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

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20 Abstract

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

32  
33 Keywords: cadmium; remobilization; sediment resuspension; water quality; Environmental  
34 Quality Standards (EQS)

## I 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 12h, a time which seems long in view of the process highlighted after a few

61 minutes for other elements (*Dang et al., 2020*). In this context, the first aim of this study was  
62 to study and compare the succession and amplitude of Cd transfers between the dissolved and  
63 particulate phases from minutes to weeks. For that, dissolved Cd concentration was measured  
64 over time during resuspension at a fixed sediment:water ratio of sediments sampled in  
65 different Mediterranean urbanized bays. Then, on the basis of the observed kinetics, the  
66 influence of the quantity of resuspended sediment on Cd release into the dissolved phase was  
67 assessed at week scale through a second experiment using different sediment:water ratios,  
68 representative of low (wind induced resuspension), medium (nautical activities) and high  
69 (dredging activities) resuspension energies. Finally, the measured dissolved Cd  
70 concentrations in the second set of experiments was compared to the maximum allowable  
71 concentration (MAC) accepted by the EU-WFD EQS.

## 72 II Experimental

### 73 II.1 Sample collection, pre-treatment and storage

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

77 For the purpose of this work, sampling campaigns were performed in three  
78 Mediterranean urbanized bays: La Spezia (coordinates 44.10482 N, 9.84737 E), Olbia  
79 (coordinates 40.92944 N, 9.52812 E) and Toulon (coordinates 43.11454 N, 5.88542 E). **The water**  
80 **depth was 12, 4 and 1.4 m for La Spezia, Olbia and Toulon, respectively.** At each sampling  
81 site, 25 L of surface seawater (0.5 m) were collected using a 4.2 L horizontal van Dorn type  
82 water sampler (Wildco, model Beta) and stored in a pre-cleaned 25 L HDPE bottle rinsed 3  
83 times with water from the site. An aliquot of each seawater sample was filtered (0.2  $\mu$ m on-  
84 line syringe filters, cellulose nitrate, Sartorius) and collected into a 125 mL FEP bottle, then  
85 acidified (0.2%v/v HNO<sub>3</sub> s.p (Merck)) before being UV-irradiated (150 W mercury lamp,

86 Hanau, Germany) for at least 24 h in order to completely decompose organic matter. Samples  
87 were then stored at ambient temperature until dissolved Cd analysis. The remaining  
88 unprocessed water was kept at ambient temperature and day light until further resuspension  
89 experiments.

90 One sediment core was sampled at each site using an interface corer (Uwitec) equipped  
91 with PVC tubes of 90 mm in diameter. The first 30 cm of the core were sliced and homogenized  
92 under inert N<sub>2</sub> atmosphere. We are aware that diagenetic processes could have led to  
93 different physical-chemical properties of the sediment within such a thick sediment slice,  
94 however, it represents well the sediment thickness targeted by sediment management  
95 operations in harbor areas. An aliquot of each homogenized sediment sample was submitted  
96 to centrifugation (4248 RCF (Relative Centrifugal Force), 20 °C for 15 min Sigma 3-18K) to  
97 separate porewater from sediment. After removing the supernatant, the pellet was weighed  
98 before and after freeze-drying in order to determine the water content of each sediment.  
99 Lyophilized sediments were finally sieved under 2 mm and crushed in a Planetary Ball Mill  
100 PM 100 (Retch). Aqua-regia digestion was performed on the lyophilized sediments using a  
101 microwave digestion (Milestone) prior to assess the Cd concentration on particles. This  
102 protocol was previously described (*Cukrov et al., 2019; Tessier et al., 2011*) and validated  
103 using a certified material (PACS-2 National Research Council of Canada; n = 20, accuracy  
104 between 0.9 and 7% according to the considered element; *Tessier et al., 2011*). In order to  
105 determine the easily exchangeable fraction of Cd, an acid extraction (1 M HCl) was performed  
106 (*Larrose et al., 2010*). The extraction was achieved by mixing 100 mg of freeze-dried  
107 homogenous sediment with 10 mL of 1 M HCl (Merck, suprapur solution) in a polypropylene  
108 tube shaken head-over-head (6 rpm, Heidolph Reax 20) for 24 h. After centrifugation (4,248  
109 RCF, 15 min), the supernatant was filtered through 0.2 µm syringe filters and stored in the

110 dark at 4 °C. Remaining homogenized and wet sediments were kept anoxic at ambient  
111 temperature until further resuspension experiment.

## 112 II.2 Laboratory resuspension experiments

113 In order to evaluate the kinetics of Cd remobilization during sediment resuspension,  
114 laboratory experiments were launched within 48 h after sampling, using pre-cleaned 5L PTFE  
115 bottles. The sediment was kept under an inter atmosphere (N<sub>2</sub>) to prevent sediment oxidation.  
116 Experiments were carried out with the same sediment:water ratio for all three sampling  
117 locations. Since the sediment collected in the different sites have different water content, the  
118 amount of sediment particles added were different, despite an identical mass of wet sediment  
119 (*Table 1*). Two different kind of resuspension experiments were performed. The first series of  
120 experiment was carried out to study the kinetics of Cd transfers between sediment and  
121 seawater. It was conducted with a sediment:water ratio of 2.5 g of wet sediment per liter of  
122 seawater (representing approximately 1 g of dry sediment per liter of seawater) in 5L PTFE  
123 bottle, submitted to continuous head-over-head shaking (15 rpm, Heidolph Reax 20). This ratio  
124 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  
126 nautical traffic. Water-sediment mixture was sub-sampled (180 mL) at exponentially  
127 increasing intervals to allow the coverage of both short and long-term Cd transfer processes:  
128 5, 15, 30 min, 1, 3, 7 h, 1, 2, days, 1 and 2 weeks. The second series of experiment was performed  
129 to quantify the impact of the quantity of resuspended sediment onto Cd transfers. Sediment  
130 and seawater were mixed in 500 mL FEP bottles during 2 weeks with 10 different  
131 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  
132 of seawater representing approximately 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 50 g of dry sediment  
133 per liter of seawater, respectively (*Table 1*). These ratios allowed to represent a large diversity  
134 of resuspension processes, from natural wind events in shallow coastal areas (<0.5 gL<sup>-1</sup>, (*Jiang*

135 *et al., 2020*) to dredging operations ( $\sim 10\text{-}50\text{ gL}^{-1}$ , (*Nichols et al., 1990*)). The water-sediment  
 136 mixture was only sampled after two weeks of mixing. For both experiments, samples were  
 137 filtered, treated and stored as described above for seawater prior to dissolved Cd  
 138 concentration measurement.

139 In parallel of the first series of experiments performed with a sediment:water ratio of  
 140  $2.5\text{ gL}^{-1}$ , pH, Eh and O<sub>2</sub> were measured at each interval sampling time and every day until the  
 141 end of the experiment in a separate 1 L HDPE bottle (with the same conditions and sediment  
 142 load) to avoid potential contamination by the probes. The pH measurement was carried out  
 143 with a combined electrode (Ag|AgCl|KCl 3 M) of the microtip type (diameter of 5 mm,  
 144 Bioblock Scientific). The latter has been calibrated beforehand (before each new set of  
 145 measurement) using buffer solution at pH 4.01, 7.01 and 10.01 (HANNA). Redox electrode was  
 146 made of Pt (Radiometer Copenhagen) coupled to the reference electrode in Hg|Hg<sub>2</sub>Cl<sub>2</sub>|KCl 3  
 147 M (Radiometer Analytical, E<sub>ref</sub> = 255 mV/NHE, 25°C), calibrated with the Zobell's solution (Eh  
 148 = 430 mV/NHE at 25°C, Thermo Scientific).

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

151 *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 ( $2.5\text{gL}^{-1}$ )	8.10	6.90	6.00
Solid/Liquid ratio ( $0.05\text{gL}^{-1}$ )	0.02	0.01	0.01
Solid/Liquid ratio ( $0.125\text{gL}^{-1}$ )	0.04	0.03	0.03
Solid/Liquid ratio ( $0.25\text{gL}^{-1}$ )	0.08	0.07	0.06
Solid/Liquid ratio ( $0.5\text{gL}^{-1}$ )	0.16	0.14	0.12
Solid/Liquid ratio ( $1.25\text{gL}^{-1}$ )	0.41	0.35	0.3



Solid/Liquid ratio (2.5gL <sup>-1</sup> )	0.81	0.69	0.6
Solid/Liquid ratio (5gL <sup>-1</sup> )	1.62	1.38	1.2
Solid/Liquid ratio (12.5gL <sup>-1</sup> )	4.05	3.45	3.0
Solid/Liquid ratio (25gL <sup>-1</sup> )	8.10	6.90	6.0
Solid/Liquid ratio (125gL <sup>-1</sup> )	40.50	34.50	30.00

### II.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  $2.11 \pm 0.14 \text{ mgkg}^{-1}$  (n=5) while the certified values is  $2.11 \pm 0.15 \text{ mgkg}^{-1}$ . The French authorities (JORF n°184 10-08-2000) have defined N1 (1.2  $\mu\text{gCdg}^{-1}$ ) and N2 (2.4  $\mu\text{gCdg}^{-1}$ ) 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 ( $0.3 \mu\text{gCdg}^{-1}$ ), 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

172 disposed of in a manner that minimizes the release of contaminants either into solution or by  
173 resuspension. Between L1 and L2 levels ( $0.3 - 0.8 \mu\text{gCd g}^{-1}$ ) with low or no adverse outcome  
174 from bioassays, sediment can be dumped in off-shores marine areas (over 3 m) or addressed  
175 in confined disposal facilities (CDF) effectively isolated from the environment. An  
176 environmental monitoring plan must be foreseen for each option listed above. Finally, above  
177 the L2 levels, sediment must be dredged and transported with care, and effectively isolated  
178 from the environment upon final disposal.

