Marine Pollution Bulletin 180 (2022) 113771

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Cd transfers during marine sediment resuspension over short and long-term period: Associated risk for coastal water quality

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ARTICLE INFO

Keywords:
Cadmium
Remobilization
Sediment resuspension
Water quality
Environmental quality standards (EQS)

ABSTRACT

Cadmium (Cd) is a highly toxic metal, regularly monitored uniformly for water quality across Europe, but scarcely for sediments. This study was designed to compare the kinetics of Cd remobilization and the amplitude of its transfers with different marine sediments. The results showed a highly reproducible transfer kinetics. Dissolved Cd was strongly and quickly removed from the dissolved phase (from 5 min up to 7 h). Then, the dissolved Cd concentration increased progressively to reach a maximal value after two weeks of mixing. The influence of the resuspension intensity representing light wind-induced resuspension up to dredging operations was observed after 2 weeks. The intensity of the sediment resuspension clearly impacted the amplitude of Cd remobilization, dissolved Cd ranging from a few ngL^{-1} to few hundreds of ngL^{-1}, exceeding the maximal dissolved Cd concentration accepted by the European Union Water Framework Directive (WFD-2008/105 32/EC).

1. Introduction

Coastal areas are of great interest for humankind, due to the huge amount of resources therein, leading to an increase in population along the coastlines. While the population increased, sanitary infrastructure did not, causing an increase of contaminants release towards the environment occurs, threatening the ecosystems, the marine species, and the human population health. To protect the marine environment, the European Union defined environmental regulations concerning both seawater and sediments. Concerning the concentration of chemical substances in the water, the European Union Water Framework Directive (WFD-2008/105/EC) has defined environmental quality standards (EQS) thresholds that must not be exceeded to limit human impact on natural ecosystems. EU member states consider sediment contamination for the management of sediments in harbor areas through very heterogeneous standards, mainly in order to limit the resuspension of chemically contaminated particles. Sediments indeed accumulate a high amount of toxic substances (El Houssainy et al., 2020; Guigue et al., 2017; Misson et al., 2016; Schintu et al., 2016, 1991). Both natural and human-induced sediment resuspension often occur in coastal areas and, during resuspension, chemical substances can easily be remobilized through the dissolved phase towards the water column (Ciffroy et al., 2019; Dang et al., 2020; de Freitas et al., 2019). The remobilization of chemical substances from sediment can therefore potentially alter water quality with regard to the EU-WFD.

Among this chemical substances, cadmium (Cd) is a non-essential, harmful trace metal, which causes serious problems due to its severe toxicity towards organisms (Miao and Wang, 2006; Satarug et al., 2003). Cadmium remobilization occurs due to the competition of major seawater cations with trace metals for specific adsorption sites and the formation of metal chloro-complexes (Calmano et al., 1993; Prause et al., 1985; Tahervand and Jalali, 2016; Zhuang et al., 1994). The kinetics of transfer found in the previous literature was only evaluated after 12 h, a time which seems long in view of the process highlighted after a few minutes for other elements (Dang et al., 2020). In this context, the first aim of this study was to study and compare the

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https://doi.org/10.1016/j.marpolbul.2022.113771
Received 11 March 2022; Received in revised form 16 May 2022; Accepted 17 May 2022

succession and amplitude of Cd transfers between the dissolved and particulate phases from minutes to weeks. For that, dissolved Cd concentration was measured over time during resuspension at a fixed sediment:water ratio of sediments sampled in different Mediterranean urbanized bays. Then, on the basis of the observed kinetics, the influence of the quantity of resuspended sediment on Cd release into the dissolved phase was assessed at week scale through a second experiment using different sediment:water ratios, representative of low (wind induced resuspension), medium (nautical activities) and high (dredging activities) resuspension energies. Finally, the measured dissolved Cd concentrations in the second set of experiments was compared to the maximum allowable concentration (MAC) accepted by the EU-WFD EQS.

2. Experimental

2.1. Sample collection, pre-treatment and storage

In order to avoid contamination, sampling devices, bottles, filters and syringes were previously acid-cleaned (10% *v*/v HCl, pro analysis, Fisher Scientific) and fully rinsed with Milli-Q water (18.2 MΩ, Millipore) at laboratory.

For the purpose of this work, sampling campaigns were performed in three Mediterranean urbanized bays: La Spezia (coordinates 44.10482 N, 9.84737 E), Olbia (coordinates 40.92944 N, 9.52812 E) and Toulon (coordinates 43.11454 N, 5.88542 E). The water depth was 12, 4 and 1.4 m for La Spezia, Olbia and Toulon, respectively. At each sampling site, 25 L of surface seawater (0.5 m) were collected using a 4.2 L horizontal van Dorn type water sampler (Wildco, model Beta) and stored in a pre-cleaned 25 L HDPE bottle rinsed 3 times with water from the site. An aliquot of each seawater sample was filtered (0.2 μm on-line syringe filters, cellulose nitrate, Sartorius) and collected into a 125 mL FEP bottle, then acidified (0.2%*v*/v HNO_3 s.p (Merck)) before being UV-irradiated (150 W mercury lamp, Hanau, Germany) for at least 24 h in order to completely decompose organic matter. Samples were then stored at ambient temperature until dissolved Cd analysis. The remaining unprocessed water was kept at ambient temperature and day light until further resuspension experiments.

