

1 **Seasonal variation and sources of dissolved trace metals in Maó Harbour, Minorca**
2 **Island**

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27

28 **Abstract**

29 The environmental conditions of semi-enclosed coastal water-bodies are directly related
30 to the catchment, human activities, and oceanographic setting in which they are located.
31 As a result of low tidal forcing, and generally weak currents, waters in Mediterranean
32 harbours are poorly renewed, leading to quality deterioration. Here, we characterise the
33 seasonal variation of trace metals (i.e. Co, Cd, Cu, Fe, Mo, Ni, Pb, and Zn) in surface
34 waters, and trace metal content in sediments from Maó Harbour, a semi-enclosed
35 coastal ecosystem in the NW Mediterranean Sea. Our results show that most of the
36 dissolved trace metals in the waters of Maó Harbour exhibit a marked inner - outer
37 concentration gradient, suggesting a permanent input into the inner part of the harbour.
38 In general, metal concentrations in the waters of Maó Harbour are higher than those in
39 offshore waters. Concentration of Cu (21 ± 8 nM), Fe (9.2 ± 3.2 nM) and Pb (1.3 ± 0.4
40 nM) are particularly high when compared with other coastal areas of the Mediterranean
41 Sea. The concentration of some metals such as Cu and Zn increases during summertime,
42 when the human population and boat traffic increase during the tourism season, and
43 when resuspension from the metal enriched sediments is higher. The evaluation of the
44 metal sources in the harbour reveals that, compared with other putative sources such as
45 runoff, aerosol deposition and fresh groundwater discharges, contaminated sediments
46 are the main source of the metals found in the water column, most likely through vessel-
47 driven resuspension events. This study contributes to the understanding of the processes
48 that control the occurrence and distribution of trace metals in Maó Harbour, thus aiding
49 in the effective management of the harbour, and enhancing the overall quality of the
50 seawater ecosystem.

51

52 **Keywords:** Maó Harbour, Trace metals, seawater, sediments, Groundwater discharge,
53 Mediterranean Sea

54 **1 Introduction**

55 Coastal regions are highly variable and complex systems, with dynamics resulting from
56 land-ocean interactions. These areas play an important role in the biogeochemical
57 cycling of nutrients and metals, and serve as buffer zones between terrestrial and marine
58 systems (Jahnke et al., 2008; Falco et al., 2010). Bays, harbours and other semi-
59 enclosed areas have reduced water renewal while integrating the loads from large
60 watersheds. These ecosystems show high sensitivity to environmental disturbances,
61 both of natural and anthropogenic origin (e.g. Lucas et al., 1999; Cloern, 1999, Cullen
62 et al., 2002).

63 Coastal marine waters are usually enriched in nutrients and trace metals compared with
64 the open ocean (e.g., Kremling and Hydes, 1988; Kremling and Pohl, 1989; De Jonge et
65 al., 1994; Nixon, 1995; Paerl, 1997; Pelley, 1998; Le Gal et al., 1999). This enrichment
66 results from the direct influence of rivers, submarine groundwater discharge (SGD),
67 atmospheric dust deposition, natural weathering, or anthropogenic sources discharging
68 along the coast (e.g. Martin and Whitfield, 1983; Nixon 1995; Paerl 1997; Cotté-Krief
69 et al., 2000; Tovar-Sanchez et al., 2014). The release of heavy metals from
70 anthropogenic activities is usually the major cause of the increase in concentrations that
71 may result in alterations to their natural geochemical cycles. Although trace metals in
72 the sea normally occur at low concentrations, they may have a considerable biological
73 effect on the coastal biota (Rainbow, 1992). Some trace metals, such as Fe, Co or Mo,
74 may influence the productivity and species composition of phytoplankton, while others
75 may have a toxic effect (e.g. Pb, Cu; Sunda, 1989, Jordi et al., 2012; Echeveste et al.,
76 2012). Moreover, above a certain threshold all bioavailable trace metals are potentially
77 toxic (Kennish, 1996).