179 To determine the organic carbon content, the crushed sediment was acidified with  
180 (Fisher Scientific, Analytical Reagent grade, 85%) to eliminate inorganic carbon. Then, the  
181 samples were measured on a CHNS flash 2000 (Thermo Electron) following the method  
182 described by Benner and Strom (1993). The total sulfur content was measured after mixing  
183 around 3 mg of freeze-dried sediments with approximately 1.5 mg of vanadium pentoxide  
184  $\text{V}_2\text{O}_5$  (Thermo Fisher Scientific). For both carbon and sulfur measurements, two reference soils  
185 were used, NC and NCS (Thermo Fisher Scientific). Each sample was analyzed in triplicate.

186 The particle size distribution was determined using a laser diffraction particle-size  
187 analyzer LS 13320 (Beckman Coulter Inc.). Wet sediment samples were dispersed in deionized  
188 water and briefly treated in an ultrasonic bath (3 min) prior to measurement. The instrument  
189 analysis ranged from 0.4 to 2000  $\mu\text{m}$ .

190 Dissolved Cd concentrations in UV-irradiated seawater samples were determined by  
191 Differential Pulse Anodic Stripping Voltammetry (DPASV). The measurements were carried  
192 out using an Autolab-III potentiostat (EcoChemie) equipped with an autosampler. A three-  
193 electrode system (663 VA Stand, Metrohm) consisting of Hg working electrode (size 3),  
194  $\text{Ag} | \text{AgCl} | 3 \text{ M KCl}$  reference electrode and Pt counter electrode was used for measurements.  
195 Automated measurements were controlled by the GPES 4.9 software (EcoChemie).  
196 Quantification of the metals concentrations was performed using the standard addition

197 method, automated using syringe burettes (Pump XE 1000, TECAN). Voltammograms were  
198 processed (peak height of 2<sup>nd</sup> derivative as analytical signal characteristic) using ECDSOFT  
199 software (*Cobelo-García et al., 2014; Omanović and Branica, 1998*). The percentage of Cd  
200 desorption from sediment was calculated by subtracting the Cd quantity in the initial seawater  
201 from the Cd quantity measured at the end of the experiment and divided by the quantity of  
202 Cd added in the mixing solution by sediment particles.

### III Results and discussion

#### III.1 Sediment and seawater initial characteristics

205 The salinity of seawater was 37.9 for La Spezia, 37.6 for Olbia and 38.2 for Toulon, while  
206 the pH values of overlying water for these three sites were 8.32, 7.55 and 7.87, respectively.  
207 The percentage of oxygen saturation of the overlying water was 89, 101 and 90.3 %. The initial  
208 pH values of the seawater used for the resuspension experiments were 8.30, 8.36 and 7.79 for  
209 La Spezia, Olbia and Toulon respectively. The initial dissolved Cd concentrations in seawater  
210 were 15.74, 7.87 and 11.24 ngL<sup>-1</sup> for La Spezia, Olbia and Toulon respectively, which is  
211 consistent with the literature for these bays or their coastal surroundings (*Breder, 1987; Coclet*  
212 *et al., 2019*). The dissolved Cd concentrations in the three harbors were below the admissible  
213 dissolved cadmium concentration in seawater (more than 200 mgL<sup>-1</sup> CaCO<sub>3</sub>) defined by the  
214 EQS (2008/105/EC).

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

220 Cadmium contents were 0.10, 0.20 and 0.37 µgg<sup>-1</sup> in the sediment of La Spezia, Olbia  
221 and Toulon respectively. Contents observed in Toulon and Olbia sediments are consistent with

222 the literature for these bays (*Schintu et al., 1991; Tessier et al., 2011*) while the content  
223 observed in La Spezia sediment were lower than that previously observed (*Breder, 1987*). The  
224 easily-exchangeable proportion of Cd in the three sediments were 63, 47 and 38% for La Spezia,  
225 Olbia and Toulon respectively. Such range of easily exchangeable Cd proportion was already  
226 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).

### III.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.

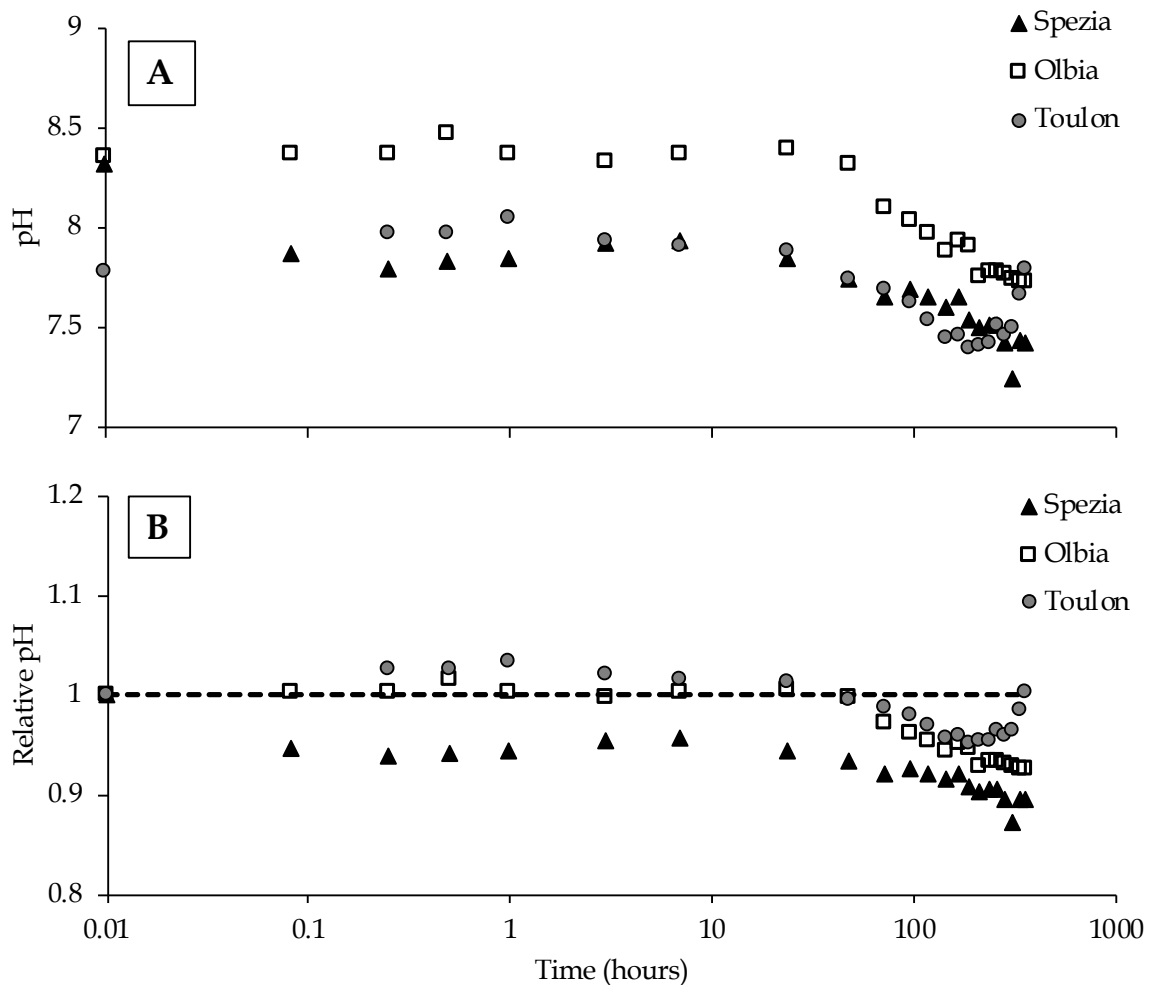
*Table 2 : Amount of total particulate and easily-exchangeable Cd expressed in ng added in each performed experiment*