One sediment core was sampled at each site using an interface corer (Uwitec) equipped with PVC tubes of 90 mm in diameter. The first 30 cm of the core were sliced and homogenized under inert N_2 atmosphere. We are aware that diagenetic processes could have leaded to different physical-chemical properties of the sediment within such a thick sediment slice, however, it represents well the sediment thickness targeted by sediment management operations in harbor areas. An aliquot of each homogenized sediment sample was submitted to centrifugation (4248 RCF (Relative Centrifugal Force), 20 °C for 15 min Sigma 3-18 K) to separate porewater from sediment. After removing the supernatant, the pellet was weighed before and after freeze-drying in order to determine the water content of each sediment. Lyophilized sediments were finally sieved under 2 mm and crushed in a Planetary Ball Mill PM 100 (Retch). Aqua-regia digestion was performed on the lyophilized sediments using a microwave digestion (Milestone) prior to assess the Cd concentration on particles. This protocol was previously described (Cukrov et al., 2019; Tessier et al., 2011) and validated using a certified material (PACS-2 National Research Council of Canada; $n = 20$, accuracy between 0.9 and 7% according to the considered element; Tessier et al., 2011). In order to determine the easily exchangeable fraction of Cd, an acid extraction (1 M HCl) was performed (Larrose et al., 2010). The extraction was achieved by mixing 100 mg of freeze-dried homogenous sediment with 10 mL of 1 M HCl (Merck, suprapur solution) in a polypropylene tube shaken head-over-head (6 rpm, Heidolph Reax 20) for 24 h. After centrifugation (4248 RCF, 15 min), the supernatant was filtered through 0.2 μm syringe filters and stored in the dark at 4 °C. Remaining homogenized and wet sediments were kept anoxic at ambient temperature until further resuspension experiment.

2.2. Laboratory resuspension experiments

In order to evaluate the kinetics of Cd remobilization during sediment resuspension, laboratory experiments were launched within 48 h after sampling, using pre-cleaned 5 L PTFE bottles. The sediment was kept under an inter atmosphere (N_2) to prevent sediment oxidation. Experiments were carried out with the same sediment:water ratio for all three sampling locations. Since the sediment collected in the different sites have different water content, the amount of sediment particles added were different, despite an identical mass of wet sediment (Table 1). Two different kind of resuspension experiments were performed. The first series of experiment was carried out to study the kinetics of Cd transfers between sediment and seawater. It was conducted with a sediment:water ratio of 2.5 g of wet sediment per liter of seawater (representing approximately 1 g of dry sediment per liter of seawater) in 5 L PTFE bottle, submitted to continuous head-over-head shaking (15 rpm, Heidolph Reax 20). This ratio was frequently used in previous studies (Dang et al., 2020; Guigue et al., 2017; Millward and Liu, 2003; Moran and Moore, 1991) and represents a resuspension event related to nautical traffic. Water-sediment mixture was sub-sampled (180 mL) at exponentially increasing intervals to allow the coverage of both short and long-term Cd transfer processes: 5, 15, 30 min, 1, 3, 7 h, 1, 2, days, 1 and 2 weeks. The second series of experiment was performed to quantify the impact of the quantity of resuspended sediment onto Cd transfers. Sediment and seawater were mixed in 500 mL FEP bottles during 2 weeks with 10 different sediment:water ratios (0.05, 0.125, 0.25, 0.5, 1.25, 2.5, 5, 12.5, 25, 125 g of wet sediment per liter of seawater representing approximately 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 50 g of dry sediment per liter of seawater, respectively (Table 1). These ratios allowed to represent a large diversity of resuspension processes, from natural wind events in shallow coastal areas (<0.5 gL^{-1}, (Jiang et al., 2020)) to dredging operations ($\sim$10–50 gL^{-1}, (Nichols et al., 1990)). The water-sediment mixture was only sampled after two weeks of mixing. For both experiments, samples were filtered, treated and stored as described above for seawater prior to dissolved Cd concentration

Table 1
: Mass of sediment particles added in the performed experiments.

Performed Experiment	Mass of added particles in La Spezia experiments (g)	Mass of added particles in Olbia experiments (g)	Mass of added particles in Toulon experiments (g)
Kinetics (2.5gL^{-1})	8.10	6.90	6.00
Solid/Liquid ratio (0.05gL^{-1})	0.02	0.01	0.01
Solid/Liquid ratio (0.125gL^{-1})	0.04	0.03	0.03
Solid/Liquid ratio (0.25gL^{-1})	0.08	0.07	0.06
Solid/Liquid ratio (0.5gL^{-1})	0.16	0.14	0.12
Solid/Liquid ratio (1.25gL^{-1})	0.41	0.35	0.3
Solid/Liquid ratio (2.5gL^{-1})	0.81	0.69	0.6
Solid/Liquid ratio (5gL^{-1})	1.62	1.38	1.2
Solid/Liquid ratio (12.5gL^{-1})	4.05	3.45	3.0
Solid/Liquid ratio (25gL^{-1})	8.10	6.90	6.0
Solid/Liquid ratio (125gL^{-1})	40.50	34.50	30.00

measurement.

In parallel of the first series of experiments performed with a sediment:water ratio of 2.5 gL^{-1}, pH, Eh and O_2 were measured at each interval sampling time and every day until the end of the experiment in a separate 1 L HDPE bottle (with the same conditions and sediment load) to avoid potential contamination by the probes. The pH measurement was carried out with a combined electrode (Ag|AgCl|KCl 3 M) of the microtip type (diameter of 5 mm, Bioblock Scientific). The latter has been calibrated beforehand (before each new set of measurement) using buffer solution at pH 4.01, 7.01 and 10.01 (HANNA). Redox electrode was made of Pt (Radiometer Copenhagen) coupled to the reference electrode in $Hg|Hg_2Cl_2|KCl$ 3 M (Radiometer Analytical, $E_{ref} = 255$ mV/NHE, 25 °C), calibrated with the Zobell's solution (Eh = 430 mV/NHE at 25 °C, Thermo Scientific).

Each experiment was performed in one replicate, therefore the standard deviation calculated for the total dissolved Cd concentrations represents the measurements variability.