78 Aerosol deposition, riverine runoff and/or SGD have been identified as the major
79 contributors to the dissolved pool of trace metals in the waters of the Mediterranean Sea
80 (Guerzoni et al., 1999; Ludwig et al., 2009; Krom et al., 2004; Tovar-Sanchez et al.,
81 2014; Rodellas et al., 2014; Trezzi et al. 2016). The study of metal fluxes from
82 sediments (e.g. through diffusion, bioturbation, bioirrigation, or resuspension events) in
83 nearshore areas have received scarce attention, even though they may represent an
84 important source of metals with a significant effect on the global dynamics and
85 functioning of phytoplankton (e.g. Lafabrie et al., 2013). This influence may be

86 exacerbated in some coastal environments such as harbours and bays, where industrial
87 activities have concentrated since the Industrial Revolution, dumping large amounts of
88 contaminants that accumulated in sediments (Garcia-Orellana, et al., 2011; Gargouri et
89 al., 2011; Lafabrie et al., 2007). Although industrial effluents are nowadays more tightly
90 controlled, the accumulated contaminants in the seabed can still represent an important
91 source of pollution, exceeding other sources.

92 Despite the importance of natural or anthropogenic disturbances, and physicochemical
93 forcing in the regulation of ecosystem biogeochemistry, there is a lack of information
94 about these processes which affect the dynamics of trace metals in low-energy confined
95 coastal systems, such as harbours. The identification of trace metal sources in coastal
96 ecosystems, and the processes controlling their seasonality are critical in the
97 understanding of the ecological functioning and the biogeochemical cycles in the coast
98 as well as for the application of government regulations on seawater quality. These
99 studies are especially critical in the nearshore waters of oligotrophic areas, as is the case
100 of the Mediterranean Sea, where a large proportion of the marine productivity is
101 regulated by the supply of terrestrial input (Tovar-Sanchez et al., 2014).

102 The natural semi-enclosed harbour of Maó (Minorca Island, NW Mediterranean Sea) is
103 a highly impacted region particularly vulnerable to variations in climate conditions and
104 where, as a consequence of the industrial activities established along the harbour during
105 the last century, metal concentrations have increased in the sediments (Garcia-Orellana
106 et al., 2011). This study aims to identify processes and quantify fluxes that control the
107 spatial and temporal distribution of trace metal composition (i.e. Cd, Co, Cu, Fe, Mo,
108 Ni, Pb, and Zn) in waters and sediments of Maó Harbour. This research will contribute
109 to the knowledge of the biogeochemical cycle of trace metals in the area which will help
110 in the appropriate management of the port (e.g. dredging, maritime traffic) and will also
111 enhance its ecological sustainability.

112

113 **2 Material and methods**

114 2.1 Site description

115 Maó Harbour (Minorca Island, Spain; 39°52'N 4°18'E; Fig. 1) is considered as one of
116 the largest natural harbours in the Mediterranean Sea, with a length of ~5.5 km, a width
117 of ~0.6 km and a depth of up to 30 m. The geomorphology of the area is conditioned by
118 a NW-SE running geological fault over which the harbour is situated. Its mouth is very
119 narrow (~300 m) and relatively shallow (~14 m), which greatly restricts the exchange
120 with offshore waters. The climate in the area is characterised by mild winters (~13°C)
121 and relatively hot and dry summers (~28°C). Annual precipitation is 563 ± 132 mm
122 (Data from the Spanish Meteorological Agency, AEMET). The harbour receives
123 terrestrial water input from different sources. Runoff from a watershed extending to the
124 north is channelled through a small stream intermittently discharging into the harbour
125 head. The input may be torrential during autumn and early winter when precipitation is
126 at its highest. Likewise, submarine groundwater discharge, which includes fresh
127 groundwater discharge through the limestone lithology extending along the southern
128 coast of the harbour and seawater recirculating through sediments, may represent a
129 source of trace metals (total flow $60 \cdot 10^3 - 180 \cdot 10^3 \text{ m}^3 \text{ d}^{-1}$; Rodellas et al., 2015a).