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 <sup>-1</sup> )	778   490	1380   649	2220   844
Solid/Liquid ratio (0.05gL <sup>-1</sup> )	1.92   1.21	2.00   0.94	3.70   1.41
Solid/Liquid ratio (0.125gL <sup>-1</sup> )	3.84   2.42	6.00   2.82	11.1   4.22
Solid/Liquid ratio (0.25gL <sup>-1</sup> )	7.68   4.84	14.0   6.58	22.2   8.44
Solid/Liquid ratio (0.5gL <sup>-1</sup> )	15.4   9.68	28.0   13.2	44.4   16.9
Solid/Liquid ratio (1.25gL <sup>-1</sup> )	39.4   24.8	70.0   32.9	111   42.2
Solid/Liquid ratio (2.5gL <sup>-1</sup> )	77.8   49.0	138   64.9	222   84.4
Solid/Liquid ratio (5gL <sup>-1</sup> )	156   98.0	276   1230	444   169
Solid/Liquid ratio (12.5gL <sup>-1</sup> )	388   245	690   324	1110   422
Solid/Liquid ratio (25gL <sup>-1</sup> )	778   490	1380   649	2220   844
Solid/Liquid ratio (125gL <sup>-1</sup> )	3888   2449	6900   3243	11100   4218

### III.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<sup>-1</sup> 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 (Figure 1), while

259 no similar early sharp decrease was observed for Olbia and Toulon (*Figure 1*). From 5<sup>th</sup>  
1  
2 260 minutes of mixing to the end of the experiment, a similar temporal variation of pH was  
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4  
5 261 observed for La Spezia and Olbia experiments (*Figure 1*, Spearman's correlation test,  $\rho = 0.936$ ,  
6  
7 262  $p < 0.05$ ). Between 48 h and the end of the experiments, the pH value dropped down to 7.40  
8  
9 263 and 7.73 for La Spezia and Olbia, respectively. pH decrease during sediment resuspension has  
10  
11 264 already been observed (*Cabrol et al., 2017; Dang et al., 2015b; Pía Di Nanno et al., 2007;*  
12  
13  
14 265 *Zouch et al., 2018*) and could suggested a relatively common process governing pH,  
15  
16 266 irrespective of the sediment composition. We have already demonstrated (*Layglon et al.,*  
17  
18  
19 267 *2021*) that the pH decrease during sediment resuspension (performed with 50 times higher  
20  
21 268 sediment content) could be abiotically controlled and therefore might result from the increase  
22  
23  
24 269 in dissolved acidic substances. Richards et al., (*2018*) suggested that the oxidation of acid  
25  
26 270 volatile sulfide (AVS) during the resuspension of anoxic sediment could induce an increasing  
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29 271 concentration of dissolved acidic substances. Surprisingly, in the experiment with samples  
30  
31 272 from Toulon, while pH values showed a similar decreasing trend until 8 days of mixing  
32  
33 273 (Spearman's correlation test,  $\rho = 0.850$ ,  $\rho = 0.899$  respectively for Toulon-La Spezia and Toulon-  
34  
35  
36 274 Olbia,  $p < 0.05$ ), pH increased from 8 days to the end of the experiment and reached values  
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38 275 similar to initial one (*Figure 1*). This observation remains unexplained for the moment.  
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277 Figure 1: Variations of pH during sediment resuspensions ( $2.5 \text{ gL}^{-1}$  sediment :water ratio). Panel A  
 278 represents its absolute variations, with initial values of seawater represented by the symbols on the Y  
 279 axis line while panel B represents its variations relatively to the initial pH of seawater before sediment  
 280 addition. As a consequence, a value above the dotted line corresponds to an increase compared to the  
 281 initial sampled seawater value, whereas a value below this line corresponds to a decrease. No pH data  
 282 could be recorded for Toulon at 5 minutes of mixing because of a technical problem.

#### 283 III.4 Kinetics of Cadmium transfers

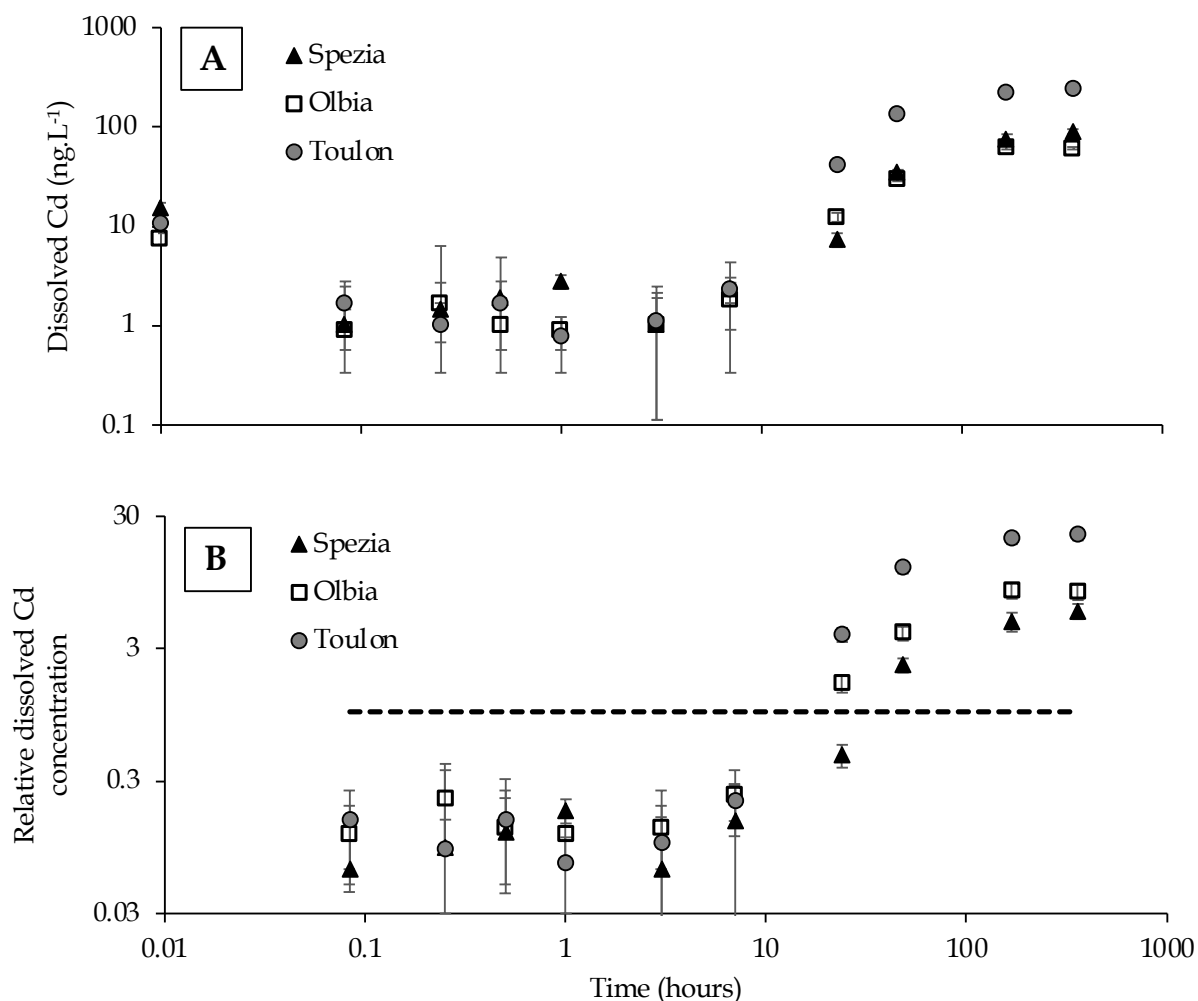
284 First, Cd experienced a strong and fast removal from the dissolved phase, observed  
 285 within a few minutes (*Figure 2A*) for all experiments. As a consequence, dissolved  
 286 concentrations were decreased by a factor 15.3, 10.8 and 8.4 for La Spezia, Toulon and Olbia,  
 287 respectively (*Figure 1B*). Cd is known to have a strong affinity for carbonates and clays  
 288 (*Pickering, 1983; Shirvani et al., 2006; Superville et al., 2015; Zheng et al., 2007*), as well as  
 289 with OM (*Tahervand and Jalali, 2016*), therefore its removal might be attributed to its  
 290 adsorption onto resuspended carbonates, OM and/or clays. Dissolved Cd concentrations then

291 remained rather stable at low concentrations up to 7 hours to 1 day of mixing. Finally,  
292 dissolved Cd concentrations increased to reach maximal and stable values after one week  
293 (*Figure 2A*), showing that dissolved Cd dynamics were similar in the three experiments. Such  
294 Cd remobilization was already explained in the literature, and is related to the competition of  
295 major seawater cations with trace metals for specific adsorption sites and the formation of  
296 metal chloro-complexes (*Calmano et al., 1993; Prause et al., 1985; Tahervand and Jalali,*  
297 *2016; Zhuang et al., 1994*).

