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

Nicolas Layglon^{1,2*}, Véronique Lenoble¹, Longo Louis¹, Sébastien
D'Onofrio¹, Stéphane Mounier¹, Jean-Ulrich Mullo³, Davide Sartori⁴,
Dario Omanović⁵, Cédric Garnier¹, Benjamin Misson¹

¹Université de Toulon, Aix Marseille Université, CNRS/INSU, IRD, MIO UM 110,
Mediterranean Institute of Oceanography, La Garde, France

²University of Geneva, Sciences II, 30 Quai E.-Ansermet, 1221 Geneva 4, Switzerland

³LASEM-Toulon, Base Navale De Toulon, BP 61, 83800 Toulon, France

⁴Institute for Environmental Protection and Research, ISPRA, Via del Cedro, 38, 57123
Livorno, Italy

⁵Center for Marine and Environmental Research, Ruđer Bošković Institute, P.O. Box 180,
10002 Zagreb, Croatia

* Corresponding author: nicolas.layglon@unige.ch

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 ngL^{-1}
30 to few hundreds of 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 Ω , 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 μ m on-
84 line syringe filters, cellulose nitrate, Sartorius) and collected into a 125 mL FEP bottle, then
85 acidified (0.2%v/v HNO₃ 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 N₂ 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 (N₂) 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*
125 *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⁻¹, (*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 gL^{-1} , pH, Eh and O₂ 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|Hg₂Cl₂|KCl 3
 147 M (Radiometer Analytical, E_{ref} = 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 (2.5gL^{-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

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 μgCdg^{-1}) and N2 (2.4 μgCdg^{-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 μgCdg^{-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 V_2O_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 μm .

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 2nd 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⁻¹ 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⁻¹ CaCO₃) 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⁻¹ 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.

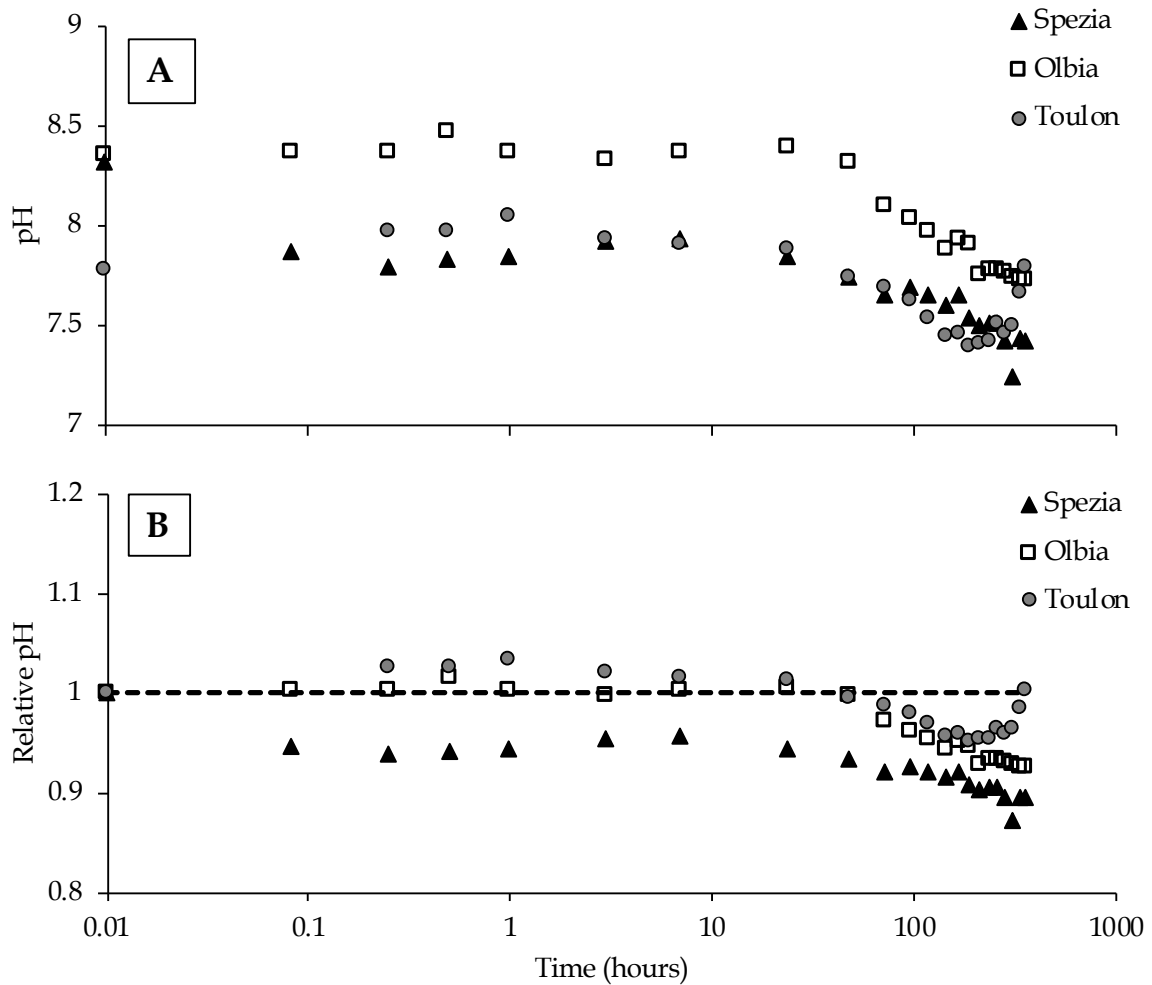
Table 2 : Amount of total particulate and easily-exchangeable Cd expressed in ng added in each performed experiment