130 Various types of industries (mainly marine, motor, textile, jewellery and footwear
131 factories) have been established around the harbour during the two last centuries and
132 have led to the dumping of waste-water into the bay, producing a progressive
133 accumulation of metals in sediments (e.g. Ag, Cd, Cu, Ni, Pb; Garcia-Orellana et al.,
134 2011). Since 1978, urban and industrial wastes are dumped into the open sea through
135 an outfall pipe. Nowadays, Maó Harbour is an important tourism destination and hosts
136 the most important industrial, maricultural (mussels) and mercantile centre of the island.
137 As a consequence, cruise boats and deep draft vessels daily transit the waters of the
138 harbour, with higher frequency during the summer.

139 2.2 *Sampling and analysis*

140 Surface water samples were collected during four surveys in July 2010, October 2010,
141 March 2011 and June 2011. In all surveys 15 stations were sampled in a longitudinal
142 transect following the main axis of the harbour (Fig. 1). At each station a SBE-25 CTD
143 was deployed from surface to the bottom in order to characterise the hydrographic

144 properties of the water column. We use practical salinity scale to report salinities and
145 therefore salinities values are expressed by dimensionless number (PSS-78, UNESCO
146 1981).

147 Water samples were collected at 1 m below the surface using a peristaltic pumping
148 system equipped with acid-washed C-Flex tubing in the pump head, and filtered in-situ
149 through an acid-cleaned polypropylene cartridge filter (0.22 μm ; MSI, Calyx®). The
150 sampling protocol has been described elsewhere (Tovar-Sánchez, 2012). Additionally,
151 samples for trace metals analysis were also collected from the stream inflowing into the
152 inner harbour (in October 2010 and March 2011) and from the waters of eight nearshore
153 wells (W1-8) (Fig. 1). Waters from these wells are assumed to be representative of the
154 groundwater inflow into the harbour (Rodellas et al., 2015a).

155 Dissolved trace metals samples were acidified to pH <2 with ultrapure grade HCl
156 (Merck) in a class-100 HEPA laminar flow hood and stored for at least 1 month before
157 extraction. Concentrations of metals (i.e. Cd, Co, Cu, Fe, Mo, Ni, Pb, and Zn) were
158 analysed with ICP-MS (PerkinElmer ELAN DRC-e) after a pre-concentration using the
159 APDC/DDDC organic extraction method (Bruland et al. 1979; Tovar-Sánchez, 2012).
160 The accuracy of the analysis was established using Coastal Seawater Reference Material
161 for trace metals (NASS-5, NRC-CNRC) (obtained recoveries of 108%, 93%, 107%,
162 93%, 97%, 92%, 88%, and 105% for Cd, Co, Cu, Fe, Mo, Ni, Pb, and Zn, respectively).
163 The limits of detection, calculated as three times the standard deviations of subsequent
164 blank measurements, were 6, 4, 141, 129, 309, 22, 4, 427, and 287 pM for Cd, Co, Cu,
165 Fe, Mo, Ni, Pb, and Zn, respectively.

166 Surface sediment samples (1-2 cm) were collected by scuba divers in June 2011, in 6
167 stations located along the harbour (Fig. 1). Samples were stored frozen in polyethylene
168 tubes until analysis. The grain size in each sample was determined with a set of stainless
169 steel sieves for six fractions with an electric sieve. Samples were treated initially with
170 hydrogen peroxide to remove the organic fraction (McManus, 1988; Walling and
171 Woodward, 1993) and dried in an oven at 60°C for two days. Approximately 50 g of
172 sample were sieved for a period of 15 min using a battery of 6 sieves with mesh sizes
173 of: 2 mm, 1 mm, 500 μm , 250 μm , 125 μm , and 63 μm . Material retained on each sieve
174 was weighed to calculate the percentage in each size fraction.

