessment of the effectiveness of clean-up activities, and as basis for future scaling-up studies on MWH of Hg-contaminated sediments.

**Keywords:** Citric acid, marine sediment, mercury (Hg), microwave heating (MWH), MGDA, non-ionic surfactant.

## 1. Introduction

Mercury (Hg)-contamination of marine sediments is a serious and global scale environmental problem, especially due to its high persistence and toxicity [1,2]. The largest industrial use of Hg during the 20<sup>th</sup> century was the chlor-alkali process, which used electrolysis (Hg being the anode) for separating chlorine and sodium from brine [3]. In Europe, one of the largest and most Hg-polluted site is Augusta Bay. It is a semi-enclosed basin with a coastal area of about 30 km<sup>2</sup>, and is included in the “Augusta - Melilli - Priolo” industrial area (East coast of Sicily). Since the early 50's, it has been affected by marine contamination from chemical industrial and petrochemical plants [4]. Due to its high state of environmental degradation, in 2002 this site was included in the National Remediation Plan by the Italian Environmental Ministry (Law No. 426/1998) [5]. The major environmental concern was due to the emission activities of a chlor-alkali plant with Hg cells, which operated until 2003, causing a severe Hg - contamination of the bottom sediments [6], especially in the southwestern (SW) zone of the bay [7]. The very high Hg-concentration in sediments, by far exceeding the standard limit reported by national and international sediment quality guidelines (SQGs), and its long-term and mutagenic effects, pose a serious risk to the environment and human health [8]. The unsuitability of the traditional management strategies, such as landfill disposal, makes the possibility to remedy Hg-contaminated sediments a key factor in term of social sustainability, and at the same time, a great challenge for scientific communities and society in general [9,10]. However marine sediment characteristics (fine texture, low permeability jointly with a high salinity and organic, sulphide and water content) make their remediation using conventional methods very difficult [11]. Limited techniques have been reported to treat heavy metal-contaminated sediments, such as washing, disposal and stabilisation/solidification. However, they have been proved inappropriate, especially for fine grained and low permeable matrices [12]. Fine textures can in fact result in low metal removals since they reduce the effectiveness of contaminant extraction processes in washing treatments, or in low mechanical resistances of stabilised/solidified matrices. Similarly, a high water content generally results in a worsening of the resistance performance of the treated matrices. Electrokinetic (EK) decontamination has been shown as being more suitable but it generally presents low removal efficiencies with high costs due to the sediment high buffering capacity [13], especially in the presence of high Hg-contamination levels [14]. On the contrary, the mineralogical composition of the sediments and the presence of a high water, as moisture content, and high salinity could represent main

advantages in the microwave (MW) technique application.

In recent years, microwave heating (MWH) has been documented as a rapid and effective technique for the remediation of soils [15–18], aquifers [19] and for the detoxification of several industrial wastes [20,21]. MWH is based on the conversion process of the MW electric field energy adsorbed by the irradiated medium into heat [22]. This leads to an increase of the matrix temperature resulting in thermal desorption processes and/or in a direct local selective vaporization of contaminants if they are much higher polar than soil. Specifically, the higher the dielectric properties of the irradiated medium, the higher the temperature increase achievable by means of MWH [23]. Minerals, generally constituting the coastal sediments [24], could have dielectric properties (dielectric constant and dielectric loss factor) higher than soil minerals (i.e.: silica, clays) [25] and this would represent a key factor for the achievement of the high temperatures needed to activate Hg thermal removal from sediments. In addition, at the radio frequency of 2.45 GHz, water and sodium chloride are excellent MW absorbers, and the high water amount (40 - 50%) and salinity, generally present in marine sediments, would allow a rapid vapour production able to increase the contaminant removal efficiency due to distillation and subsequent stripping processes [26,27]. Therefore, MWH may provide an alternative technique for Hg-contaminated marine sediment remediation. However, this has never been investigated. Furthermore, high organic matter and sulphide content or the strength of contaminant - sediment bonds could limit the Hg-removal mechanisms requiring temperatures higher than 600 °C [28]. Consequently, the possibility to develop a novel method to lower the temperature at which Hg can be reduced to below the regulatory limit of 1 mg kg<sup>-1</sup>, or to maximize the removal efficiency, and consequently reduce energy requirements, CO<sub>2</sub> footprints and costs, could represent an important alternative in contaminated sediment treatment activities. In addition, the possibility to use specific agents to enhance the MWH removal mechanisms, especially contaminant stripping by distillation, could be a further advantage.

Synthetic chelates, such as ethylenediamine tetraacetic acid (EDTA) or diethylene triamine pentaacetic acid (DTPA), have largely been employed as enhancing agents in washing [29], EK [30–33] or phytoextraction [34] treatments. However, they have a relatively high environmental persistence and toxicity as well as a thermal instability at high temperatures [35]. On the other hand, the methylglycinediacetic acid (MGDA) is a relatively novel chelate, much more biodegradable than others jointly with the essential advantage of having a stable thermal behaviour under a wide range of temperatures [35]. Likewise, surfactants with low toxicity

and favourable biodegradability, such as Polyoxyethylene (20) sorbitan monooleate, also known as Tween<sup>®</sup> 80 [36,37], have been extensively used in organic and inorganic contaminant removal treatments [11,38,39]. Recently, citric acid (CA) has also been used to enhance conventional thermal applications [28].

The main aim of this study was to investigate at lab- scale the capability of a novel hybrid MWH treatment for the removal of mercury from real contaminated bottom sediments, which includes the use of a biodegradable chelate (C) MGDA, surfactant (S) Tween<sup>®</sup> 80 and citric acid (CA). The influence of the enhancing agent contact time and dose on the Hg removal efficiency was also evaluated. Novel findings from experiments are expected to provide useful basic information for future scaling-up and real scale studies on the enhanced MWH treatment for the successful remediation of marine Hg-contaminated sediments.

## **2. Materials and Methods**

### **2.1 Sediment sampling and characterization**

The contaminated sediments were collected from the SW part of Augusta Bay in April 2014 (Figure 1). After the sampling procedures, the sediments were stored in a sealed refrigerated (-4 °C) box for their transportation to the laboratory. After air-drying (72 h), sieving (2 mm) and homogenizing procedures, the sediment physico-chemical features, as well as the contaminant concentration, were evaluated. The density was assessed using the ASTM D854-92 method, while moisture and organic matter were obtained according to the ASTM D2974-14 method. Sediment salinity was measured as total dissolved salts (TDS) at 25°C from a sediment aqueous solution. Specifically, 1:5 sediment:deionised water was prepared by adding 20 g of air-dried sediments to 100 mL deionised water. The solution was then mechanically shaken in a closed system for 30 min to dissolve soluble salts before measuring TDS by means of a PCE-PHD 1 conductivity meter. Heavy metal concentration, including Hg, was obtained with US-EPA 6020A and 3051A methods, using ICP-MS. PAHs were determined with US-EPA SW 3541, SW 3620 and 8270 methods coupled with GC-MS analysis. Total petrol hydrocarbon (TPH) concentration was measured by GC-MS using the US-EPA 8270-C method. The concentration of all contaminants was expressed as mg kg<sub>dw</sub><sup>-1</sup>.