2.3. Chemical analyses

The concentration of Cd in sediment after aqua-regia digestion or acid extraction were measured by HR-ICP-MS after 20-fold dilution. A certified material was used (PACS-2, National Research Council of Canada) for the validation of the aqua-regia digestion. The measured Cd concentration was PACS-2 was 2.11 ± 0.14 $mgkg^{-1}$ ($n = 5$) while the certified values is 2.11 ± 0.15 $mgkg^{-1}$. The French authorities (JORF n°184 10-08-2000) have defined N1 (1.2 $\mu g_{Cd}g^{-1}$) and N2 (2.4 $\mu g_{Cd}g^{-1}$) levels to evaluate the potential impact of sediment onto the environment. Below N1 level, the potential impact of the sediment is considered neutral or negligible, meaning that the management of the sediment does not therefore require any particular precaution. Between N1 and N2, further investigation may be necessary; the assessments of the overall toxicity of the sediments should be performed. Above N2 Level, an impact on the environment is expected, and the dredged sediment is considered as a hazardous waste which must be stored in appropriate dump. The Italian Ministerial Decree 173/2016 has defined L1 (the lowest chemical level of reference) and L2 (the highest chemical level of reference) levels which, together with the outcome of toxicological tests (weight of evidence criteria), contributes to the classification and identification of appropriate management for marine and brackish sediments to be dredged. Below L1 level (0.3 $\mu g_{Cd}g^{-1}$), with low or no adverse results from ecotoxicological tests, sediment can be dredged and used for beach nourishment, dumped in offshore marine areas (over 3mn), or transported and disposed of in a manner that minimizes the release of contaminants either into solution or by resuspension. Between L1 and L2 levels (0.3–0.8 $\mu g_{Cd}g^{-1}$) with low or no adverse outcome from bioassays, sediment can be dumped in off-shores marine areas (over 3 m) or addressed in confined disposal facilities (CDF) effectively isolated from the environment. An environmental monitoring plan must be foreseen for each option listed above. Finally, above the L2 levels, sediment must be dredged and transported with care, and effectively isolated from the environment upon final disposal.

To determine the organic carbon content, the crushed sediment was acidified with (Fisher Scientific, Analytical Reagent grade, 85%) to eliminate inorganic carbon. Then, the samples were measured on a CHNS flash 2000 (Thermo Electron) following the method described by Benner and Strom (1993). The total sulfur content was measured after mixing around 3 mg of freeze-dried sediments with approximately 1.5 mg of vanadium pentoxide V_2O_5 (Thermo Fisher Scientific). For both carbon and sulfur measurements, two reference soils were used, NC and NCS (Thermo Fisher Scientific). Each sample was analyzed in triplicate.

The particle size distribution was determined using a laser diffraction particle-size analyzer LS 13320 (Beckman Coulter Inc.). Wet sediment samples were dispersed in deionized water and briefly treated in an ultrasonic bath (3 min) prior to measurement. The instrument analysis ranged from 0.4 to 2000 μm.

Dissolved Cd concentrations in UV-irradiated seawater samples were determined by Differential Pulse Anodic Stripping Voltammetry (DPASV). The measurements were carried out using an Autolab-III potentiostat (EcoChemie) equipped with an autosampler. A three-electrode system (663 VA Stand, Metrohm) consisting of Hg working electrode (size 3), Ag|AgCl|3 M KCl reference electrode and Pt counter electrode was used for measurements. Automated measurements were controlled by the GPES 4.9 software (EcoChemie). Quantification of the metals concentrations was performed using the standard addition method, automated using syringe burettes (Pump XE 1000, TECAN). Voltammograms were processed (peak height of 2nd derivative as analytical signal characteristic) using ECDSOFT software (Cobelo-García et al., 2014; Omanović and Branica, 1998). The percentage of Cd desorption from sediment was calculated by subtracting the Cd quantity in the initial seawater from the Cd quantity measured at the end of the experiment and divided by the quantity of Cd added in the mixing solution by sediment particles.

3. Results and discussion

3.1. Sediment and seawater initial characteristics

The salinity of seawater was 37.9 for La Spezia, 37.6 for Olbia and 38.2 for Toulon, while the pH values of overlying water for these three sites were 8.32, 7.55 and 7.87, respectively. The percentage of oxygen saturation of the overlying water was 89, 101 and 90.3%. The initial pH values of the seawater used for the resuspension experiments were 8.30, 8.36 and 7.79 for La Spezia, Olbia and Toulon respectively. The initial dissolved Cd concentrations in seawater were 15.74, 7.87 and 11.24 ngL^{-1} for La Spezia, Olbia and Toulon respectively, which is consistent with the literature for these bays or their coastal surroundings (Breder, 1987; Coclet et al., 2019). The dissolved Cd concentrations in the three harbors were below the admissible dissolved cadmium concentration in seawater (more than 200 mgL^{-1} $CaCO_3$) defined by the EQS (2008/105/EC).

The sediment from La Spezia was equally composed of clay and sand (44 and 46%) while the silt fraction represented only 10%. The sediment from La Olbia and Toulon were mainly composed of clay (65 and 52% respectively) while the sand fraction represented 28 and 40% respectively. Finally, the silt fraction was the lowest one with only 7 and 8% in the sediment from Olbia and Toulon.

Cadmium contents were 0.10, 0.20 and 0.37 μgg^{-1} in the sediment of La Spezia, Olbia and Toulon respectively. Contents observed in Toulon and Olbia sediments are consistent with the literature for these bays (Schintu et al., 1991; Tessier et al., 2011) while the content observed in La Spezia sediment were lower than that previously observed (Breder, 1987). The easily-exchangeable proportion of Cd in the three sediments were 63, 47 and 38% for La Spezia, Olbia and Toulon respectively. Such range of easily exchangeable Cd proportion was already observed in the literature (Dang et al., 2015a; El Houssainy et al., 2020).

The percentage of organic carbon in the sediment was 0.42, 2.12 and 2.39% for La Spezia, Olbia and Toulon respectively. The percentage of total sulfur was 0.35, 0.91% and 0.27% in La Spezia, Olbia and Toulon respectively.

Given that the sediments were sampled in France and Italy, we compared their Cd contents to national laws framing marine sediment management. Sediment from Toulon presented Cd content lower than the regulatory N1 level defined by the French authorities (JORF n°184 10-08-2000). As a consequence, its potential impact regarding Cd is considered neutral or negligible and the management of the sediment does not require any particular precaution. The Cd content in La Spezia and Olbia were below the Italian lower chemical exceedance Level and could thus be dredged, transported and disposed if the release of contaminants into solution or by resuspension is minimized (Italian Ministerial Decree 173/2016).