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 ⁻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	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⁻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 (Figure 1), while

259 no similar early sharp decrease was observed for Olbia and Toulon (*Figure 1*). From 5th
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2 260 minutes of mixing to the end of the experiment, a similar temporal variation of pH was
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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
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9 263 and 7.73 for La Spezia and Olbia, respectively. pH decrease during sediment resuspension has
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11 264 already been observed (*Cabrol et al., 2017; Dang et al., 2015b; Pía Di Nanno et al., 2007;*
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13
14 265 *Zouch et al., 2018*) and could suggested a relatively common process governing pH,
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16 266 irrespective of the sediment composition. We have already demonstrated (*Layglon et al.,*
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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
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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
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31 272 from Toulon, while pH values showed a similar decreasing trend until 8 days of mixing
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33 273 (Spearman's correlation test, $\rho = 0.850$, $\rho = 0.899$ respectively for Toulon-La Spezia and Toulon-
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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 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.

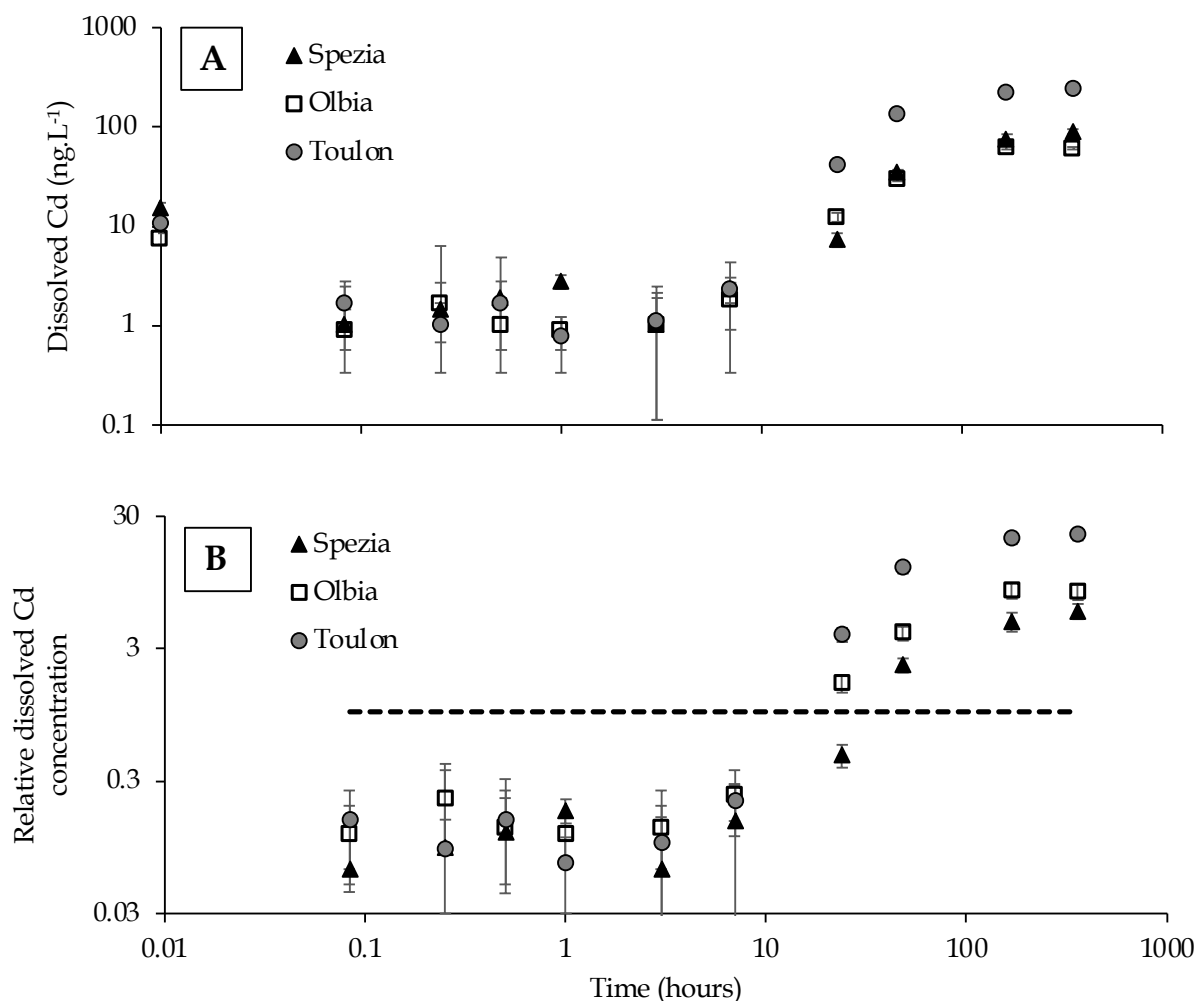
283 III.4 Kinetics of Cadmium transfers

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⁻¹ 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⁻¹) than in La Spezia (74 ngL⁻¹)
304 and the lowest value was found for Olbia (53 ngL⁻¹). 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 ± 0.20 compared
314 to 7.70 ± 0.08 and 7.63 ± 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⁻¹*
 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⁻¹, 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⁻¹ 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⁻¹), 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⁻¹ 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
20
21 340 (*Figure 3*). Therefore, the maximal concentration accepted by the EQS (2008/105/EC)
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23 341 (1500 ngL⁻¹ in water containing more than 200 mgL⁻¹ CaCO₃) 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
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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
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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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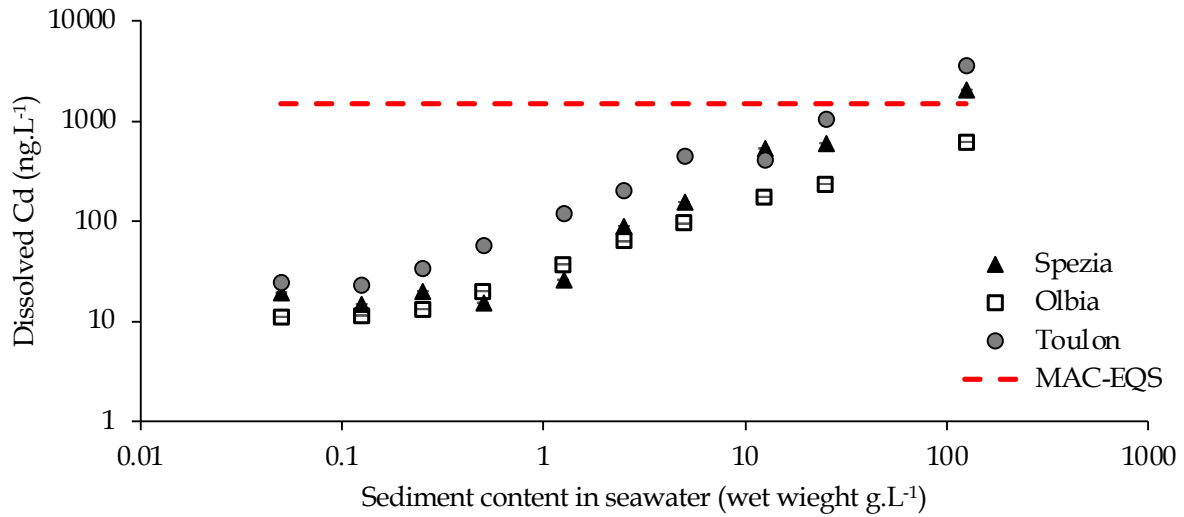