Mineralogical composition of the sediments was also investigated using x-ray analysis (Bruker AXS D5000), where Cu-K $\alpha$  radiation operated at 40 mA and 45 kV (6 - 60 °2 $\theta$  range with a 0.02 °2 $\theta$  step size and a rate of 0.5 s step<sup>-1</sup>). Semi-quantitative analyses on XRD pattern were carried out using a specific MATLAB

coding. The dielectric features as dielectric constant ( $\epsilon'$ ) and dielectric loss factor ( $\epsilon''$ ) were measured at the frequency of 2.45 GHz by means of the cavity perturbation method [40]. The mercury fractionation was also obtained by means of modified Tessier sequential extraction procedure [6]. Specifically, five fractions were determined as detailed in Table 1. In order to assess the influence of the sediment salinity on the sediment ability to increase the temperature when irradiated, several sediment samples with a gradual increase in pore water salinity values (from 0 to 10% and different from the initial natural value of 4.3%) were obtained. The procedure included a preliminary sediment washing with deionised water for a complete salinity removal, followed by a different NaCl dosage to the system [41].

## 2.2 Experimental apparatus and procedures

In this study a MWH treatment (MW) and MWH treatment enhanced by the use of MGDA (MW + C), Tween<sup>®</sup> 80 (MW + S), their mixture (MW + C + S) or citric acid (MW + CA) were applied to Hg - contaminated sediment samples. For hybrid treatment tests, MGDA (as Na<sub>3</sub>-MGDA), Tween<sup>®</sup> 80, MGDA - Tween<sup>®</sup> 80 mixture (1 : 1) and citric acid were premixed at different concentrations considering a contact time in the 5 - 720 min range. In order to better understand the role of the water amount in Hg-removal mechanisms, MWH tests were also carried out on dried sediment samples (MW - dry). The experimental matrix is given in Table 2. MWH was simulated at lab-scale by means of a dedicated MW setup. It mainly includes an oven cavity where a sediment sample was placed to be irradiated. The cavity was connected by a waveguide to a magnetron able to generate a 2.45 GHz MW irradiation and operating at the maximum power of 1 kW. A flexible type-k thermocouple ( $\varnothing = 1.5$  mm) was used for recording the sediment sample temperature profiles.. The volatile compounds produced during the treatment were captured by a dedicated exhaust gas line, which consists of a unit for the condensate collecting, an activated carbon filter and an electric vacuum pump. For each test, 25 g of sediment sample were treated for an irradiation time ( $t$ ) of 0.5, 1, 3, 5 and 7 min at a selected power ( $P$ ) of 0.65 kW. At bench-scale, MW irradiation is generally applied at powers up to a maximum value of 1000 W, which is generally required to totally remove organic pollutants from soils [26]. The temperature variation was also obtained for MW treatment (irradiation time = 3 min) of sediments as a function of their pore water salinity. After the treatment, the sediment samples were cooled down, then stored sealed at -4 °C before analysis. Residual moisture values, sediment sample temperature profiles and Hg residual concentrations ( $C$ ) as mg kg<sub>dw</sub><sup>-1</sup> were obtained for each condition investigated. To

better comprehend the effect of the single MWH treatments on the Hg removal mechanisms, Hg sequential extraction of the sediments after their MW irradiation at 7 min was also conducted. Contaminant removal ( $R$ ) was calculated according to the following expression:

$$R_{\%} = \frac{C_0 - C}{C_0} \cdot 100 \quad (1)$$

where  $C_0$  is the initial Hg concentration. Triplicated tests were carried out for each condition and mean values were reported. During MWH, hundreds of Hg species can be obtained from thermal desorption of Hg-contaminated matrices (even if in absence of chelant agents or surfactants), and this makes the development and application of dedicated tools strictly needed to obtain their identification [42]. The addition of compounds such as MGDA, Tween<sup>®</sup> 80 or citric acid and, over all, the use of real contaminated sediment samples, would make the problem even more complex. Total Hg amount in the condensate and filters were obtained using ICP-MS analysis.

### 3. Results and discussion

#### 3.1 Sediment characterization and Hg-speciation

Results from sediment characterization are reported in Table 3. Data confirm a high moisture of ~ 42% and a high content of organic matter (7.4 wt%) and sulphides (43.6 mg kg<sup>-1</sup>). The mineralogical composition showed calcite (CaCO<sub>3</sub>), as dominant phase (70.5 %), quartz (SiO<sub>2</sub>) (19.5%) and other silicates, among which montmorillonite, muscovite and illite (8.8%). The sediments included a predominant biogenic component (MgO + CaO) with SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> as major constituents [24]. From grain size analysis, sediments are classified as silt due to the concentration of silt higher than 88%. The high pore water salt concentration of 4.3% also confirmed the high salinity of the marine sediments. Contamination analysis revealed a high Hg concentration of 43.2 mg kg<sup>-1</sup>, whereas PAH and TPH levels of 2.45 and 6.34 mg kg<sup>-1</sup> were detected, respectively. PAH, TPH and heavy metal concentrations were below the Italian regulatory limits, whereas the Hg level was much higher than the limit of 1 mg kg<sup>-1</sup>. Physical characterization and the nature of the contamination found are consistent with characteristics of coastal sediments of the SW zone of Augusta Bay [4,24,43]. In terms of dielectric properties, the observed relatively high dielectric constant ( $\epsilon'$ ) and loss factor ( $\epsilon''$ ) of 11.3 and 0.6, respectively, are due to the high percentage of CaCO<sub>3</sub> and the presence of Al and Fe oxides in the sediment composition. These compounds are known to have dipolar features much

higher than minerals, such as SiO<sub>2</sub>, which generally constitute sandy or silty soils [25]. CaCO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> were shown to have  $\epsilon''$  values  $\sim 3$ ,  $\sim 20$  and  $\sim 30$  fold higher than SiO<sub>2</sub> [44]. Table 4 shows the relative distribution of Hg-fractions assessed by sequential extraction procedure. Hg-carbonate (50.5%), Hg-organic (36.3%) and Hg-sulphides (10.3%) were found to be the major fractions. This is in agreement with the findings of Orecchio and Polizzotto [6]. Observed Hg-speciation further confirms that Hg-removal is a main challenge and its removal processes using conventional chemical-physical techniques could be strictly inhibited [30]. On the other hand, the high water amount and dielectric properties of sediments could make MWH a perfect candidate to successfully desorb Hg from marine sediments.