3.2. Quantity and partitioning of Cd from resuspended sediments in the different experiments

The amount of total particulate and easily-exchangeable Cd added in each experiment are given in Table 2. The input of particulate Cd was 1.6–2.8 times higher in Toulon experiments compared to that of Olbia and La Spezia and the exchangeable fraction was 1.3–1.7 times higher in Toulon experiments compared to that of Olbia and La Spezia.

3.3. Variations of physical-chemical parameters over time

The percentage of dissolved oxygen remained above 100% all along the experiments for both Olbia and Toulon. Unfortunately, the dissolved oxygen couldn't be measured in La Spezia experiment due to a sensor failure. The redox potential (Eh) started 359, 322 and 291 mV in La Spezia, Olbia and Toulon experiments respectively. During the very first three hours Eh dropped down to 125, 53.7 and 170 mV in La Spezia, Olbia and Toulon experiments respectively. Then, Eh started to slightly increase but stayed below the initial seawater values for La Spezia and Toulon experiments, while it reached back the initial seawater value in Olbia experiment. The percentage of dissolved Cd species is greatly influenced by the pH value of seawater (Andreas and Zhang, 2014). Thus, the variations of pH value over time were observed with a 2.5 gL^{-1} sediment:water ratio. The pH value in La Spezia experiment dropped from 8.30 down to 7.87 the first minutes right after the addition of sediment (Fig. 1), while no similar early sharp decrease was observed for Olbia and Toulon (Fig. 1). From 5th minutes of mixing to the end of the experiment, a similar temporal variation of pH was observed for La Spezia and Olbia experiments (Fig. 1, Spearman's correlation test, $\rho = 0.936$, $p < 0.05$). Between 48 h and the end of the experiments, the pH value dropped down to 7.40 and 7.73 for La Spezia and Olbia, respectively. pH decrease during sediment resuspension has already been observed (Cabrol et al., 2017; Dang et al., 2015b; Pía Di Nanno et al., 2007; Zouch et al., 2018) and could suggested a relatively common process governing pH, irrespective of the sediment composition. We have already demonstrated (Layglon et al., 2021) that the pH decrease during sediment resuspension (performed with 50 times higher sediment content) could be abiotically controlled and therefore might result from the increase in dissolved acidic substances. Richards et al. (2018) suggested that the oxidation of acid volatile sulfide (AVS) during the resuspension of anoxic sediment could induce an increasing concentration of dissolved acidic substances. Surprisingly, in the experiment with samples from Toulon, while pH values showed a similar decreasing trend until 8 days of mixing (Spearman's correlation test, $\rho = 0.850$, $\rho = 0.899$ respectively for Toulon-La Spezia and Toulon-Olbia, $p < 0.05$), pH increased from 8 days to the end of the experiment and reached values similar to initial one (Fig. 1). This observation remains unexplained for the moment.

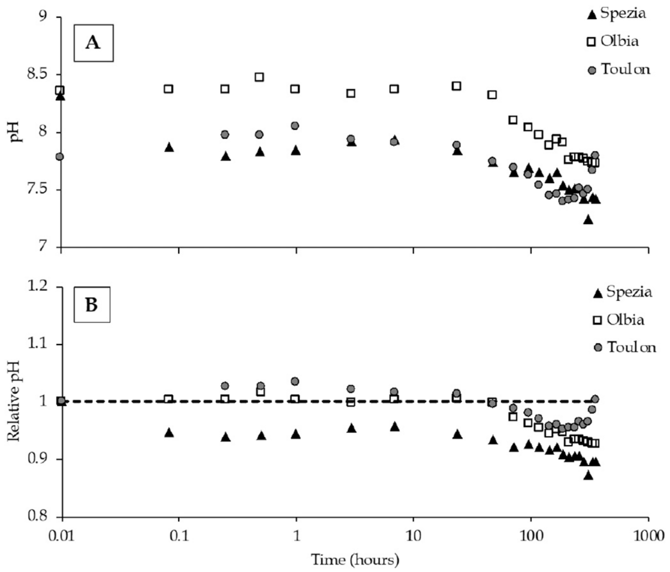

Fig. 1. Variations of pH during sediment resuspensions (2.5 gL^{-1} sediment: water ratio). Panel A represents its absolute variations, with initial values of seawater represented by the symbols on the Y axis line while panel B represents its variations relatively to the initial pH of seawater before sediment addition. As a consequence, a value above the dotted line corresponds to an increase compared to the initial sampled seawater value, whereas a value below this line corresponds to a decrease. No pH data could be recorded for Toulon at 5 min of mixing because of a technical problem.

3.4. Kinetics of Cadmium transfers

First, Cd experienced a strong and fast removal from the dissolved phase, observed within a few minutes (Fig. 2A) for all experiments. As a consequence, dissolved concentrations were decreased by a factor 15.3, 10.8 and 8.4 for La Spezia, Toulon and Olbia, respectively (Fig. 1B). Cd is known to have a strong affinity for carbonates and clays (Pickering, 1983; Shirvani et al., 2006; Superville et al., 2015; Zheng et al., 2007), as well as with OM (Tahervand and Jalali, 2016), therefore its removal might be attributed to its adsorption onto resuspended carbonates, OM and/or clays. Dissolved Cd concentrations then remained rather stable at low concentrations up to 7 h to 1 day of mixing. Finally, dissolved Cd concentrations increased to reach maximal and stable values after one week (Fig. 2A), showing that dissolved Cd dynamics were similar in the three experiments. Such Cd remobilization was already explained in the literature, and is related to the competition of major seawater cations with trace metals for specific adsorption sites and the formation of metal chloro-complexes (Calmano et al., 1993; Prause et al., 1985; Tahervand and Jalali, 2016; Zhuang et al., 1994).