298 At the end of the experiments, the maximal dissolved Cd concentrations were 90.0, 60.8  
299 and 240.6 ngL<sup>-1</sup> for La Spezia, Olbia and Toulon experiments, respectively (*Figure 2A*),  
300 representing a huge increase in concentration compared to the initial seawater concentrations  
301 (5.8-fold, 8.1-fold and 22.1-fold higher in La Spezia, Olbia and Toulon, respectively). When  
302 focusing on the absolute Cd concentration (*Figure 2A*), during the desorption step, the  
303 maximal increase in dissolved Cd was higher in Toulon (229 ngL<sup>-1</sup>) than in La Spezia (74 ngL<sup>-1</sup>)  
304 and the lowest value was found for Olbia (53 ngL<sup>-1</sup>). As seen above, the input of particulate  
305 Cd was 1.6 and 2.8 times higher in Toulon experiments compared to that of La Spezia and  
306 Olbia, respectively. The percentage of desorbed Cd was similar in La Spezia and Toulon  
307 experiments (47 and 51% respectively) and was found to be smaller in Olbia experiment (20%).  
308 The difference in the percentage of desorbed Cd did neither correspond to differences in Cd  
309 total content between the three sediments, nor to their differences in easily-exchangeable  
310 fraction of Cd. Therefore, none of total Cd content and Cd easily-extractable fraction appeared  
311 as the main parameter leading to Cd remobilization when, however, they are the most  
312 commonly measured parameters and those used for the management of sediments. The more  
313 alkaline pH measured in the experiment carried out with Olbia sediment ( $8.1 \pm 0.20$  compared  
314 to  $7.70 \pm 0.08$  and  $7.63 \pm 0.16$  for La Spezia and Toulon, respectively) could explain the lowest  
315 Cd release into seawater (*Figure 1: Figure 1 (Andreas and Zhang, 2014)*). While the kinetics



316 of Cd remobilization were similar in the three experiments, the amplitude of Cd  
 317 adsorption/desorption were dependent on the mixing (*Figure 2*).



318  
 319 *Figure 2 : Variations of dissolved Cd concentration during sediment resuspensions (2.5 gL<sup>-1</sup>*  
 320 *sediment:water ratio). Panel A represents its absolute variation while Panel B represents its relative*  
 321 *variation. As a consequence, a value above the black dotted line will correspond to an increase compared*  
 322 *to Cd in initial seawater, whereas a value below this line will correspond to a decrease. Note that the x*  
 323 *and y axis are on log scale. The dissolved Cd concentration indicated at x = 0.01 in panel A represents*  
 324 *Cd concentration of the initial seawater before the addition of sediment.*

325 III.5 Effects of the quantity of resuspended particles onto cadmium transfers

326 Using a ratio of 2.5 gL<sup>-1</sup>, we showed that the kinetics of Cd remobilization was similar  
 327 with different initial samples, and that the maximal dissolved Cd concentrations was observed  
 328 after 2 weeks of mixing. Therefore, we evaluated the impact of sediment resuspension  
 329 intensity after 2 weeks of mixing by varying the sediment:water ratio. The increase of

330 suspended particulate matter led to an increase in final dissolved Cd concentrations in the  
1  
2 331 three experiments (*Figure 3*). However, the increase in dissolved Cd concentration was not  
3  
4 332 linearly linked to the increase of suspended particulate matter and thus of the quantity of total  
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6  
7 333 or easily extractable Cd (*Figure 3*), pointing out a threshold effect that remains to be explained.  
8  
9 334 The dissolved Cd concentrations obtained with a ratio of 2.5 gL<sup>-1</sup> are consistent with the one  
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11 335 observed in the previous kinetics experiments (*Figure 2* and *Figure 3*). For the highest S/L  
12  
13 336 ratio (i.e. 125 gL<sup>-1</sup>), representative of a suspended particulate matter concentration in seawater  
14  
15 337 during dredging operations (*Nichols et al., 1990*), dissolved Cd increased up to 615, 2050 and  
16  
17 338 3624 ngL<sup>-1</sup> in Olbia, La Spezia and Toulon experiments, respectively, corresponding to a 82-  
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19 339 fold, 132-fold and 330-fold increase when compared to the initial concentration in seawater  
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21 340 (*Figure 3*). Therefore, the maximal concentration accepted by the EQS (2008/105/EC)  
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23 341 (1500 ngL<sup>-1</sup> in water containing more that 200 mgL<sup>-1</sup> CaCO<sub>3</sub>) was exceeded for experiments of  
24  
25 342 La Spezia (by a factor 1.4) and Toulon (by a factor 2.4) experiments. These experiments showed  
26  
27 343 that the EQS were punctually overpassed even if the Cd contents were lower than the N1 and  
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29 344 L1 levels for La Spezia, and below the N1 and L2 levels for Toulon sediments. Although this  
30  
31 345 was very punctual and result of a laboratory simulation, this work demonstrated the potential  
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33 346 contribution of sediment resuspension to the dissolved Cd contamination, especially in case  
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35 347 of strong resuspension by human activities. Once dissolved, the remobilized Cd can poison  
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37 348 biota or be exported towards the open sea and therefore contribute to its large-scale dispersion.  
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39 349 In addition, this study was performed with slightly contaminated sediment, while more  
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41 350 contaminated sediments could perhaps challenge the EQS at lower sediment:water ratio  
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43 351 therefore events of lower energy (storm, nautical traffic, ...) (*Abi-Ghanem et al., 2014; Dang*  
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45 352 *et al., 2015a; El Houssainy et al., 2020; Schintu et al., 2016*).  
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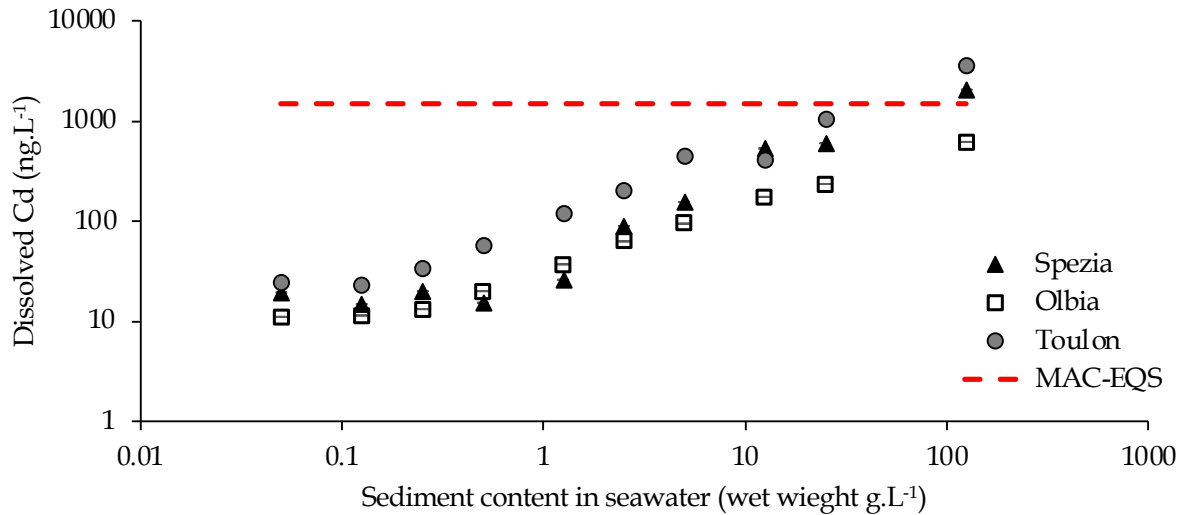


Figure 3 : Variations of dissolved Cd as a function of the sediment content (wet weight in g.L<sup>-1</sup>) in seawater. The red dotted line represents the maximum allowable concentration (MAC-EQS) defined by the Environmental Quality Standards (EQS) in seawater. Both axis are presented in log scale to better visualize data.

#### IV 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 hours of mixing time, leading to a clear contamination of the initial seawater after 24 hours, 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

1 373 results clearly put forward the need to better characterize the processes leading to Cd  
2 374 remobilization and controlling the magnitude of the contamination induced. An effort toward  
3  
4 375 mixing conditions better representing field conditions is now required to confront more  
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7 376 realistic data to regulation thresholds and to contribute to regulation harmonization between  
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9 377 countries. This study provides new bases for decision-makers and local authorities concerned  
10  
11  
12 378 by sediment management and water quality protection.

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17  
18 380 The authors declare that they have no known competing financial interests or personal  
19  
20 381 relationships that could have appeared to influence the work reported in this paper.