### **3.2 MWH and enhanced MWH treatments**

#### **3.2.1 Sediment temperature profiles**

The sediment temperature ( $T$ ) profiles with time, recorded for each experimental condition investigated, are given in Figure 2. In all cases, results showed an increase in  $T$  with time, due to the capacity of the irradiated samples to absorb the energy of the electric field generated by MW irradiation and convert it into heat. Fundamentals on MWH report that temperature increase ratio is proportional to the loss factor ( $\epsilon''$ ) of the irradiated matrix [45], and this is confirmed by the linear increase of temperature observed for sediment samples pre-dried before the MWH treatment. In this case, the maximum  $T$  of about 450 °C was recorded at the end of the irradiation, which highlighted that the presence of higher polar compounds, respect to those observed for soils, resulted in a more rapid temperature increase. Specifically, after the same remediation time, a maximum temperature of about 160 °C was observed for MW treatment of sandy soils. Much lower temperatures were observed in the case of silty or clayey soils. In any case, temperatures not higher than  $\sim 270$  °C were found also with higher operating powers, up to 1.0 kW, and much longer times, up to 60 min [25]. For all the moisturised sediment treatments, at the beginning of the MW irradiation, the  $T$  increase was limited by the presence of water, due to the higher energy required for its evaporation. Specifically, the sediment temperature kept constant at  $\sim 100$  °C between 0.5 and 2.0 min, until almost all the water evaporated (Table 4). However, final temperatures in the range 422 – 437 °C (not much lower than that found for dry sediments) were observed. No relevant differences between the treatments with or without enhancing agent addition were found. Overall, the observed strong passive ability of sediments to convert a relatively low power irradiation energy into a rapid and large temperature increase (maximum  $T$  increase rate

of  $\sim 64 \text{ }^\circ\text{C min}^{-1}$ ) undoubtedly represents a key factor in the whole remediation process. This also depended on the high salinity, in addition to the large concentration of calcite in the mineralogical composition of the sediments, as confirmed by investigated influence of sediment salinity on  $T$  variation (Figure 3). An almost linear  $T$  increase was in fact found with sediment pore water salinity up to the value of 4.3%, which corresponded to the natural salinity content. Higher salinity values did not lead to a further  $T$  increase. At the frequency of 2.45 GHz, sodium chloride was shown to have dielectric properties higher than those of soil or sediment minerals, which also greatly increase for temperatures higher than  $90 \text{ }^\circ\text{C}$ . This allowed a relevant increase in the dielectric constants of geological materials respect to increasing values of salinity [46,47].

### 3.2.2 Hg removal kinetics in unenhanced treatments

Figure 4 shows the Hg residual concentration ( $C$ ) in sediments after MW treatments at different irradiation times. Results were observed to have a maximum error of  $\pm 5.8\%$ . As expected,  $C$  decreased with  $t$  for all the treatments, and the rate of removal strictly depended on the specific treatment applied and the temperature profile achieved. In the case of irradiation of dried sediment samples,  $C$  was higher than  $29 \text{ mg kg}^{-1}$ , corresponding to a percentage removal ( $R$ ) of  $\sim 33\%$ , when the temperature was below  $162 \text{ }^\circ\text{C}$  ( $t = 2 \text{ min}$ ). When  $T$  was higher than  $233 \text{ }^\circ\text{C}$ ,  $C$  dramatically decreased up to a minimum value of  $15 \text{ mg kg}^{-1}$  ( $R = 65.3\%$ ), which was found for the highest observed  $T$  of  $452 \text{ }^\circ\text{C}$  ( $t = 7 \text{ min}$ ). The increase in temperature resulted in Hg-thermal desorption phenomena also capable of destroying forces existing between the contaminant and sediments. Lower  $C$  values were generally observed for the moisturised sediment samples. In this case,  $C$  was higher than  $15.6 \text{ mg kg}^{-1}$  ( $R = \sim 64\%$ ) when the temperature was below  $192 \text{ }^\circ\text{C}$  ( $t = 3 \text{ min}$ ), whereas it decreased to its minimum value of  $12.6 \text{ mg kg}^{-1}$  ( $R = \sim 72\%$ ) when  $T$  was  $437 \text{ }^\circ\text{C}$  ( $t = 7 \text{ min}$ ). During MWH, the water in the moisturised sediments changed its phase into vapour. This produced an additional Hg removal action due to the activation of stripping processes, which moved mercury from the sediment to the gas phase, leading to a greater Hg removal [48]. In the presence of pore-water, a thermal treatment may produce an entrainment gas stream, which enhances the removal of Hg gas phase and other compounds that are not normally considered volatile [42]. The improved effectiveness of the MWH can be also ascribable to the increase in the sediment permeability caused by the vapour hot flow, which provides uniform vapour flow patterns for superheated mercury in fine texture matrices [42]. Results also showed a progressive reduction in the slope of Hg removal kinetics, which is typical for conventional thermal

desorption treatments [49]. However, it was also due to the progressive reduction of the residual water content observed during the MWH (Table 4). The higher removal efficiencies found for the moistured sediments respect to the dry ones, clearly highlighted that the Hg removal process is strongly enhanced by the water as sediment moisture [18,26]. This was also verified by the high removal observed for the F1 fraction (Table 5). The relatively low removals achievable at the end of the unenhanced MW treatment mainly depended on the high percentage of carbonates, organic matter and sulphides (Table 3), which resulted in tight bounds with mercury [42], as confirmed by the Hg residual concentrations of 3.33 (27.2%), 4.42 (36.1%) and 4.02 mg kg<sup>-1</sup> (32.8%) in the carbonate, organic/metallic and sulphides fractions, respectively (Table 5). Hg(II) forms extremely strong complexes with organic matter adsorbed onto the sediment surface [50] and reduced sulphur [14], affecting Hg transport and removal mechanisms. Temperatures higher than 500 °C can be required to convert compounds such as HgS and HgCO<sub>3</sub> into gaseous elemental mercury [51]. Ma et al. [28] reported that organic carbon in Hg-contaminated soils treated at 400 °C was 65% respect to its initial value, whereas organic carbon was reduced to 0.02% after a heating at 700 °C. These findings indicate that irradiation alone can't effectively reduce residual Hg to levels below the maximum allowed concentration. Results are in agreement with those from previous studies. Ma et al. [52] found a Hg soil concentration reduction from ~70 to 11 mg kg<sup>-1</sup> when treated at 500 °C. Data were also in agreement with Reis et al. [53] and Rumayor et al. [54].

### **3.2.3 Hg removal kinetics in enhanced treatments**

The effect of the addition of MGDA on Hg-residual concentration was also assessed and results were compared with the application of MWH only (Figure 4). Data were observed to have a maximum margin of error of ±6.9%. Similar to MW treatment, results showed a clear dependence of Hg removal on the related sediment temperature profile. Specifically, after 2 min of MGDA - enhanced treatment (MW + C), a residual Hg content of 27.2 mg kg<sup>-1</sup> was observed, whereas a further decrease up to 12.1, 7.7 and 5.4 was achieved for longer times of 3, 5 and 7 min, respectively. Observed residual concentrations corresponded to a percentage reduction in the range 10 – 56 % respect to the MWH without MGDA addition. An improvement in Hg removal rate depended on synergetic action of both stripping process and Hg enhanced mobility due to the strong chelating ability of MGDA in forming Me(II)-MGDA stable complexes also in high temperature and wide pH range environments. More details on MGDA metal chelation mechanisms can be found in

Jachula et al. [55]. In particular, observed chelating action was found to have a specific action on Hg bound to carbonates, oxides and sulphides for which a reduction from 3.33, 0.44 and 4.02 mg kg<sup>-1</sup> to 0.33, 0.20 and 0.93 mg kg<sup>-1</sup> was respectively observed at the end of the test (Table 5). This is in accordance with Peters et al. [56]. Otherwise, no relevant reduction in organo-Hg-complexes was found due to the interference of organic matter with MGDA chelant action [50].