At the end of the experiments, the maximal dissolved Cd

Table 2

: Amount of total particulate and easily-exchangeable Cd expressed in ng added in each performed experiment.

Performed Experiment	Amount of total particulate and easily-exchangeable Cd in La Spezia (ng)	Amount of total particulate and easily-exchangeable Cd in Olbia (ng)	Amount of total particulate and easily-exchangeable Cd in Toulon (ng)
Kinetics (2.5gL^{-1})	778 | 490	1380 | 649	2220 | 844
Solid/Liquid ratio (0.05gL^{-1})	1.92 | 1.21	2.00 | 0.94	3.70 | 1.41
Solid/Liquid ratio (0.125gL^{-1})	3.84 | 2.42	6.00 | 2.82	11.1 | 4.22
Solid/Liquid ratio (0.25gL^{-1})	7.68 | 4.84	14.0 | 6.58	22.2 | 8.44
Solid/Liquid ratio (0.5gL^{-1})	15.4 | 9.68	28.0 | 13.2	44.4 | 16.9
Solid/Liquid ratio (1.25gL^{-1})	39.4 | 24.8	70.0 | 32.9	111 | 42.2
Solid/Liquid ratio (2.5gL^{-1})	77.8 | 49.0	138 | 64.9	222 | 84.4
Solid/Liquid ratio (5gL^{-1})	156 | 98.0	276 | 1230	444 | 169
Solid/Liquid ratio (12.5gL^{-1})	388 | 245	690 | 324	1110 | 422
Solid/Liquid ratio (25gL^{-1})	778 | 490	1380 | 649	2220 | 844
Solid/Liquid ratio (125gL^{-1})	3888 | 2449	6900 | 3243	11,100 | 4218

concentrations were 90.0, 60.8 and 240.6 ngL^{-1} for La Spezia, Olbia and Toulon experiments, respectively (Fig. 2A), representing a huge increase in concentration compared to the initial seawater concentrations (5.8-fold, 8.1-fold and 22.1-fold higher in La Spezia, Olbia and Toulon, respectively). When focusing on the absolute Cd concentration (Fig. 2A), during the desorption step, the maximal increase in dissolved Cd was higher in Toulon (229 ngL^{-1}) than in La Spezia (74 ngL^{-1}) and the lowest value was found for Olbia (53 ngL^{-1}). As seen above, the input of particulate Cd was 1.6 and 2.8 times higher in Toulon experiments compared to that of La Spezia and Olbia, respectively. The percentage of desorbed Cd was similar in La Spezia and Toulon experiments (47 and 51% respectively) and was found to be smaller in Olbia experiment (20%). The difference in the percentage of desorbed Cd did neither correspond to differences in Cd total content between the three sediments, nor to their differences in easily-exchangeable fraction of Cd. Therefore, none of total Cd content and Cd easily-extractable fraction appeared as the main parameter leading to Cd remobilization when, however, they are the most commonly measured parameters and those used for the management of sediments. The more alkaline pH measured in the experiment carried out with Olbia sediment (8.1 ± 0.20 compared to 7.70 ± 0.08 and 7.63 ± 0.16 for La Spezia and Toulon, respectively) could explain the lowest Cd release into seawater (Fig. 1) (Andreas and Zhang, 2014). While the kinetics of Cd remobilization were similar in the three experiments, the amplitude of Cd adsorption/desorption were dependent on the mixing (Fig. 2).

3.5. *Effects of the quantity of resuspended particles onto cadmium transfers*

Using a ratio of 2.5 gL^{-1}, we showed that the kinetics of Cd remobilization was similar with different initial samples, and that the maximal dissolved Cd concentrations was observed after 2 weeks of mixing. Therefore, we evaluated the impact of sediment resuspension intensity after 2 weeks of mixing by varying the sediment:water ratio. The increase of suspended particulate matter led to an increase in final dissolved Cd concentrations in the three experiments (Fig. 3). However, the increase in dissolved Cd concentration was not linearly linked to the increase of suspended particulate matter and thus of the quantity of total or easily extractable Cd (Fig. 3), pointing out a threshold effect that remains to be explained. The dissolved Cd concentrations obtained with a ratio of 2.5 gL^{-1} are consistent with the one observed in the previous kinetics experiments (Figs. 2 and 3). For the highest S/L ratio (*i.e.* 125 gL^{-1}), representative of a suspended particulate matter concentration in seawater during dredging operations (Nichols et al., 1990), dissolved Cd increased up to 615, 2050 and 3624 ngL^{-1} in Olbia, La Spezia and Toulon experiments, respectively, corresponding to a 82-fold, 132-fold and 330-fold increase when compared to the initial concentration in seawater (Fig. 3). Therefore, the maximal concentration accepted by the EQS (2008/105/EC) (1500 ngL^{-1} in water containing more than 200 mgL^{-1} $CaCO_3$) was exceeded for experiments of La Spezia (by a factor 1.4) and Toulon (by a factor 2.4) experiments. These experiments showed that the EQS were punctually overpassed even if the Cd contents were lower than the N1 and L1 levels for La Spezia, and below the N1 and L2 levels for Toulon sediments. Although this was very punctual and result of a laboratory simulation, this work demonstrated the potential contribution of sediment resuspension to the dissolved Cd contamination, especially in case of strong resuspension by human activities. Once dissolved, the remobilized Cd can poison biota or be exported towards the open sea and therefore contribute to its large-scale dispersion. In addition, this study was performed with slightly contaminated sediment, while more contaminated sediments could perhaps challenge the EQS at lower sediment:water ratio therefore events of lower energy (storm, nautical traffic, …) (Abi-Ghanem et al., 2014; Dang et al., 2015a; El Houssainy et al., 2020; Schintu et al., 2016).