175 Metal concentrations in surface sediments (i.e. Cd, Co, Cu, Fe, Mo, Ni, Pb, and Zn)
176 were determined by ICP-OES (Perkin Elmer ICP-OES Optima 5300 DV). Samples
177 were dried in an oven at 60°C for two days and subsequently ground in a zirconia ball
178 mill (10 min at 170 rpm) before analysis. Metals were extracted with a microwave acid
179 digestion system (CEM model Mars 5) according to the SW-846 EPA Method 3051A
180 (US EPA 1987), which involved the digestion of 0.2 g of sediment sample by triplicate
181 with 10 mL of nitric acid (65%, Suprapur quality) in Teflon vessels. After digestion,
182 samples were diluted to 50 mL using Milli-Q water and then analysed. The accuracy of
183 the analysis was checked with the certified reference material PACS-2 (National
184 Research Council Canada), with recoveries of 99.4%, 99.9%, 90.9%, 86.7%, 92.6%,
185 89.8%, 91.6%, and 93.3% for Cd, Co, Cu, Fe, Mo, Ni, Pb, and Zn respectively.

186 *2.3 Statistical analysis*

187 Statistical evaluation was performed using SigmaPlot 12.0 for Windows. Previous to the
188 selection of the statistic test a Shapiro-Wilk test was previously performed for each case
189 to evaluate the normality of the data distribution. The non-parametric Kruskal-Wallis
190 One Way Analysis of Variance on Ranks was carried out to determine differences in
191 average metal concentrations between the four surveys. Because the small number of
192 data for each survey and their normal distributions, a Student's t-test was employed to
193 identify differences in metal concentrations between inner and outer harbour.
194 Correlations between ²²⁴Ra and trace metals through the four surveys were tested using
195 a linear regression model that also involved the calculation of Pearson Product Moment
196 Correlation Coefficient. A confidence interval of 95% was adopted and results for all
197 tests were considered significant if associated p values were <0.05.

198

199 **3 Results and discussion**

200 *3.1 Hydrologic characteristics*

201 Marked seasonal differences in seawater temperature and salinity were observed
202 between surveys (Fig. 2). During summer (July 2010 and June 2011), and in the deepest
203 parts of the harbour, the water column presented a marked thermal stratification (Fig.
204 2A and G), varying from 25 °C in the surface to <17 °C near the bottom. The

205 thermocline was located at 14.0 ± 1.6 m and presented a strong temperature gradient.
206 Lower temperatures were measured during October 2010 (~ 20 °C) and March 2011
207 (~ 14 °C) and when the water column was more homogeneously mixed with a small
208 temperature variation of < 2 °C between the sea surface and the bottom (Fig. 2C and E).
209 Salinity in the harbour waters ranged between 38.1 in July 2010 and 37.4 in March 2011
210 when a reduced salinity layer was observed in the upper 5 m of the water column, which
211 was indicative of enhanced runoff. Differences in salinity between the harbour and
212 offshore waters were also observed in July 2010 and October 2010 (t-test: t value 6.62
213 and -7.72 for July 2010 and October 2010, respectively. p value: < 0.001 , degrees of
214 freedom (DF): 13, n 'inner': 7, n 'outer': 8). The inner part experienced increased
215 salinities in July, possibly as a consequence of intense evaporation (Fig. 2B).
216 Conversely, precipitation and runoff decreased the salinity during October (Fig. 2D).
217 These salinity differences suggest water confinement in the harbour and, consequently,
218 the environmental conditions appear to be driven by local processes rather than by
219 general oceanographic conditions.