Figure 3 : Variations of dissolved Cd as a function of the sediment content (wet weight in g.L⁻¹) in seawater. The red dotted line represents the maximum allowable concentration (MAC-EQS) defined by the Environmental Quality Standards (EQS) in seawater. Both axis are presented in log scale to better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

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
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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
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11
12 378 by sediment management and water quality protection.

15 379 **Declaration of competing interest**

17
18 380 The authors declare that they have no known competing financial interests or personal
19
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Cd transfers during marine sediment resuspension over short and long-term period: associated risk for coastal water quality

Nicolas Layglon^{1,2*}, Véronique Lenoble¹, Longo Louis¹, Sébastien
D'Onofrio¹, Stéphane Mounier¹, Jean-Ulrich Mullo³, Davide Sartori⁴,
Dario Omanović⁵, Cédric Garnier¹, Benjamin Misson¹

¹Université de Toulon, Aix Marseille Université, CNRS/INSU, IRD, MIO UM 110,
Mediterranean Institute of Oceanography, La Garde, France

²University of Geneva, Sciences II, 30 Quai E.-Ansermet, 1221 Geneva 4, Switzerland

³LASEM-Toulon, Base Navale De Toulon, BP 61, 83800 Toulon, France

⁴Institute for Environmental Protection and Research, ISPRA, Via del Cedro, 38, 57123
Livorno, Italy

⁵Center for Marine and Environmental Research, Ruđer Bošković Institute, P.O. Box 180,
10002 Zagreb, Croatia

* Corresponding author: nicolas.layglon@unige.ch

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 ngL^{-1}
30 to few hundreds of 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,*
48
49 55 *2006; Satarug et al., 2003*). Cadmium remobilization occurs due to the competition of major
50
51 56 seawater cations with trace metals for specific adsorption sites and the formation of metal
52
53 57 chloro-complexes (*Calmano et al., 1993; Prause et al., 1985; Tahervand and Jalali, 2016;*
54
55 58 *Zhuang et al., 1994*). The kinetics of transfer found in the previous literature was only
56
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 Ω , 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 μ m on-
83 line syringe filters, cellulose nitrate, Sartorius) and collected into a 125 mL FEP bottle, then
84 acidified (0.2%v/v HNO₃ 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 N₂ 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 (N₂) 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⁻¹, (*Jiang*

134 *et al., 2020*) to dredging operations (~10-50 gL⁻¹, (*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⁻¹, pH, Eh and O₂ 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|Hg₂Cl₂|KCl 3
 146 M (Radiometer Analytical, E_{ref} = 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 ⁻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

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 μgCdg^{-1}) and N2 (2.4 μgCdg^{-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 V_2O_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 μm .

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 2nd 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⁻¹ 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⁻¹ CaCO₃) 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⁻¹ 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 ⁻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	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⁻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 (Figure 1), while

258 no similar early sharp decrease was observed for Olbia and Toulon (*Figure 1*). From 5th
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.