The addition of Tween<sup>®</sup> 80 alone (MW + S) led to higher residual Hg values of 27.1, 14.2, 11.1 and 9.0 mg kg<sup>-1</sup> after 2, 3, 5 and 7 min of MW irradiation, respectively (Figure 4). As shown in Table 5, this corresponded to a great reduction (~65%) of F4 fraction. This depended on the specific action of Tween<sup>®</sup> 80 on the removal of organo-Hg-complexes. Tween<sup>®</sup> 80 structure includes a lipophilic part with a very high affinity for the organic compounds and a hydrophilic part, which, on the contrary, tends to be attracted by the moisturised mineral particles [57]. Consequently, its addition to the sediments resulted in the solubilisation of the organic matter and its complexes with Hg, which in turn led to an increase of their transfer to the liquid phase [39,57]. On the other hand, limited reduction achieved for F2 (carbonates) and F5 (sulphides) remarks that their removal strictly depends on the activation of complexation and/or ionic exchange processes. However, these require the ionic nature of the surfactant. Another reason for the low Hg removals observed could be the temperature dependent behaviour of the Tween<sup>®</sup> 80, which tends to lose its hydrophilic character at high temperatures [37]. In both cases (MGDA or Tween<sup>®</sup> 80), results again revealed residual Hg levels higher than the regulatory limit.

When Tween<sup>®</sup> 80 and MGDA were simultaneously added (MW + S + C), an enhancement of the solubilisation removal mechanisms was observed due to their synergetic action. This led to a final residual Hg concentration of 0.56 mg kg<sup>-1</sup> (R = 99%) (Figure 4), which allowed the regulatory limit to be met. A corresponding strong reduction of all Hg fractions investigated was also observed (Table 5). A probable reason is the improvement of the Hg chelant action of MGDA due to the specific action of the surfactant on the removal of organic matter and F4 fraction (Table 5), which are known to reduce the chelant action [50,58]. Chelating agents were shown to be very good synergists in combined use with surfactants. In this case, the addition of MGDA to Tween<sup>®</sup> 80 also gave it an ionic behaviour, which then, acted as an ionic surfactant with the advantages of the non-ionic one (i.e.: low critic micelle concentration and lipophilic behavior) [39].

When the citric acid was added to the sediments (MW + CA), a general remarkable improvement of Hg removal was observed (Figure 4). This allowed the achievement of a residual Hg concentration lower than the limit of  $1 \text{ mg kg}^{-1}$  ( $R = 99\%$ ) in a shorter irradiation time of 5 min. kinetic also exhibited a higher slope respect to all previous cases between 1 and 2 min, which corresponded to the duration for which the temperature remained almost constant due to the water evaporation. This probably indicated that a different Hg removal mechanism took place. The addition of chelates or surfactant resulted an improvement of the solubilisation process, which in turn helped Hg removal by distillation. In this case, the addition of citric acid facilitated the chemical action in destroying the Hg-sediment bounds due to the ability of citric acid to dissolve the  $\text{CaCO}_3$  [28], which is the main mineral constituent of the sediments and offers adsorption sites for Hg and organic matter. A total removal of F4 fraction was in fact observed at the end of this treatment (Table 5). Therefore, the presence of citric acid clearly helped Hg desorption via thermal and stripping processes. Obtained results are in agreement with Hahladakis et al. [38] who reported that metal removal from sediments by EK can be enhanced using citric acid in the anodic chamber due to its strong ability to remove the organic matter and the metals adsorbed onto it.

Total mercury analysis from the off-gas treatment system revealed that for all experiments the overall recovery was in the 88 - 99% range. Specifically, the major part was entrapped in the condenser unit (~74%), whereas ~26% was collected by the filtering system. This is in agreement with Kunkel et al. [59]. Although the development of specific models is strictly required for the identification of several Hg species produced during the treatment, based on literature findings, main Hg forms that are expected to be found in exhaust - gas traps are  $\text{Hg}^0$ ,  $\text{HgCl}_2$ ,  $\text{HgO}$ ,  $\text{Hg}_2\text{SO}_4$  and  $\text{Hg}(\text{OH})_2$ . Hg released from mineral bounds, may also generate secondary Hg phases such as andtiemannite ( $\text{HgSe}$ ), corderoite ( $\text{Hg}_3\text{S}_2\text{Cl}_2$ ), laffittite ( $\text{AgHgAsS}_3$ ), metacinnabar ( $\text{HgS}$ ), schuetteite ( $\text{Hg}_3(\text{SO}_4)\text{O}_2$ ) and shakhovite ( $\text{Hg}_4\text{SbO}_5(\text{OH})_3$ ). However precipitated cinnabar generally represents the predominant phase in solid phase-mercury. At the same time, carbonate minerals decompose to the oxide or basic carbonates with the production of  $\text{CO}_2$  [42].

#### **3.2.4 Influence of enhancing agent dose and contact time on MWH effectiveness**

The influence of Tween<sup>®</sup>-MGDA mixture and citric acid dose on the Hg removal kinetics was evaluated for an irradiation time of 3 min and a contact time of 60 min. Results are given in Figures 5. Data were observed to have a maximum margin of error of  $\pm 5.8\%$  and showed that in MW + S + C treatment any relevant

variation of temperature or contaminant removal did not occur with increasing the concentration of the enhancing agent. Only a slight difference in evaporation behaviour was recorded between only water and the solutions at 2 and 4% (Table 4). This was probably due to the increase of the solute concentration in the interstitial solution, which, consequently, would have produced a lowering of the vapour pressure. In terms of Hg removal, it is clear that the increase in agent amount, from 2 to 4% did not enhance the performance of the system. On the other hand, a marked increase in Hg removal was observed when the citric acid dose increased from 0.1 to 0.2 M (MW + CA) (Figure 6). However, a further increase to 0.3 did not lead to higher Hg removals. Again, no variation of temperature occurred with increasing the citric acid dose. Obtained findings highlighted that 2% and 0.2M can be considered as optimal doses for Tween<sup>®</sup>-MGDA mixture and citric acid, respectively.

Results also demonstrated that in MW + S + C (2%) and MW + CA (0.2M) treatments the variation of the enhancing agent contact time influenced the Hg removal process (Figure 7). In both cases, an increase in Hg removal was found when contact time increased from 5 to 60 min. Higher contact times did not result in an improvement of the performance of the system. This confirms that 1 h is a sufficient time because the enhancing chemical reactions, described in the previous section, took place resulting in the maximum Hg removal rate. This is in agreement with other studies [60,61] investigating the effect of surfactant or chelant contact time on Hg removal.