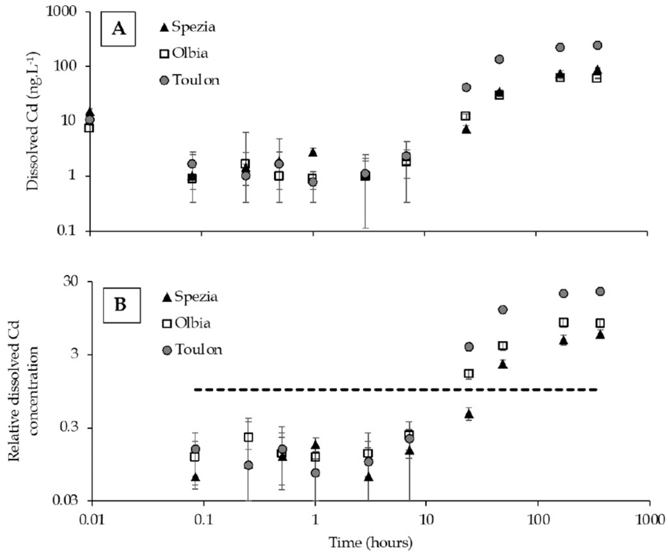

Fig. 2. Variations of dissolved Cd concentration during sediment resuspensions (2.5 gL^{-1} sediment:water ratio). Panel A represents its absolute variation while Panel B represents its relative variation. As a consequence, a value above the black dotted line will correspond to an increase compared to Cd in initial seawater, whereas a value below this line will correspond to a decrease. Note that the x and y axis are on log scale. The dissolved Cd concentration indicated at x = 0.01 in panel A represents Cd concentration of the initial seawater before the addition of sediment.

4. Conclusion

The aim of this study was to compare the kinetics of Cd remobilization and the amplitude of its transfers with different marine sediments resuspended at different sediment:water ratios. The results of the study showed that after initial decrease of dissolved Cd, the sharp increase in Cd concentration occurred after ~7 h of mixing time, leading to a clear contamination of the initial seawater after 24 h, reaching the maximal value after 1 week of mixing. The kinetics of the adsorption/desorption processes seemed similar, regardless of the sediment quality, but the amplitude of Cd concentration decrease/increase was dependent of the sediment characteristics. The amplitude of Cd remobilization was only partially related to the total and easily-exchangeable Cd contents in the sediment as well as the pH value of mixing. The intensity of the sediment resuspension (*i.e.* the amount of resuspended sediment in seawater) modified the amplitude of Cd remobilization. The maximum allowable concentration (MAC) accepted by the EU-WFD EQS was largely exceeded when the quantity of resuspended sediment was close to the one encountered during dredging operations, leading to an increase of dissolved Cd concentration by several orders of magnitude. These results

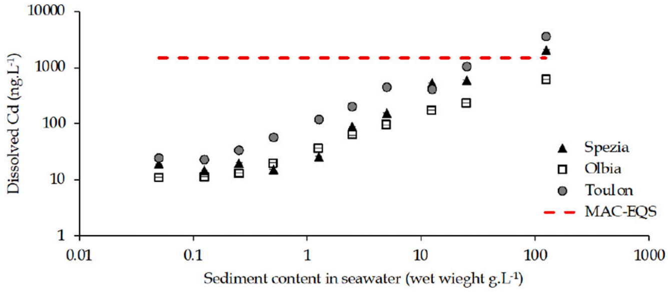

Fig. 3. Variations of dissolved Cd as a function of the sediment content (wet weight in gL^{-1}) in seawater. The red dotted line represents the maximum allowable concentration (MAC-EQS) defined by the Environmental Quality Standards (EQS) in seawater. Both axis are presented in log scale to better visualize data.

clearly put forward the need to better characterize the processes leading to Cd remobilization and controlling the magnitude of the contamination induced. An effort towards mixing conditions better representing field conditions is now required to confront more realistic data to regulation thresholds and to contribute to regulation harmonization between countries. This study provides new bases for decision-makers and local authorities concerned by sediment management and water quality protection.

Funding

This study was supported by SE.D.RI.PORT. (SEdimenti, Dragagi e RIschi PORTuali, Interreg Marittimo IT/FR 2017–2020, co-funded by European Regional Development Fund). This work was realized also as a part of the project "New methodological approach in biogeochemical studies of trace metal speciation in coastal aquatic ecosystems" (MEBTRACE) (IP-2014-09-7530), financially supported by the Croatian Science Foundation. N. Layglon PhD was partly funded by Sud region and supported by LASEM Toulon.

CRediT authorship contribution statement

Nicolas Layglon: Methodology, Investigation, Validation, Formal analysis, Data interpretation and curation, Visualization, Writing – original draft, Writing – Review & Editing.

Véronique Lenoble: Methodology, Investigation, Validation, Data Curation, Writing – Review & Editing.

Louis Longo: Conceptualization, Investigation, Formal analysis, Review & Editing.

Sébastien D'Onofrio: Conceptualization, Investigation, Formal analysis, Review & Editing.

Stéphane Mounier: Methodology, Investigation, Validation, Data Curation, Writing – Review & Editing.

J-U Mullot: Resources, Review & Editing.

Davide Sartori: Resources, Review & Editing.

Dario Omanović: Methodology, Investigation, Validation, Data Curation, Writing – Review & Editing.

Cédric Garnier: Conceptualization, Methodology, Funding acquisition.

Benjamin Misson: Conceptualization, Methodology, Investigation, Validation, Formal analysis, Data interpretation, Writing – Review & Editing, Supervision, Project coordination, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors want to thank Erwan Tessier, the French Navy, Aurélie Portas, Emilie Pasero and Alexis Canino for their help regarding the sampling as well as Christian Martino for instrumentation repairs. The authors are thankful to the ARPAL and ISPRA institutions as well as the Olbia's mussel cooperative for the organization of the sampling campaign in Italy. This work is dedicated to our colleague and friend Cédric Garnier, prematurely gone.

References

Abi-Ghanem, C., Khalaf, G., Najjar, E., 2014. Distribution of Lead, cadmium, and vanadium in lebanese coastal sediments and mussels. J. Coast. Res. 297, 1074–1080. https://doi.org/10.2112/JCOASTRES-D-12-00187.1.