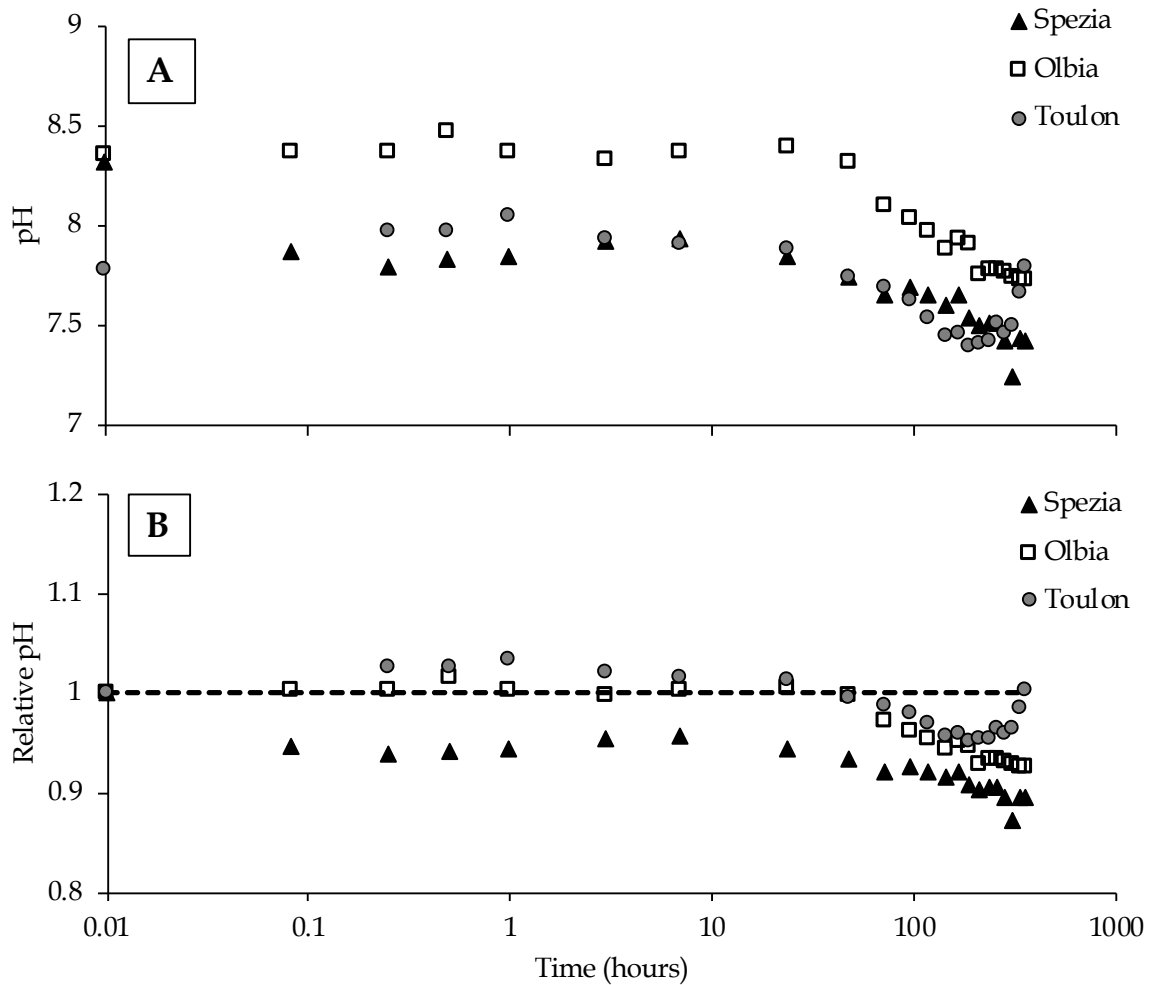


Figure 1: Variations of pH during sediment resuspensions (2.5 gL^{-1} sediment :water ratio). Panel A represents its absolute variations, with initial values of seawater represented by the symbols on the Y axis line while panel B represents its variations relatively to the initial pH of seawater before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