### **3.3 Comparison to other clean-up alternatives**

An almost total Hg removal from sediments observed in such a short time is hardly achievable by other remediation techniques, which often require multi-step processes. This is also due to the features of the studied treatment that acted simulating a high effective multi-step process, where a pure thermal desorption (after drying) is followed by an initial combined sediment washing and thermal desorption treatment. A further advantage respect to conventional sediment treatments is that there is neither need for initial water addition nor to treat the final wastewater containing the by-products of the contaminant removal. In addition, the heating process allows a very effective dewatering treatment, strictly required as pre-treatment for marine sediment decontamination. Generally, centrifuges, filter presses, plate or diaphragm-plate filter or gravity thickening can be used for dewatering purposes; however, these methods are not suitable for silt or clay [62].

Results from a study by He et al. [63] showed that ultrasound and alga biomass (2AMT-2) combined technique was effective to remove ~24% of mercury from sediments with a certified initial content of 3.04 mg kg<sup>-1</sup>. Careghini et al. [43] reported a maximum Hg removal of 63% from marine sediments dredged from Augusta Bay applying a sequential S/S and thermal process for 4 h. Similar removals were found by Comuzzi et al. [64] testing a decontamination procedure of Hg-polluted dredged sludge from Marano-Grado Lagoon (NE Italy), based on cationic exchange associated with low temperature thermal desorption. Hg removals between 24 and 60% were observed when the samples were treated with a 15% solution of tetrabutyl-ammonium chloride. The range depended on the nature of the slurry (Hg pollution ranging from 20 to 200 ppm). Relatively low Hg removal was also found by treating marine sediments with EK despite the initial Hg content being very low (1.17 mg kg<sup>-1</sup>) [11]. Authors reported the highest removal of ~46% when EK was applied for 30 days (voltage = 3 V cm<sup>-1</sup>) using H<sub>2</sub>O<sub>2</sub> and EDTA solution as processing fluids. More recently, Falciglia et al. [65] reported that a 400-h EK treatment led to a limited Hg removal of ~71%, which did not match with the desired regulatory limit for Augusta bay. Literature has demonstrated that only conventional thermal treatments can be effective, but require high temperatures and fuel costs in the range of US\$ 650 - 1000 ton<sup>-1</sup> [1,62]. On the other hand, recent literature [66] demonstrated that low energy costs in the 18 - 27 € ton<sup>-1</sup> range are required in MWH treatments of contaminated soils. Because MWH was shown to be more effective in sediment remediation rather than soils, obtained results make MWH a potential cost-effective alternative to conventional thermal desorption.

#### 4. Conclusions

Based on results obtained from experiments, the following conclusions can be drawn:

- Simulated MWH allowed the achievement of a very rapid heating (maximum  $\Delta T$  rate = ~64 °C min<sup>-1</sup>) and high sediment temperature (maximum  $T = \sim 450$  °C), mainly due to the mineral composition of the sediments and high salinity, and consequently, their dielectric properties, which were much higher than those generally observed for soils. No relevant differences of temperature between treatments with or without enhancing agent addition were found. In addition the heating process allowed a very rapid and effective dewatering, strictly required as pre-treatment for marine sediment decontamination.

- For the MWH without enhancing agent addition, relatively low Hg removals were achieved. In this case, Hg removal is activated by thermal desorption and stripping processes. Specifically, a residual concentration of 15.6 ( $R = \sim 64\%$ ) and 12.6 mg kg<sup>-1</sup> ( $R = \sim 72\%$ ) was found after a 3 or 7 min irradiation time, respectively. The application of MGDA led to a further Hg concentration reduction in the range 10 – 56 %, due to the MGDA chelating ability, with minimal value of 5.4 mg kg<sup>-1</sup> ( $R = \sim 87\%$ ) being achieved for longest time investigated. Lower Hg-removals were observed for the surfactant enhanced MWH. For the treatment including the simultaneous addition of both the enhancing additives (chelating agent + surfactant), their synergetic action and stripping processes led to a very low residual Hg concentration of 0.56 mg kg<sup>-1</sup> after 7-min treatment, corresponding to a contaminant removal of  $\sim 99\%$ . The addition of citric acid resulted in a remarkable improvement of Hg removal kinetics, which allows the achievement of a residual Hg concentration lower than the limit of 1 mg kg<sup>-1</sup> in a shorter irradiation time of 5 min.
- None relevant variation of temperature or contaminant removal occurred with increasing the concentration of the Tween<sup>®</sup>-MGDA mixture from 2 to 4%. On the other hand, a marked increase in Hg removal was observed when the citric acid dose increased from 0.1 to 0.2 M. However, a higher citric acid dose did not lead to higher Hg removals. Obtained findings highlighted that 2% and 0.2M can be considered as optimal doses for Tween<sup>®</sup>-MGDA mixture and citric acid, respectively. Results also exhibited that in MW + S + C and MW + CA treatments the variation of the enhancing agent contact time influenced the Hg removal. In both cases, a contact time of 1 h can be considered as optimal.
- Achieved Hg removals in such a short time are hardly possible by other remediation techniques. This is also due to the features of the enhanced MWH that operated as a high effective multi-step technique (washing + pure thermal desorption). The observed strong passive ability of sediments to convert a low power irradiation energy into a rapid and large temperature increase undoubtedly represents a key factor in the whole remediation process, potentially able to reduce the energy costs. A further advantage is that there is no need to treat the final wastewater for by-product removal.
- Observed kinetic data can be suitable for the preliminary assessment of the effectiveness of clean-up activities for contaminated sediment remediation. The investigated Hg-removal mechanisms can

also serve as basis for future scaling-up works on enhanced MWH of Hg-contaminated sediments or for the creation of novel hybrid techniques based on MW irradiation processes.