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

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20 Abstract

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

32 Keywords: cadmium; remobilization; sediment resuspension; water quality; Environmental  
33 Quality Standards (EQS)

## 34 I Introduction

1 Coastal areas are of great interest for humankind, due to the huge amount of resources  
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4 36 therein, leading to an increase in population along the coastlines. While the population  
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6 37 increased, sanitary infrastructure did not, causing an increase of contaminants release towards  
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8 38 the environment occurs, threatening the ecosystems, the marine species, and the human  
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10 39 population health. To protect the marine environment, the European Union defined  
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12 40 environmental regulations concerning both seawater and sediments. Concerning the  
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14 41 concentration of chemical substances in the water, the European Union Water Framework  
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16 42 Directive (WFD-2008/105/ EC) has defined environmental quality standards (EQS) thresholds  
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18 43 that must not be exceeded to limit human impact on natural ecosystems. EU member states  
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20 44 consider sediment contamination for the management of sediments in harbor areas through  
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22 45 very heterogeneous standards, mainly in order to limit the resuspension of chemically  
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24 46 contaminated particles. Sediments indeed accumulate a high amount of toxic substances (*El*  
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26 47 *Houssainy et al., 2020; Guigue et al., 2017; Misson et al., 2016; Schintu et al., 2016, 1991*).  
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28 48 Both natural and human-induced sediment resuspension often occur in coastal areas and,  
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30 49 during resuspension, chemical substances can easily be remobilized through the dissolved  
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32 50 phase towards the water column (*Ciffroy et al., 2019; Dang et al., 2020; de Freitas et al.,*  
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34 51 *2019*). The remobilization of chemical substances from sediment can therefore potentially alter  
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36 52 water quality with regard to the EU-WFD.  
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45 53 Among this chemical substances, cadmium (Cd) is a non-essential, harmful trace metal,  
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47 54 which causes serious problems due to its severe toxicity towards organisms (*Miao and Wang,*  
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49 55 *2006; Satarug et al., 2003*). Cadmium remobilization occurs due to the competition of major  
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51 56 seawater cations with trace metals for specific adsorption sites and the formation of metal  
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53 57 chloro-complexes (*Calmano et al., 1993; Prause et al., 1985; Tahervand and Jalali, 2016;*  
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55 58 *Zhuang et al., 1994*). The kinetics of transfer found in the previous literature was only  
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57 59 evaluated after 12h, a time which seems long in view of the process highlighted after a few  
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60 minutes for other elements (*Dang et al., 2020*). In this context, the first aim of this study was  
61 to study and compare the succession and amplitude of Cd transfers between the dissolved and  
62 particulate phases from minutes to weeks. For that, dissolved Cd concentration was measured  
63 over time during resuspension at a fixed sediment:water ratio of sediments sampled in  
64 different Mediterranean urbanized bays. Then, on the basis of the observed kinetics, the  
65 influence of the quantity of resuspended sediment on Cd release into the dissolved phase was  
66 assessed at week scale through a second experiment using different sediment:water ratios,  
67 representative of low (wind induced resuspension), medium (nautical activities) and high  
68 (dredging activities) resuspension energies. Finally, the measured dissolved Cd  
69 concentrations in the second set of experiments was compared to the maximum allowable  
70 concentration (MAC) accepted by the EU-WFD EQS.

## II Experimental

### II.1 Sample collection, pre-treatment and storage

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

76 For the purpose of this work, sampling campaigns were performed in three  
77 Mediterranean urbanized bays: La Spezia (coordinates 44.10482 N, 9.84737 E), Olbia  
78 (coordinates 40.92944 N, 9.52812 E) and Toulon (coordinates 43.11454 N, 5.88542 E). **The water**  
79 **depth was 12, 4 and 1.4 m for La Spezia, Olbia and Toulon, respectively.** At each sampling  
80 site, 25 L of surface seawater (0.5 m) were collected using a 4.2 L horizontal van Dorn type  
81 water sampler (Wildco, model Beta) and stored in a pre-cleaned 25 L HDPE bottle rinsed 3  
82 times with water from the site. An aliquot of each seawater sample was filtered (0.2  $\mu$ m on-  
83 line syringe filters, cellulose nitrate, Sartorius) and collected into a 125 mL FEP bottle, then  
84 acidified (0.2%v/v HNO<sub>3</sub> s.p (Merck)) before being UV-irradiated (150 W mercury lamp,

85 Hanau, Germany) for at least 24 h in order to completely decompose organic matter. Samples  
86 were then stored at ambient temperature until dissolved Cd analysis. The remaining  
87 unprocessed water was kept at ambient temperature and day light until further resuspension  
88 experiments.

89 One sediment core was sampled at each site using an interface corer (Uwitec) equipped  
90 with PVC tubes of 90 mm in diameter. The first 30 cm of the core were sliced and homogenized  
91 under inert N<sub>2</sub> atmosphere. We are aware that diagenetic processes could have led to  
92 different physical-chemical properties of the sediment within such a thick sediment slice,  
93 however, it represents well the sediment thickness targeted by sediment management  
94 operations in harbor areas. An aliquot of each homogenized sediment sample was submitted  
95 to centrifugation (4248 RCF (Relative Centrifugal Force), 20 °C for 15 min Sigma 3-18K) to  
96 separate porewater from sediment. After removing the supernatant, the pellet was weighed  
97 before and after freeze-drying in order to determine the water content of each sediment.  
98 Lyophilized sediments were finally sieved under 2 mm and crushed in a Planetary Ball Mill  
99 PM 100 (Retch). Aqua-regia digestion was performed on the lyophilized sediments using a  
100 microwave digestion (Milestone) prior to assess the Cd concentration on particles. This  
101 protocol was previously described (*Cukrov et al., 2019; Tessier et al., 2011*) and validated  
102 using a certified material (PACS-2 National Research Council of Canada; n = 20, accuracy  
103 between 0.9 and 7% according to the considered element; *Tessier et al., 2011*). In order to  
104 determine the easily exchangeable fraction of Cd, an acid extraction (1 M HCl) was performed  
105 (*Larrose et al., 2010*). The extraction was achieved by mixing 100 mg of freeze-dried  
106 homogenous sediment with 10 mL of 1 M HCl (Merck, suprapur solution) in a polypropylene  
107 tube shaken head-over-head (6 rpm, Heidolph Reax 20) for 24 h. After centrifugation (4,248  
108 RCF, 15 min), the supernatant was filtered through 0.2 µm syringe filters and stored in the



109 dark at 4 °C. Remaining homogenized and wet sediments were kept anoxic at ambient  
110 temperature until further resuspension experiment.

## 111 II.2 Laboratory resuspension experiments

112 In order to evaluate the kinetics of Cd remobilization during sediment resuspension,  
113 laboratory experiments were launched within 48 h after sampling, using pre-cleaned 5L PTFE  
114 bottles. The sediment was kept under an inter atmosphere (N<sub>2</sub>) to prevent sediment oxidation.  
115 Experiments were carried out with the same sediment:water ratio for all three sampling  
116 locations. Since the sediment collected in the different sites have different water content, the  
117 amount of sediment particles added were different, despite an identical mass of wet sediment  
118 (*Table 1*). Two different kind of resuspension experiments were performed. The first series of  
119 experiment was carried out to study the kinetics of Cd transfers between sediment and  
120 seawater. It was conducted with a sediment:water ratio of 2.5 g of wet sediment per liter of  
121 seawater (representing approximately 1 g of dry sediment per liter of seawater) in 5L PTFE  
122 bottle, submitted to continuous head-over-head shaking (15 rpm, Heidolph Reax 20). This ratio  
123 was frequently used in previous studies (*Dang et al., 2020; Guigue et al., 2017; Millward*  
124 *and Liu, 2003; Moran and Moore, 1991*) and represents a resuspension event related to  
125 nautical traffic. Water-sediment mixture was sub-sampled (180 mL) at exponentially  
126 increasing intervals to allow the coverage of both short and long-term Cd transfer processes:  
127 5, 15, 30 min, 1, 3, 7 h, 1, 2, days, 1 and 2 weeks. The second series of experiment was performed  
128 to quantify the impact of the quantity of resuspended sediment onto Cd transfers. Sediment  
129 and seawater were mixed in 500 mL FEP bottles during 2 weeks with 10 different  
130 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  
131 of seawater representing approximately 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 50 g of dry sediment  
132 per liter of seawater, respectively (*Table 1*). These ratios allowed to represent a large diversity  
133 of resuspension processes, from natural wind events in shallow coastal areas (<0.5 gL<sup>-1</sup>, (*Jiang*

134 *et al., 2020*) to dredging operations (~10-50 gL<sup>-1</sup>, (*Nichols et al., 1990*)). The water-sediment  
 135 mixture was only sampled after two weeks of mixing. For both experiments, samples were  
 136 filtered, treated and stored as described above for seawater prior to dissolved Cd  
 137 concentration measurement.

138 In parallel of the first series of experiments performed with a sediment:water ratio of  
 139 2.5 gL<sup>-1</sup>, pH, Eh and O<sub>2</sub> were measured at each interval sampling time and every day until the  
 140 end of the experiment in a separate 1 L HDPE bottle (with the same conditions and sediment  
 141 load) to avoid potential contamination by the probes. The pH measurement was carried out  
 142 with a combined electrode (Ag|AgCl|KCl 3 M) of the microtip type (diameter of 5 mm,  
 143 Bioblock Scientific). The latter has been calibrated beforehand (before each new set of  
 144 measurement) using buffer solution at pH 4.01, 7.01 and 10.01 (HANNA). Redox electrode was  
 145 made of Pt (Radiometer Copenhagen) coupled to the reference electrode in Hg|Hg<sub>2</sub>Cl<sub>2</sub>|KCl 3  
 146 M (Radiometer Analytical, E<sub>ref</sub> = 255 mV/NHE, 25°C), calibrated with the Zobell's solution (Eh  
 147 = 430 mV/NHE at 25°C, Thermo Scientific).