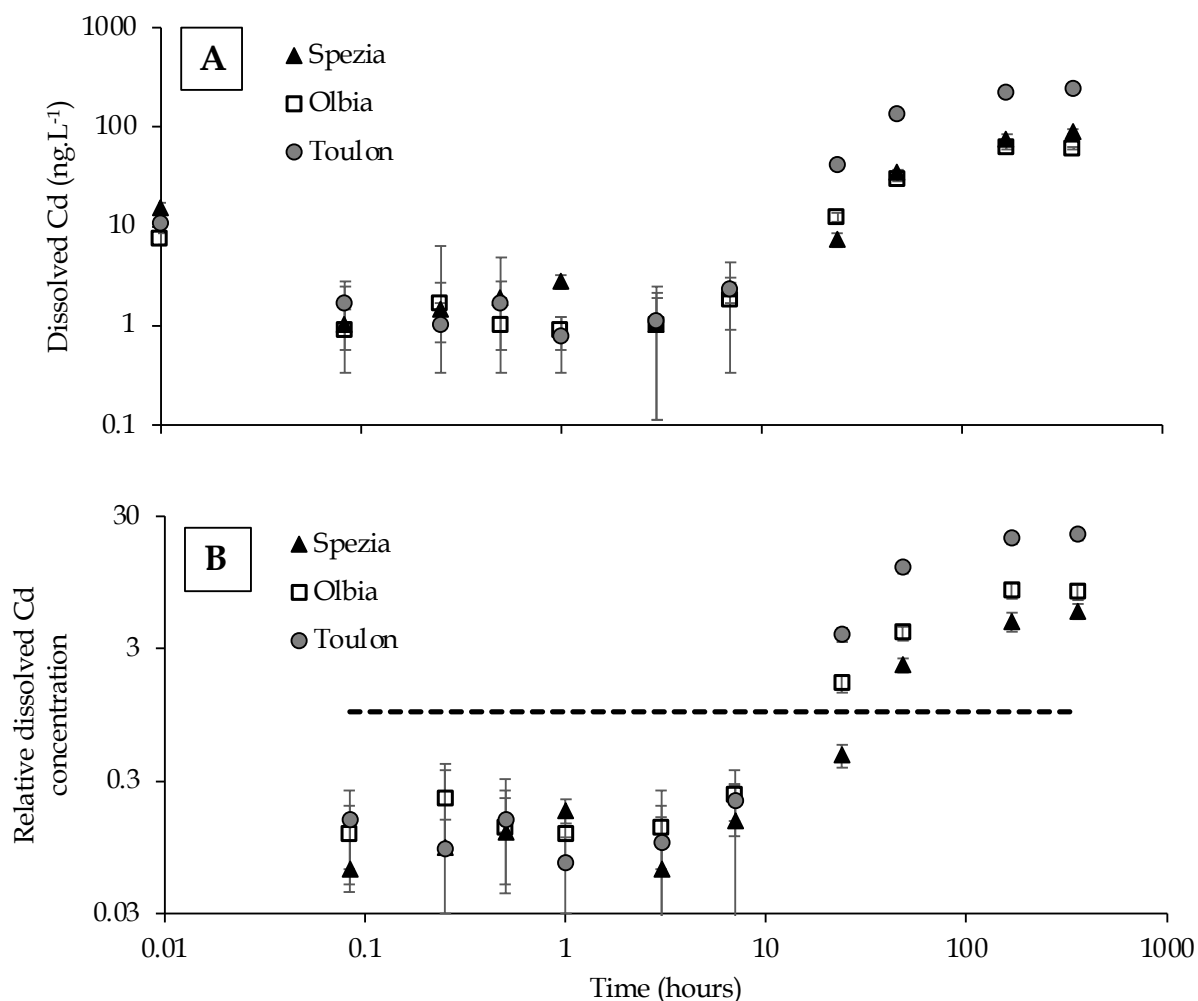
III.4 Kinetics of Cadmium transfers

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⁻¹ 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⁻¹) than in La Spezia (74 ngL⁻¹)
303 and the lowest value was found for Olbia (53 ngL⁻¹). 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 ± 0.20 compared
313 to 7.70 ± 0.08 and 7.63 ± 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⁻¹*
 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⁻¹, 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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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⁻¹ are consistent with the one
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11 334 observed in the previous kinetics experiments (*Figure 2* and *Figure 3*). For the highest S/L
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13 335 ratio (i.e. 125 gL⁻¹), representative of a suspended particulate matter concentration in seawater
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15 336 during dredging operations (*Nichols et al., 1990*), dissolved Cd increased up to 615, 2050 and
16
17 337 3624 ngL⁻¹ in Olbia, La Spezia and Toulon experiments, respectively, corresponding to a 82-
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19 338 fold, 132-fold and 330-fold increase when compared to the initial concentration in seawater
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21 339 (*Figure 3*). Therefore, the maximal concentration accepted by the EQS (2008/105/EC)
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23 340 (1500 ngL⁻¹ in water containing more than 200 mgL⁻¹ CaCO₃) was exceeded for experiments of