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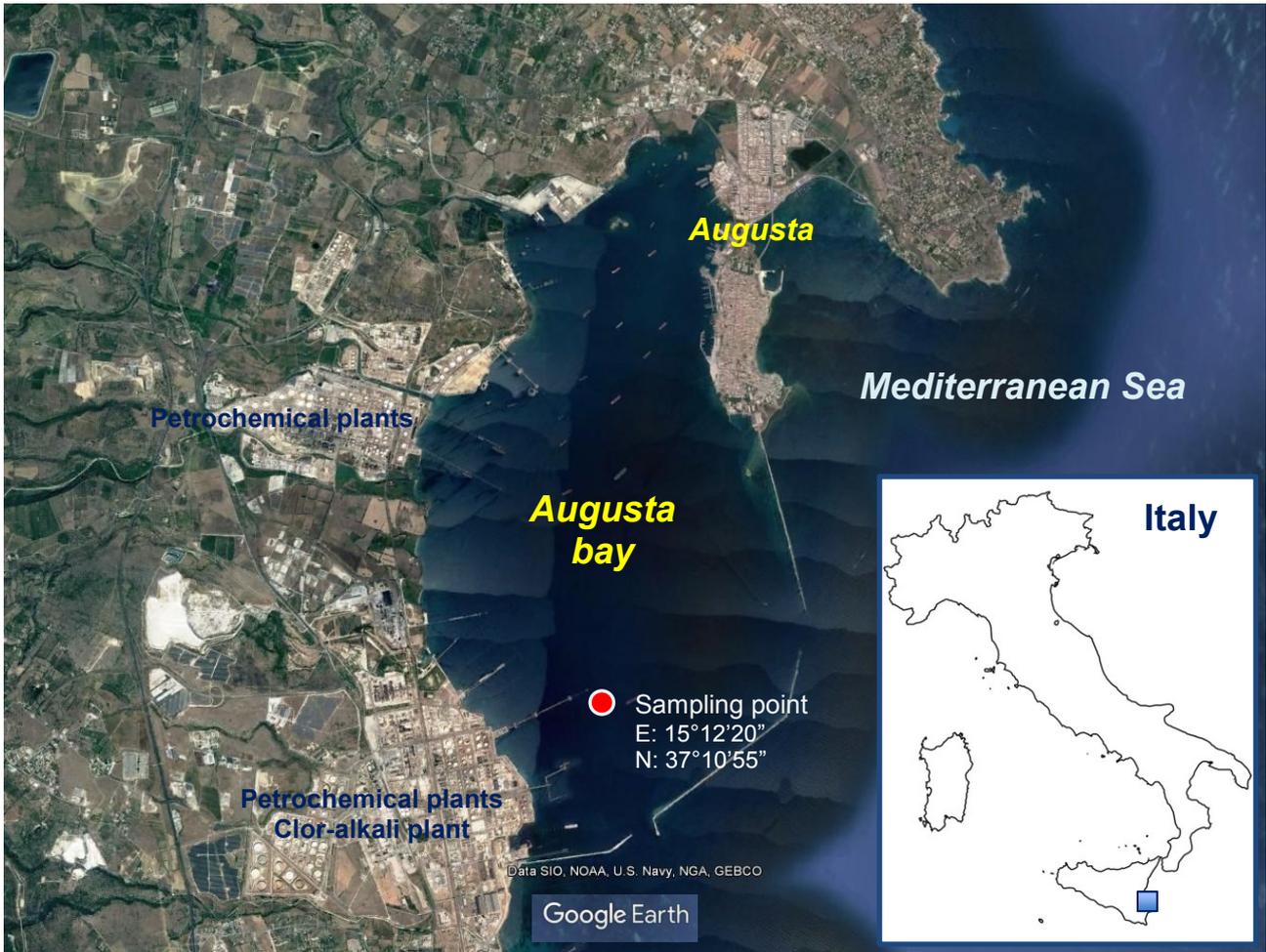
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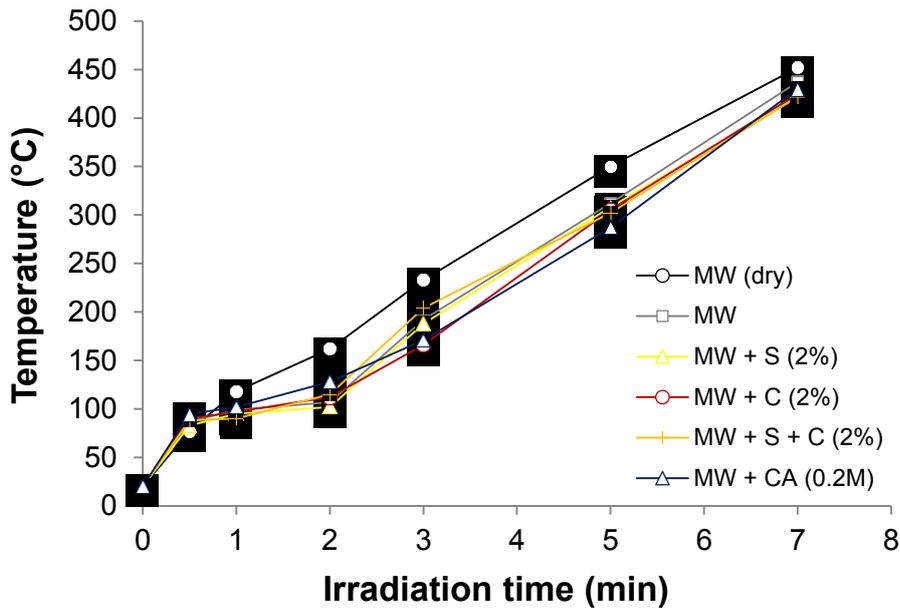
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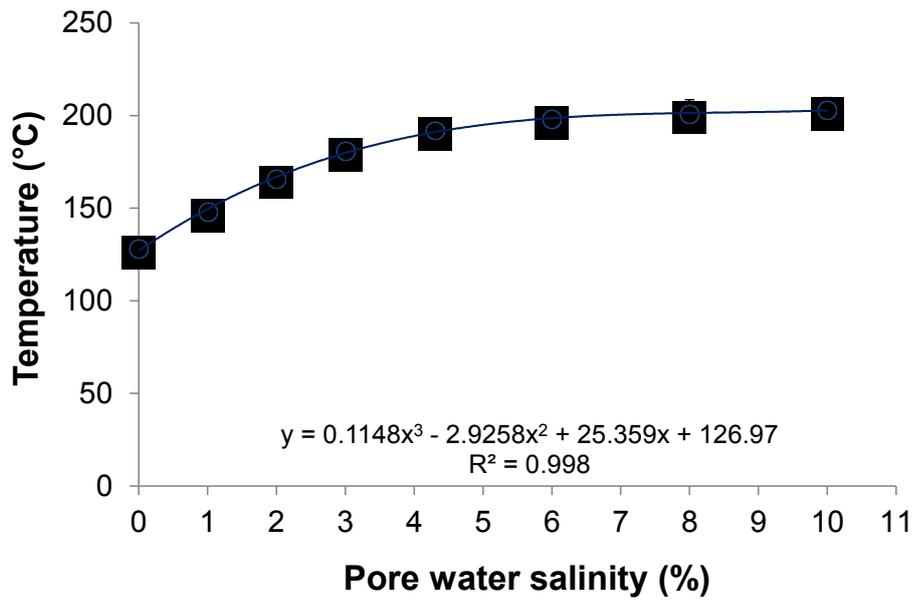
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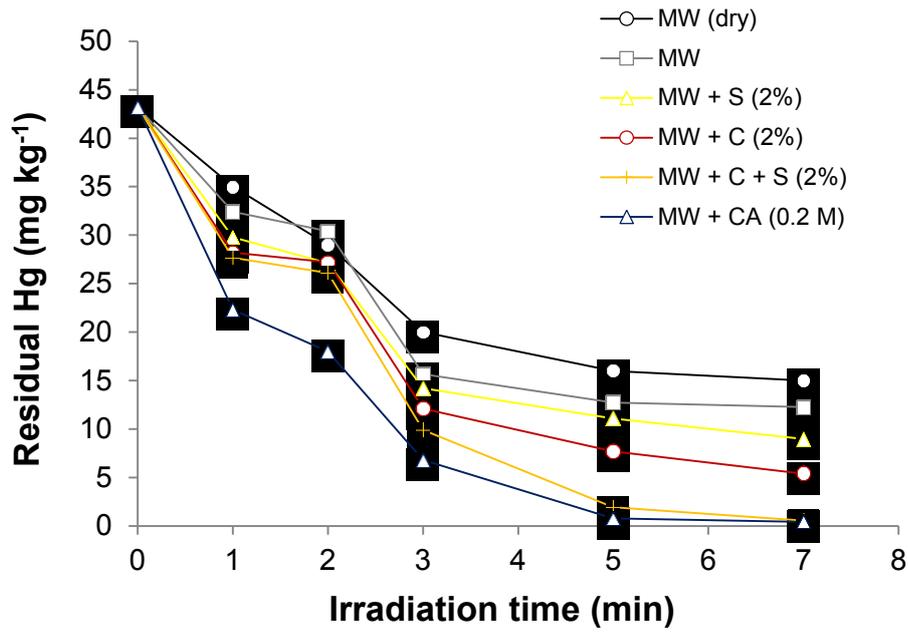
**Figure 1.** Augusta Bay (Italy) and location of the sediment sampling point (Google Earth®).