Andreas, R., Zhang, J., 2014. Characteristics of adsorption interactions of Cadmium(II) onto humin from peat soil in freshwater and seawater media. Bull. Environ. Contam. Toxicol. 92, 352–357. https://doi.org/10.1007/s00128-014-1205-x.

Benner, R., Strom, M., 1993. A critical evaluation of the analytical blank associated with DOC measurements by high-temperature catalytic oxidation. Mar. Chem. 41, 153–160. https://doi.org/10.1016/0304-4203(93)90113-3.

Breder, R., 1987. Distribution of heavy metals in ligurian and tyrrhenian coastal waters. Sci. Total Environ. 60, 197–212. https://doi.org/10.1016/0048-9697(87)90416-5.

Cabrol, L., Quéméneur, M., Misson, B., 2017. Inhibitory effects of sodium azide on microbial growth in experimental resuspension of marine sediment. J. Microbiol. Methods 133, 62–65. https://doi.org/10.1016/j.mimet.2016.12.021.

Calmano, W., Förstner, U., Hong, J., 1993. Mobilization and scavenging of heavy metals following resuspension of anoxic sediments from the Elbe River. In: Alpers, C.N., Blowes, D.W. (Eds.), Environmental Geochemistry of Sulfide Oxidation, pp. 298–321. https://doi.org/10.1021/bk-1994-0550.ch021.

Ciffroy, P., Monnin, L., Garnier, J.-M., Ambrosi, J.-P., Radakovitch, O., 2019. Modelling geochemical and kinetic processes involved in lead (Pb) remobilization during resuspension events of contaminated sediments. Sci. Total Environ. 679, 159–171. https://doi.org/10.1016/j.scitotenv.2019.04.192.

Cobelo-García, A., Santos-Echeandía, J., López-Sánchez, D.E., Almécija, C., Omanović, D., 2014. Improving the voltammetric quantification of ill-defined peaks using second derivative signal transformation: example of the determination of platinum in water and sediments. Anal. Chem. 86, 2308–2313. https://doi.org/10.1021/ac403558y.

Coclet, C., Garnier, C., Durrieu, G., Omanović, D., D'Onofrio, S., Le Poupon, C., Mullot, J.-U., Briand, J.-F., Misson, B., 2019. Changes in bacterioplankton communities resulting from direct and indirect interactions with trace metal gradients in an urbanized marine coastal area. Front. Microbiol. 10, 257. https://doi.org/10.3389/fmicb.2019.00257.

Cukrov, Nuša, Doumandji, N., Garnier, C., Tucaković, I., Dang, D.H., Omanović, D., Cukrov, Neven, 2019. Anthropogenic mercury contamination in sediments of Krka River estuary (Croatia). Environ. Sci. Pollut. Res. https://doi.org/10.1007/s11356-019-07475-y.

Dang, D.H., Lenoble, V., Durrieu, G., Omanović, D., Mullot, J.-U., Mounier, S., Garnier, C., 2015a. Seasonal variations of coastal sedimentary trace metals cycling: insight on the effect of manganese and iron (oxy)hydroxides, sulphide and organic matter. Mar. Pollut. Bull. 92, 113–124. https://doi.org/10.1016/j.marpolbul.2014.12.048.

Dang, D.H., Schäfer, J., Brach-Papa, C., Lenoble, V., Durrieu, G., Dutruch, L., Chiffoleau, J.-F., Gonzalez, J.-L., Blanc, G., Mullot, J.-U., Mounier, S., Garnier, C., 2015b. Evidencing the impact of coastal contaminated sediments on mussels through pb stable isotopes composition. Environ. Sci. Technol. 49, 11438–11448. https://doi.org/10.1021/acs.est.5b01893.

Dang, D.H., Layglon, N., Ferretto, N., Omanović, D., Mullot, J.-U., Lenoble, V., Mounier, S., Garnier, C., 2020. Kinetic processes of copper and lead remobilization during sediment resuspension of marine polluted sediments. Sci. Total Environ. 698, 134120 https://doi.org/10.1016/j.scitotenv.2019.134120.

de Freitas, A.R., Rodrigues, A.P.de C., Monte, C.do N., Freire, A.S., Santelli, R.E., Machado, W., Sabadini-Santos, E., 2019. Increase in the bioavailability of trace metals after sediment resuspension. SN Appl. Sci. 1, 1288. https://doi.org/10.1007/s42452-019-1276-8.

El Houssainy, A., Abi-Ghanem, C., Dang, D.H., Mahfouz, C., Omanović, D., Khalaf, G., Mounier, S., Garnier, C., 2020. Distribution and diagenesis of trace metals in marine sediments of a coastal Mediterranean area: st Georges bay (Lebanon). Mar. Pollut. Bull. 155, 111066 https://doi.org/10.1016/j.marpolbul.2020.111066.

Guigue, C., Tedetti, M., Dang, D.H., Mullot, J.-U., Garnier, C., Goutx, M., 2017. Remobilization of polycyclic aromatic hydrocarbons and organic matter in seawater during sediment resuspension experiments from a polluted coastal environment: insights from Toulon Bay (France. Environ. Pollut. 229, 627–638. https://doi.org/10.1016/j.envpol.2017.06.090.

Jiang, M., Pang, C., Liu, Z., Jiang, J., 2020. Sediment resuspension in winter in an exceptional low suspended sediment concentration area off Qinhuangdao in the Bohai Sea. Estuar. Coast. Shelf Sci. 245, 106859 https://doi.org/10.1016/j.ecss.2020.106859.

Larrose, A., Coynel, A., Schäfer, J., Blanc, G., Massé, L., Maneux, E., 2010. Assessing the current state of the gironde estuary by mapping priority contaminant distribution and risk potential in surface sediment. Appl. Geochem. 25, 1912–1923. https://doi.org/10.1016/j.apgeochem.2010.10.007.

Layglon, N., Misson, B., Gallois, N., D'Onofrio, S., Lenoble, V., Mounier, S., Omanović, D., Garnier, C., 2021. Negligible microbial heterotrophic quantitative contribution onto trace metals remobilization during marine sediment resuspension - insights from a Mediterranean urbanized bay. Mar. Chem. 103981 https://doi.org/10.1016/j.marchem.2021.103981.