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25 341 La Spezia (by a factor 1.4) and Toulon (by a factor 2.4) experiments. These experiments showed
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27 342 that the EQS were punctually overpassed even if the Cd contents were lower than the N1 and
28
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
34
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
42
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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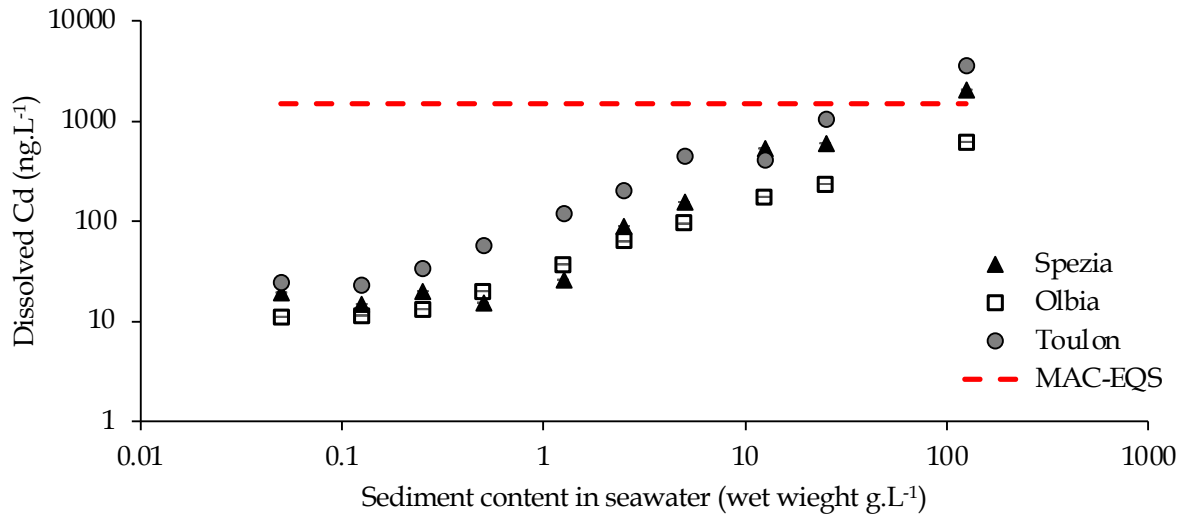


Figure 3 : Variations of dissolved Cd as a function of the sediment content (wet weight in $g.L^{-1}$) in seawater. The red dotted line represents the maximum allowable concentration (MAC-EQS) defined by the Environmental Quality Standards (EQS) in seawater. Both axis are presented in log scale to better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

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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6
7 375 realistic data to regulation thresholds and to contribute to regulation harmonization between
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9 376 countries. This study provides new bases for decision-makers and local authorities concerned
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11
12 377 by sediment management and water quality protection.
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15 378 **Declaration of competing interest**

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Declaration of competing interest

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CRedit author 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.