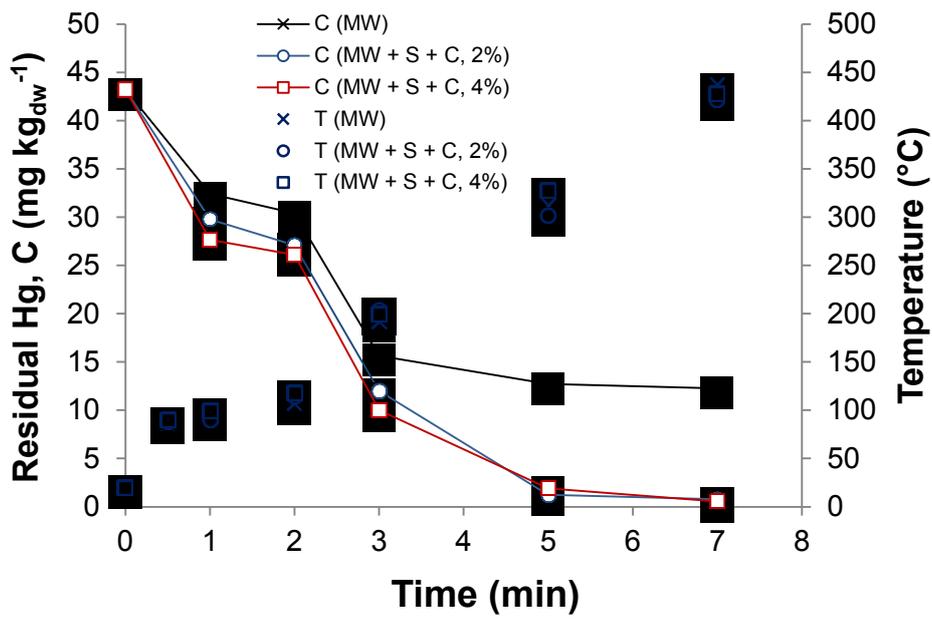
**Figure 2.** Sediment temperature variation as a function of the irradiation time for all the MWH treatments investigated.



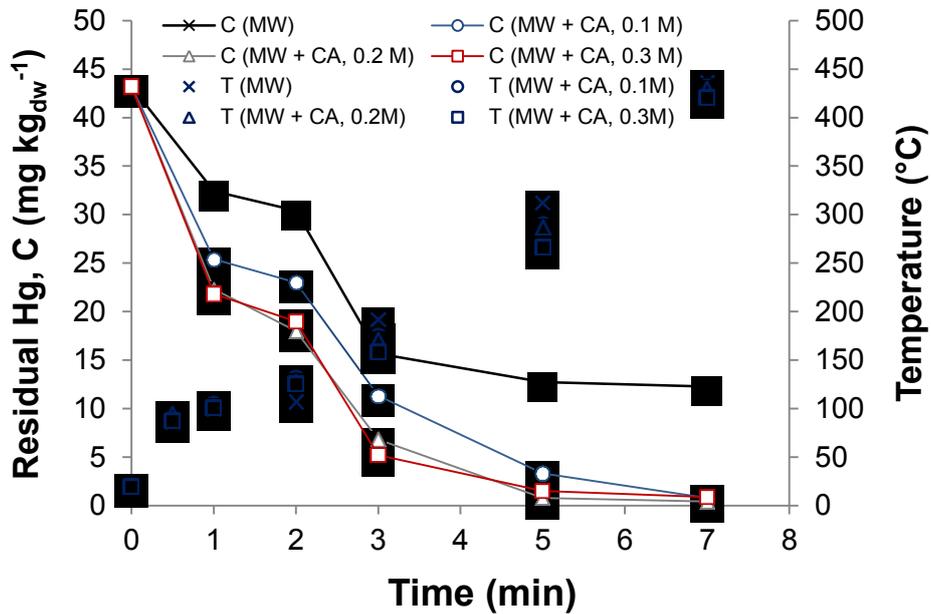
**Figure 3.** Sediment temperature variation as a function of the pore water salinity (MW treatment, irradiation time = 3 min).



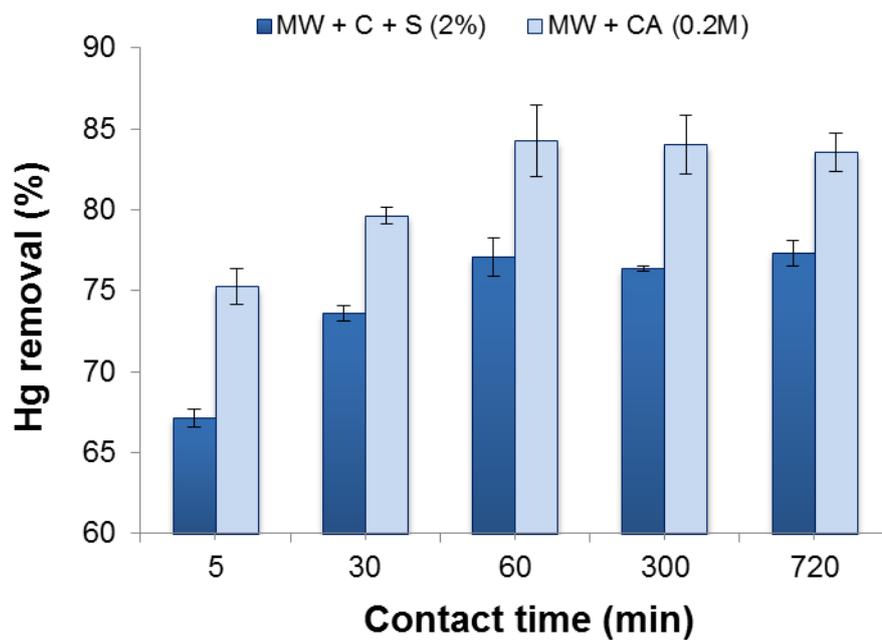
**Figure 4.** Hg residual concentration as a function of the irradiation time during all MWH treatments.