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

150 *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 <sup>-1</sup> )	8.10	6.90	6.00
Solid/Liquid ratio (0.05gL <sup>-1</sup> )	0.02	0.01	0.01
Solid/Liquid ratio (0.125gL <sup>-1</sup> )	0.04	0.03	0.03
Solid/Liquid ratio (0.25gL <sup>-1</sup> )	0.08	0.07	0.06
Solid/Liquid ratio (0.5gL <sup>-1</sup> )	0.16	0.14	0.12
Solid/Liquid ratio (1.25gL <sup>-1</sup> )	0.41	0.35	0.3

Solid/Liquid ratio (2.5gL <sup>-1</sup> )	0.81	0.69	0.6
Solid/Liquid ratio (5gL <sup>-1</sup> )	1.62	1.38	1.2
Solid/Liquid ratio (12.5gL <sup>-1</sup> )	4.05	3.45	3.0
Solid/Liquid ratio (25gL <sup>-1</sup> )	8.10	6.90	6.0
Solid/Liquid ratio (125gL <sup>-1</sup> )	40.50	34.50	30.00

### II.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  $2.11 \pm 0.14 \text{ mgkg}^{-1}$  (n=5) while the certified values is  $2.11 \pm 0.15 \text{ mgkg}^{-1}$ . The French authorities (JORF n°184 10-08-2000) have defined N1 (1.2  $\mu\text{gCdg}^{-1}$ ) and N2 (2.4  $\mu\text{gCdg}^{-1}$ ) 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 ( $0.3 \mu\text{gCdg}^{-1}$ ), 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

171 disposed of in a manner that minimizes the release of contaminants either into solution or by  
172 resuspension. Between L1 and L2 levels ( $0.3 - 0.8 \mu\text{gCd g}^{-1}$ ) with low or no adverse outcome  
173 from bioassays, sediment can be dumped in off-shores marine areas (over 3 m) or addressed  
174 in confined disposal facilities (CDF) effectively isolated from the environment. An  
175 environmental monitoring plan must be foreseen for each option listed above. Finally, above  
176 the L2 levels, sediment must be dredged and transported with care, and effectively isolated  
177 from the environment upon final disposal.

178 To determine the organic carbon content, the crushed sediment was acidified with  
179 (Fisher Scientific, Analytical Reagent grade, 85%) to eliminate inorganic carbon. Then, the  
180 samples were measured on a CHNS flash 2000 (Thermo Electron) following the method  
181 described by Benner and Strom (1993). The total sulfur content was measured after mixing  
182 around 3 mg of freeze-dried sediments with approximately 1.5 mg of vanadium pentoxide  
183  $\text{V}_2\text{O}_5$  (Thermo Fisher Scientific). For both carbon and sulfur measurements, two reference soils  
184 were used, NC and NCS (Thermo Fisher Scientific). Each sample was analyzed in triplicate.

185 The particle size distribution was determined using a laser diffraction particle-size  
186 analyzer LS 13320 (Beckman Coulter Inc.). Wet sediment samples were dispersed in deionized  
187 water and briefly treated in an ultrasonic bath (3 min) prior to measurement. The instrument  
188 analysis ranged from 0.4 to 2000  $\mu\text{m}$ .

189 Dissolved Cd concentrations in UV-irradiated seawater samples were determined by  
190 Differential Pulse Anodic Stripping Voltammetry (DPASV). The measurements were carried  
191 out using an Autolab-III potentiostat (EcoChemie) equipped with an autosampler. A three-  
192 electrode system (663 VA Stand, Metrohm) consisting of Hg working electrode (size 3),  
193  $\text{Ag} | \text{AgCl} | 3 \text{ M KCl}$  reference electrode and Pt counter electrode was used for measurements.  
194 Automated measurements were controlled by the GPES 4.9 software (EcoChemie).  
195 Quantification of the metals concentrations was performed using the standard addition

196 method, automated using syringe burettes (Pump XE 1000, TECAN). Voltammograms were  
197 processed (peak height of 2<sup>nd</sup> derivative as analytical signal characteristic) using ECDSOFT  
198 software (*Cobelo-García et al., 2014; Omanović and Branica, 1998*). The percentage of Cd  
199 desorption from sediment was calculated by subtracting the Cd quantity in the initial seawater  
200 from the Cd quantity measured at the end of the experiment and divided by the quantity of  
201 Cd added in the mixing solution by sediment particles.

### III Results and discussion

#### III.1 Sediment and seawater initial characteristics

204 The salinity of seawater was 37.9 for La Spezia, 37.6 for Olbia and 38.2 for Toulon, while  
205 the pH values of overlying water for these three sites were 8.32, 7.55 and 7.87, respectively.  
206 The percentage of oxygen saturation of the overlying water was 89, 101 and 90.3 %. The initial  
207 pH values of the seawater used for the resuspension experiments were 8.30, 8.36 and 7.79 for  
208 La Spezia, Olbia and Toulon respectively. The initial dissolved Cd concentrations in seawater  
209 were 15.74, 7.87 and 11.24 ngL<sup>-1</sup> for La Spezia, Olbia and Toulon respectively, which is  
210 consistent with the literature for these bays or their coastal surroundings (*Breder, 1987; Coclet*  
211 *et al., 2019*). The dissolved Cd concentrations in the three harbors were below the admissible  
212 dissolved cadmium concentration in seawater (more than 200 mgL<sup>-1</sup> CaCO<sub>3</sub>) defined by the  
213 EQS (2008/105/EC).

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

219 Cadmium contents were 0.10, 0.20 and 0.37 µgg<sup>-1</sup> in the sediment of La Spezia, Olbia  
220 and Toulon respectively. Contents observed in Toulon and Olbia sediments are consistent with

221 the literature for these bays (*Schintu et al., 1991; Tessier et al., 2011*) while the content  
222 observed in La Spezia sediment were lower than that previously observed (*Breder, 1987*). The  
223 easily-exchangeable proportion of Cd in the three sediments were 63, 47 and 38% for La Spezia,  
224 Olbia and Toulon respectively. Such range of easily exchangeable Cd proportion was already  
225 observed in the literature (*Dang et al., 2015a; El Houssainy et al., 2020*).

226 The percentage of organic carbon in the sediment was 0.42, 2.12 and 2.39 % for La  
227 Spezia, Olbia and Toulon respectively. The percentage of total sulfur was 0.35, 0.91 % and  
228 0.27 % in La Spezia, Olbia and Toulon respectively.

229 Given that the sediments were sampled in France and Italy, we compared their Cd  
230 contents to national laws framing marine sediment management. Sediment from Toulon  
231 presented Cd content lower than the regulatory N1 level defined by the French authorities  
232 (JORF n°184 10-08-2000). As a consequence, its potential impact regarding Cd is considered  
233 neutral or negligible and the management of the sediment does not require any particular  
234 precaution. The Cd content in La Spezia and Olbia were below the Italian lower chemical  
235 exceedance Level and could thus be dredged, transported and disposed if the release of  
236 contaminants into solution or by resuspension is minimized (Italian Ministerial Decree  
237 173/2016).

### 238 III.2 Quantity and partitioning of Cd from resuspended sediments in the different 239 experiments

240 The amount of total particulate and easily-exchangeable Cd added in each experiment  
241 are given in *Table 2*. The input of particulate Cd was 1.6-2.8 times higher in Toulon  
242 experiments compared to that of Olbia and La Spezia and the exchangeable fraction was 1.3-  
243 1.7 times higher in Toulon experiments compared to that of Olbia and La Spezia.

244 *Table 2 : Amount of total particulate and easily-exchangeable Cd expressed in ng added in each*  
245 *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 <sup>-1</sup> )	778   490	1380   649	2220   844
Solid/Liquid ratio (0.05gL <sup>-1</sup> )	1.92   1.21	2.00   0.94	3.70   1.41
Solid/Liquid ratio (0.125gL <sup>-1</sup> )	3.84   2.42	6.00   2.82	11.1   4.22
Solid/Liquid ratio (0.25gL <sup>-1</sup> )	7.68   4.84	14.0   6.58	22.2   8.44
Solid/Liquid ratio (0.5gL <sup>-1</sup> )	15.4   9.68	28.0   13.2	44.4   16.9
Solid/Liquid ratio (1.25gL <sup>-1</sup> )	39.4   24.8	70.0   32.9	111   42.2
Solid/Liquid ratio (2.5gL <sup>-1</sup> )	77.8   49.0	138   64.9	222   84.4
Solid/Liquid ratio (5gL <sup>-1</sup> )	156   98.0	276   1230	444   169
Solid/Liquid ratio (12.5gL <sup>-1</sup> )	388   245	690   324	1110   422
Solid/Liquid ratio (25gL <sup>-1</sup> )	778   490	1380   649	2220   844
Solid/Liquid ratio (125gL <sup>-1</sup> )	3888   2449	6900   3243	11100   4218

### III.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<sup>-1</sup> 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 (Figure 1), while

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258 no similar early sharp decrease was observed for Olbia and Toulon (*Figure 1*). From 5<sup>th</sup>  
259 minutes of mixing to the end of the experiment, a similar temporal variation of pH was  
260 observed for La Spezia and Olbia experiments (*Figure 1*, Spearman's correlation test,  $\rho = 0.936$ ,  
261  $p < 0.05$ ). Between 48 h and the end of the experiments, the pH value dropped down to 7.40  
262 and 7.73 for La Spezia and Olbia, respectively. pH decrease during sediment resuspension has  
263 already been observed (*Cabrol et al., 2017; Dang et al., 2015b; Pía Di Nanno et al., 2007;*  
264 *Zouch et al., 2018*) and could suggested a relatively common process governing pH,  
265 irrespective of the sediment composition. We have already demonstrated (*Layglon et al.,*  
266 *2021*) that the pH decrease during sediment resuspension (performed with 50 times higher  
267 sediment content) could be abiotically controlled and therefore might result from the increase  
268 in dissolved acidic substances. Richards et al., (*2018*) suggested that the oxidation of acid  
269 volatile sulfide (AVS) during the resuspension of anoxic sediment could induce an increasing  
270 concentration of dissolved acidic substances. Surprisingly, in the experiment with samples  
271 from Toulon, while pH values showed a similar decreasing trend until 8 days of mixing  
272 (Spearman's correlation test,  $\rho = 0.850$ ,  $\rho = 0.899$  respectively for Toulon-La Spezia and Toulon-  
273 Olbia,  $p < 0.05$ ), pH increased from 8 days to the end of the experiment and reached values  
274 similar to initial one (*Figure 1*). This observation remains unexplained for the moment.