Miao, A., Wang, W., 2006. Cadmium toxicity to two marine phytoplankton under different nutrient conditions. Aquat. Toxicol. 78, 114–126. https://doi.org/10.1016/j.aquatox.2006.02.008.

Millward, G., Liu, Y., 2003. Modelling metal desorption kinetics in estuaries. Sci. Total Environ. 314–316, 613–623. https://doi.org/10.1016/S0048-9697(03)00077-9.

Misson, B., Garnier, C., Lauga, B., Dang, D.H., Ghiglione, J.-F., Mullot, J.-U., Duran, R., Pringault, O., 2016. Chemical multi-contamination drives benthic prokaryotic diversity in the anthropized Toulon Bay. Sci. Total Environ. 556, 319–329. https://doi.org/10.1016/j.scitotenv.2016.02.038.

Moran, S.B., Moore, R.M., 1991. The potential source of dissolved aluminum from resuspended sediments to the North Atlantic deep water. Geochim. Cosmochim. Acta 55, 2745–2751. https://doi.org/10.1016/0016-7037(91)90441-7.

Nichols, M., Diaz, R.J., Schaffner, L.C., 1990. Effects of hopper dredging and sediment dispersion, Chesapeake bay. Environ. Geol. Water Sci. 15, 31–43. https://doi.org/10.1007/BF01704879.

Omanović, D., Branica, M., 1998. Automation of voltammetric measurements by polarographic analyser PAR 384B. Croat. Chem. Acta 71, 421–433.

Pía Di Nanno, M., Curutchet, G., Ratto, S., 2007. Anaerobic sediment potential acidification and metal release risk assessment by chemical characterization and batch resuspension experiments. J. Soils Sediments 7, 187–194. https://doi.org/10.1065/jss2007.04.220.

Pickering, W.F., 1983. Extraction of copper, lead, zinc or cadmium ions sorbed on calcium carbonate. Water Air Soil Pollut. 20 https://doi.org/10.1007/BF00284635.

Prause, B., Rehm, E., Schulz-Baldes, M., 1985. The remobilization of pb and cd from contaminated dredge spoil after dumping in the marine environment. Environ. Technol. Lett. 6, 261–266. https://doi.org/10.1080/09593338509384343.

Richards, C.M., van Puffelen, J.L., Pallud, C., 2018. Effects of sediment resuspension on the oxidation of acid-volatile sulfides and release of metals (iron, manganese, zinc) in pescadero estuary (CA, USA): effects of sediment resuspension on AVS oxidation. Environ. Toxicol. Chem. 37, 993–1006. https://doi.org/10.1002/etc.4047.

Satarug, S., Baker, J.R., Urbenjapol, S., Haswell-Elkins, M., Reilly, P.E.B., Williams, D.J., Moore, M.R., 2003. A global perspective on cadmium pollution and toxicity in non-occupationally exposed population. Toxicol. Lett. 137, 65–83. https://doi.org/10.1016/S0378-4274(02)00381-8.

Schintu, M., Meloni, P., Kudo, A., Contu, A., 1991. Trace metals in sediments from Olbia Bay, Italy. Mar. Pollut. Bull. 22, 360–362.

Schintu, M., Marrucci, A., Marras, B., Galgani, F., Buosi, C., Ibba, A., Cherchi, A., 2016. Heavy metal accumulation in surface sediments at the port of Cagliari (Sardinia, western Mediterranean): environmental assessment using sequential extractions and benthic foraminifera. Mar. Pollut. Bull. 111, 45–56. https://doi.org/10.1016/j.marpolbul.2016.07.029.

Shirvani, M., Shariatmadari, H., Kalbasi, M., Nourbakhsh, F., Najafi, B., 2006. Sorption of cadmium on palygorskite, sepiolite and calcite: equilibria and organic ligand affected kinetics. Colloids Surf. Physicochem. Eng. Asp. 287, 182–190. https://doi.org/10.1016/j.colsurfa.2006.03.052.

Superville, P.-J., Prygiel, E., Mikkelsen, O., Billon, G., 2015. Dynamic behaviour of trace metals in the Deûle River impacted by recurrent polluted sediment resuspensions: from diel to seasonal evolutions. Sci. Total Environ. 506–507, 585–593. https://doi.org/10.1016/j.scitotenv.2014.11.044.

Tahervand, S., Jalali, M., 2016. Sorption, desorption, and speciation of cd, ni, and fe by four calcareous soils as affected by pH. Environ. Monit. Assess. 188 https://doi.org/10.1007/s10661-016-5313-4.

Tessier, E., Garnier, C., Mullot, J.-U., Lenoble, V., Arnaud, M., Raynaud, M., Mounier, S., 2011. Study of the spatial and historical distribution of sediment inorganic contamination in the Toulon bay (France). Mar. Pollut. Bull. 62, 2075–2086. https://doi.org/10.1016/j.marpolbul.2011.07.022.

Zheng, W., Li, X., Yang, Q., Zeng, G., Shen, X., Zhang, Y., Liu, J., 2007. Adsorption of Cd (II) and Cu(II) from aqueous solution by carbonate hydroxylapatite derived from eggshell waste. J. Hazard. Mater. 147, 534–539. https://doi.org/10.1016/j.jhazmat.2007.01.048.

Zhuang, Y., Allen, H.E., Fu, G., 1994. Effect of aeration of sediment on cadmium binding. Environ. Toxicol. Chem. 13, 717–724. https://doi.org/10.1002/etc.5620130505.

Zouch, H., Cabrol, L., Chifflet, S., Tedetti, M., Karray, F., Zaghden, H., Sayadi, S., Quéméneur, M., 2018. Effect of acidic industrial effluent release on microbial diversity and trace metal dynamics during resuspension of coastal sediment. Front. Microbiol. 9 https://doi.org/10.3389/fmicb.2018.03103.