**Figure 5.** Influence of the enhancing agent dose (Tween<sup>®</sup> 80 - MGDA mixture) on sediment temperature profiles and Hg removal kinetics in MW + S + C treatment (irradiation time = 3 min; contact time = 60 min).



**Figure 6.** Influence of the enhancing agent dose (citric acid) on sediment temperature profiles and Hg removal kinetics in MW + CA treatment (irradiation time = 3 min; contact time = 60 min).



**Figure 7.** Influence of the contact time on Hg removal in MW + S + C and MW + CA treatments (irradiation time = 3 min; Tween<sup>®</sup> 80 - MGDA mixture dose = 2%; citric acid dose = 0.2M).

**Table 1.** Sequential extraction procedure with selected Hg fractions [4].

Fraction		Method
F1	Soluble Hg	Deionised water (100 °C). Exchangeable Hg: 1 M C <sub>2</sub> H <sub>3</sub> NaO <sub>2</sub>
F2	Hg bound to carbonates	CH <sub>3</sub> COONa/CH <sub>3</sub> COOH (pH = 5)
F3	Hg bound to Fe and Mn oxides	NH <sub>3</sub> (OH)Cl 0.04 mol L <sup>-1</sup> in 25% CH <sub>3</sub> COOH (96 °C)
F4	Elemental Hg and Hg bound to organic matter	Heating (180 °C) (Hg bound to organic matter); 6 mL HNO <sub>3</sub> + 1 mL 30% H <sub>2</sub> O <sub>2</sub> + MW digestion (Hg bound to organic matter + elemental Hg)
F5	Hg bound to sulphides	6 mL HCl + HNO <sub>3</sub> (3 : 1) + MW digestion

**Table 2.** Experimental matrix.

Experiment	Enhancing agent	Concentration	C : S ratio	Sample moisture (%)
MW (dry)	-	-	-	0
MW	-	-	-	42.2
MW + C	MGDA	2.0%	-	42.2
MW + S	Tween <sup>®</sup> 80	2.0%	-	42.2
MW + C + S (2%)	MGDA, Tween <sup>®</sup> 80	2.0%	1 : 1	42.2
MW + C + S (4%)	MGDA, Tween <sup>®</sup> 80	4.0%	1 : 1	42.2
MW + CA (0.1M)	Citric acid	0.1M	-	42.2
MW + CA (0.2M)	Citric acid	0.2M	-	42.2
MW + CA (0.3M)	Citric acid	0.3M	-	42.2

MW = Microwave.

C = Chelate.

S = Surfactant.

MGDA = Methylglycinediacetic acid.

**Table 3.** Physico - chemical properties of the sediments.

<i>Physical properties</i>	Value
Density (g cm <sup>-3</sup> )	2.37
pH	8.11
Moisture content (%)	42.2
Organic matter (%)	7.4
Sulphides (mg kg <sub>dw</sub> <sup>-1</sup> )	43.6
Salinity (%)	4.3
Dielectric constant ( $\epsilon'$ )	11.3
Loss factor ( $\epsilon''$ )	0.6
<i>Main minerals</i>	Percentage (%)
Calcite	70.5
Quartz	19.5
Clay minerals	8.8
Other	1.2
<i>Heavy metals</i>	Concentration (mg kg <sub>dw</sub> <sup>-1</sup> )
Hg	43.2
As	8.2
Cd	0.4
Cr tot	49.2
Ni	29.8
Pb	28.8
Cu	51.4
Zn	88.2
<i>Organic contaminants</i>	Concentration (mg kg <sub>dw</sub> <sup>-1</sup> )
∑PAHs	2.45
TPHs	6.34

**Table 4.** Residual moisture (%) after different irradiation times for all treatments (initial sediment moisture 42.2%).

Experiment	0.5 min	1 min	2 min	3 min	5 min	7 min
MW	31.6±1.2	5.8±0.3	1.1±0.1	0.6±0.1	0.0±0.0	0.0±0.0
MW + C (2%)	36.1±0.7	7.6±0.7	2.7±0.4	1.5±0.1	0.0±0.0	0.0±0.0
MW + S (2%)	35.2±1.3	7.1±0.4	2.5±0.2	1.2±0.2	0.0±0.0	0.0±0.0
MW + C + S (2%)	32.1±2.1	6.1±0.2	1.5±0.2	0.55±0.1	0.0±0.0	0.0±0.0
MW + C + S (4%)	34.2±2.4	6.7±0.8	2.9±0.7	1.4±0.3	0.0±0.0	0.0±0.0
MW + CA (0.1M)	33.4±1.2	8.1±0.4	2.1±0.2	0.9±0.2	0.0±0.0	0.0±0.0
MW + CA (0.2M)	34.7±1.6	9.1±0.7	1.4±0.3	0.8±0.2	0.0±0.0	0.0±0.0
MW + CA (0.3M)	34.6±1.1	8.8±0.9	1.6±0.1	1.1±0.1	0.0±0.0	0.0±0.0

**Table 5.** Mercury concentration in sediment fractions by sequential extraction before and after MWH.

Fraction	F1 Labile		F2 Carbonate		F3 Oxides		F4 Organic/ Metallic		F5 Sulphides		Total	
	mg kg <sub>dw</sub> <sup>-1</sup>	%	mg kg <sub>dw</sub> <sup>-1</sup>	%	mg kg <sub>dw</sub> <sup>-1</sup>	%	mg kg <sub>dw</sub> <sup>-1</sup>	%	mg kg <sub>dw</sub> <sup>-1</sup>	%	mg kg <sub>dw</sub> <sup>-1</sup>	%
Untreated	0.48± 0.07	1.1	21.82± 1.2	50.5	0.78± 0.03	1.8	15.68± 1.3	36.3	4.45± 0.3	10.3	43.2± 2.2	100.0
MW	0.05± 0.1	0.4	3.33± 0.4	27.2	0.44± 0.05	3.6	4.42± 0.5	36.1	4.02± 0.7	32.8	12.26± 1.3	100.0
MW + C (2%)	0.00± 0.0	0.0	0.33± 0.02	6.0	0.20± 0.03	3.7	4.01± 0.6	73.3	0.93± 0.03	17.0	5.47± 0.6	100.0
MW + S (2%)	0.00± 0.0	0.0	2.68± 0.3	29.9	0.52± 0.06	5.8	1.44± 0.05	16.1	4.33± 0.05	48.3	8.97± 0.7	100.0
MW + C + S (2%)	0.00± 0.0	0.0	0.00± 0.0	0.0	0.00± 0.0	0.0	0.10± 0.05	17.9	0.46± 0.03	82.1	0.56± 0.02	100.0
MW + CA (0.2M)	0.00± 0.0	0.0	0.00± 0.0	0.0	0.00± 0.0	0.0	0.00± 0.0	0.0	0.43± 0.01	100.0	0.43± 0.08	100.0