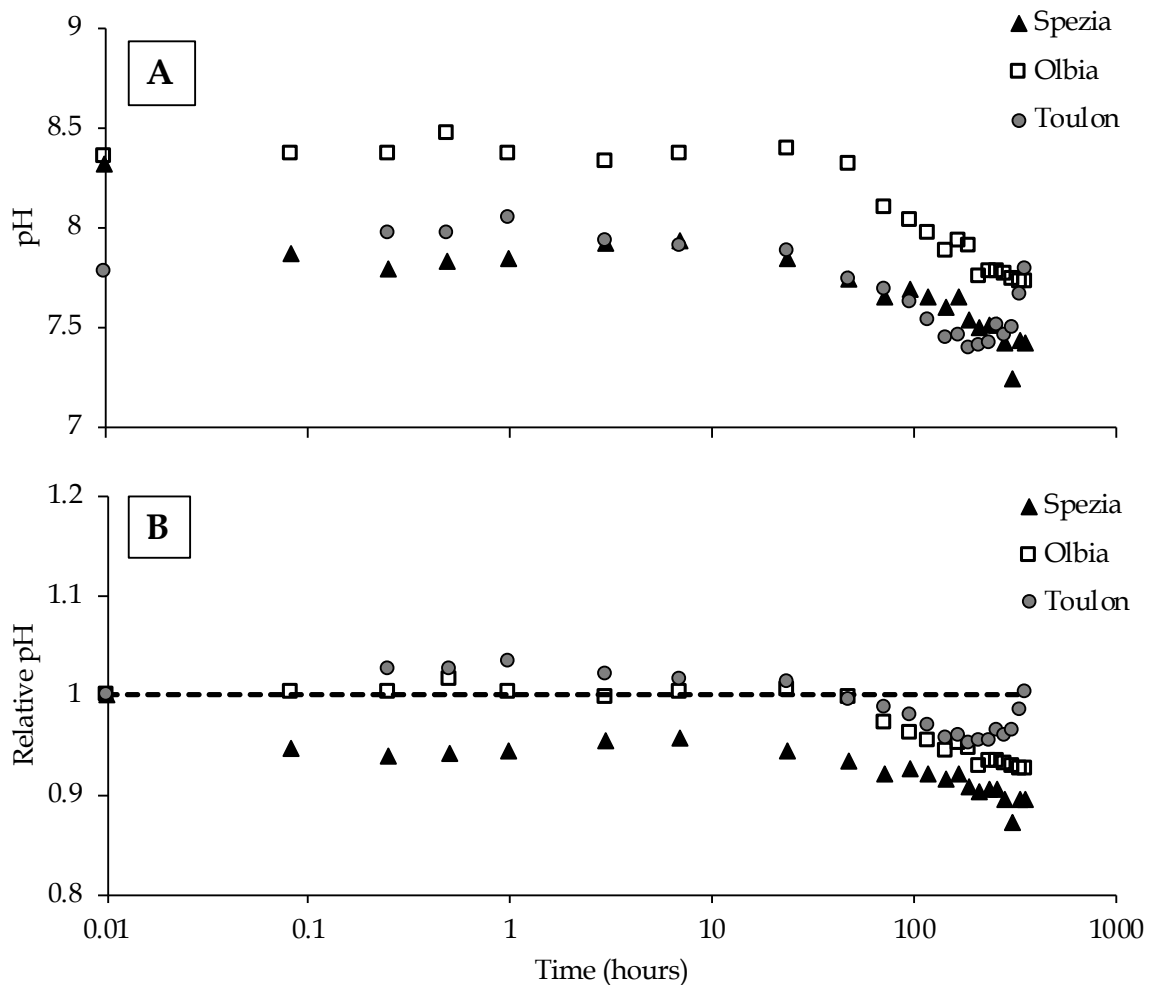


Figure 1: Variations of pH during sediment resuspensions ( $2.5 \text{ gL}^{-1}$  sediment :water ratio). Panel A represents its absolute variations, with initial values of seawater represented by the symbols on the Y axis line while panel B represents its variations relatively to the initial pH of seawater 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 minutes of mixing because of a technical problem.

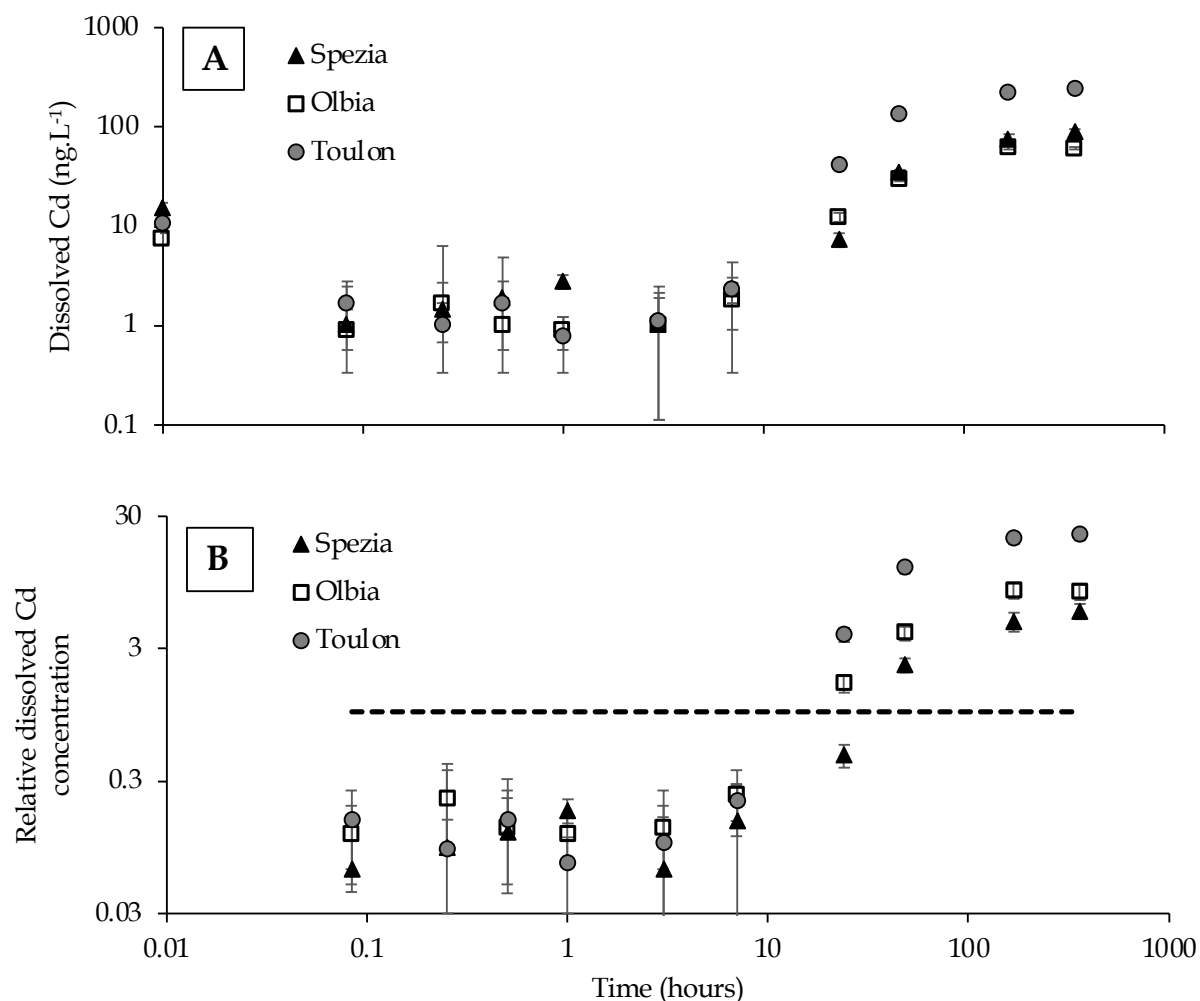
#### III.4 Kinetics of Cadmium transfers

First, Cd experienced a strong and fast removal from the dissolved phase, observed within a few minutes (Figure 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 (Figure 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

290 remained rather stable at low concentrations up to 7 hours to 1 day of mixing. Finally,  
291 dissolved Cd concentrations increased to reach maximal and stable values after one week  
292 (*Figure 2A*), showing that dissolved Cd dynamics were similar in the three experiments. Such  
293 Cd remobilization was already explained in the literature, and is related to the competition of  
294 major seawater cations with trace metals for specific adsorption sites and the formation of  
295 metal chloro-complexes (*Calmano et al., 1993; Prause et al., 1985; Tahervand and Jalali,*  
296 *2016; Zhuang et al., 1994*).

297 At the end of the experiments, the maximal dissolved Cd concentrations were 90.0, 60.8  
298 and 240.6 ngL<sup>-1</sup> for La Spezia, Olbia and Toulon experiments, respectively (*Figure 2A*),  
299 representing a huge increase in concentration compared to the initial seawater concentrations  
300 (5.8-fold, 8.1-fold and 22.1-fold higher in La Spezia, Olbia and Toulon, respectively). When  
301 focusing on the absolute Cd concentration (*Figure 2A*), during the desorption step, the  
302 maximal increase in dissolved Cd was higher in Toulon (229 ngL<sup>-1</sup>) than in La Spezia (74 ngL<sup>-1</sup>)  
303 and the lowest value was found for Olbia (53 ngL<sup>-1</sup>). As seen above, the input of particulate  
304 Cd was 1.6 and 2.8 times higher in Toulon experiments compared to that of La Spezia and  
305 Olbia, respectively. The percentage of desorbed Cd was similar in La Spezia and Toulon  
306 experiments (47 and 51% respectively) and was found to be smaller in Olbia experiment (20%).  
307 The difference in the percentage of desorbed Cd did neither correspond to differences in Cd  
308 total content between the three sediments, nor to their differences in easily-exchangeable  
309 fraction of Cd. Therefore, none of total Cd content and Cd easily-extractable fraction appeared  
310 as the main parameter leading to Cd remobilization when, however, they are the most  
311 commonly measured parameters and those used for the management of sediments. The more  
312 alkaline pH measured in the experiment carried out with Olbia sediment ( $8.1 \pm 0.20$  compared  
313 to  $7.70 \pm 0.08$  and  $7.63 \pm 0.16$  for La Spezia and Toulon, respectively) could explain the lowest  
314 Cd release into seawater (*Figure 1: Figure 1*) (*Andreas and Zhang, 2014*). While the kinetics

315 of Cd remobilization were similar in the three experiments, the amplitude of Cd  
 316 adsorption/desorption were dependent on the mixing (*Figure 2*).



317  
 318 *Figure 2 : Variations of dissolved Cd concentration during sediment resuspensions (2.5 gL<sup>-1</sup>*  
 319 *sediment:water ratio). Panel A represents its absolute variation while Panel B represents its relative*  
 320 *variation. As a consequence, a value above the black dotted line will correspond to an increase compared*  
 321 *to Cd in initial seawater, whereas a value below this line will correspond to a decrease. Note that the x*  
 322 *and y axis are on log scale. The dissolved Cd concentration indicated at x = 0.01 in panel A represents*  
 323 *Cd concentration of the initial seawater before the addition of sediment.*

### 324 III.5 Effects of the quantity of resuspended particles onto cadmium transfers

325 Using a ratio of 2.5 gL<sup>-1</sup>, we showed that the kinetics of Cd remobilization was similar  
 326 with different initial samples, and that the maximal dissolved Cd concentrations was observed  
 327 after 2 weeks of mixing. Therefore, we evaluated the impact of sediment resuspension  
 328 intensity after 2 weeks of mixing by varying the sediment:water ratio. The increase of

329 suspended particulate matter led to an increase in final dissolved Cd concentrations in the  
1  
2 330 three experiments (*Figure 3*). However, the increase in dissolved Cd concentration was not  
3  
4 331 linearly linked to the increase of suspended particulate matter and thus of the quantity of total  
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6  
7 332 or easily extractable Cd (*Figure 3*), pointing out a threshold effect that remains to be explained.  
8  
9 333 The dissolved Cd concentrations obtained with a ratio of 2.5 gL<sup>-1</sup> are consistent with the one  
10  
11 334 observed in the previous kinetics experiments (*Figure 2* and *Figure 3*). For the highest S/L  
12  
13 335 ratio (i.e. 125 gL<sup>-1</sup>), representative of a suspended particulate matter concentration in seawater  
14  
15 336 during dredging operations (*Nichols et al., 1990*), dissolved Cd increased up to 615, 2050 and  
16  
17 337 3624 ngL<sup>-1</sup> in Olbia, La Spezia and Toulon experiments, respectively, corresponding to a 82-  
18  
19 338 fold, 132-fold and 330-fold increase when compared to the initial concentration in seawater  
20  
21 339 (*Figure 3*). Therefore, the maximal concentration accepted by the EQS (2008/105/EC)  
22  
23 340 (1500 ngL<sup>-1</sup> in water containing more than 200 mgL<sup>-1</sup> CaCO<sub>3</sub>) was exceeded for experiments of  
24  
25 341 La Spezia (by a factor 1.4) and Toulon (by a factor 2.4) experiments. These experiments showed  
26  
27 342 that the EQS were punctually overpassed even if the Cd contents were lower than the N1 and  
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29 343 L1 levels for La Spezia, and below the N1 and L2 levels for Toulon sediments. Although this  
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31 344 was very punctual and result of a laboratory simulation, this work demonstrated the potential  
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33 345 contribution of sediment resuspension to the dissolved Cd contamination, especially in case  
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35 346 of strong resuspension by human activities. Once dissolved, the remobilized Cd can poison  
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37 347 biota or be exported towards the open sea and therefore contribute to its large-scale dispersion.  
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39 348 In addition, this study was performed with slightly contaminated sediment, while more  
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41 349 contaminated sediments could perhaps challenge the EQS at lower sediment:water ratio  
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43 350 therefore events of lower energy (storm, nautical traffic, ...) (*Abi-Ghanem et al., 2014; Dang*  
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45 351 *et al., 2015a; El Houssainy et al., 2020; Schintu et al., 2016*).  
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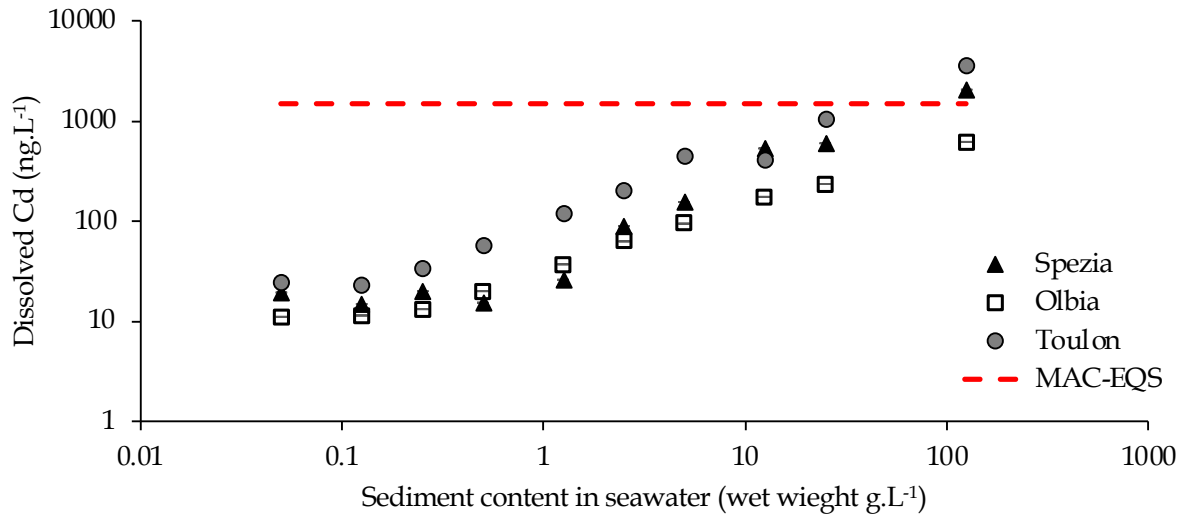


Figure 3 : Variations of dissolved Cd as a function of the sediment content (wet weight in gL<sup>-1</sup>) in seawater. The red dotted line represents the maximum allowable concentration (MAC-EQS) defined by the Environmental Quality Standards (EQS) in seawater. Both axis are presented in log scale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

#### IV 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 hours of mixing time, leading to a clear contamination of the initial seawater after 24 hours, 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

372 results clearly put forward the need to better characterize the processes leading to Cd  
1 remobilization and controlling the magnitude of the contamination induced. An effort toward  
2 373 remobilization and controlling the magnitude of the contamination induced. An effort toward  
3  
4 374 mixing conditions better representing field conditions is now required to confront more  
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7 375 realistic data to regulation thresholds and to contribute to regulation harmonization between  
8  
9 376 countries. This study provides new bases for decision-makers and local authorities concerned  
10  
11  
12 377 by sediment management and water quality protection.  
13

#### 15 378 **Declaration of competing interest**

17  
18 379 The authors declare that they have no known competing financial interests or personal  
19  
20 380 relationships that could have appeared to influence the work reported in this paper.  
21  
22

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**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.

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