220 *3.2 Trace metals in Maó Harbour*

221 *3.2.1 Metals in surface seawater*

222 With the exception of Cd and Mo, all dissolved metals exhibited an inshore-offshore
223 negative gradient with significantly (t-test: t values range from 7.51 for Cu to 2.48 for
224 Fe. p value: < 0.001 , DF = 13, n 'inner': 7, n 'outer': 8) higher concentration of Co (0.39
225 ± 0.05 nM), Cu (20 ± 4 nM), Fe (12 ± 5 nM), Ni (4.8 ± 0.3 nM), Pb (1.6 ± 0.2 nM) and
226 Zn (34 ± 6 nM) in the inner basin of the harbour (stations 1 to 7), relative to those
227 concentrations measured at the outer basin (stations 8 to 15; Co: 0.22 ± 0.04 nM, Cu:
228 13.1 ± 4.3 nM, Fe: 7.2 ± 1.6 nM, Ni: 3.8 ± 0.3 nM, Pb: 1.0 ± 0.2 nM, and Zn: 14 ± 5
229 nM) (Figs. 3 and 4). The enhanced concentrations in the inner harbour suggest that the
230 main sources of trace metals were likely located at this site. Cobalt, Cu, Ni and Zn
231 correlated well in the four surveys (coefficient of determination $r^2 > 0.83$), suggesting a
232 common origin. Copper and Zn proportionally increased during the summer (July 2010
233 and June 2011) when tourist population increases, and when navigation in the harbour is
234 at its highest. In general, lower variations were measured during March 2011, which is
235 attributed to an increased flushing of surface waters during winter rainfall episodes.

236 While in most of the cases metal concentrations decreased linearly offshore, in some
237 other cases marked variations occurred between St 9 and St10. This was noticeable
238 during March 2011 when the concentrations of Co, Ni, Pb and Zn increased at this
239 location and, more remarkably, in the case of Pb in October 2010. These variations
240 suggest a point source in this area either related to uncontrolled urban discharge or to
241 enhanced groundwater flow. This last source is less likely since the well W7, located in
242 this area, did not show particularly high Pb concentrations (i.e. 2.3 - 2.7 nM).

243 Unlike other metals, concentrations of Mo and Cd showed a rather constant distribution
244 along the harbour, but with a remarkable seasonal variation (Kuskal Wallis test: H
245 values 48.72 for Cd and 43.43 for Mo, p value: <0.001, DF: 3, n: 15). The highest
246 concentrations were found in March 2011 (Cd: 0.39 ± 0.01 nM and Mo: 137 ± 3 nM)
247 and the lowest in July 2010 for Cd (0.17 ± 0.02 nM) and July 2011 for Mo (108 ± 5 nM)
248 (Figs. 3A and 4A). The distribution and behaviour of Cd and Mo are consistent with
249 those found in other studies showing that in estuarine and coastal areas, the input from
250 rivers and terrestrial sources is not the origin of these elements (Tovar-Sanchez and
251 Sañudo-Wilhelmy, 2011). Seasonal variations may be controlled by other chemical and
252 environmental conditions such as solubility, complexation by organic ligands,
253 atmospheric inputs, etc. (Migon et al., 2002; Heimbürger et al., 2014).

254 The concentrations of dissolved metal in the waters of Maó Harbour are higher than
255 those reported for different areas of the Mediterranean Sea and Spanish coasts with the
256 highest differences measured for Cu (21 ± 8 nM), Fe (9 ± 3 nM) and Pb (1.3 ± 0.4 nM)
257 (Table 1). The progressive sediment contamination by metals (i.e. Pb and Cu) due to the
258 various types of industry established around the harbour (Garcia-Orellana et al. 2011)
259 could be the cause of these high concentrations measured in its waters.

260

261 *3.2.2 Metals in surface sediments*

262 Trace metals concentrations in surface sediments of Maó Harbour varied between 1 - 6
263 $\mu\text{g g}^{-1}$ (Co), 2 - 81 $\mu\text{g g}^{-1}$ (Cu), 0.2 - 2.3% (Fe), 1 - 22 $\mu\text{g g}^{-1}$ (Ni), 14 - 124 $\mu\text{g g}^{-1}$ (Pb),
264 17 - 134 $\mu\text{g g}^{-1}$ (Zn), (Table 2). The dominant grain size in most samples was silty-
265 sands although, in the inner basin, in proximity to the urban area (C2 and C3 at Fig. 1),
266 the proportion of silts exceeded 50% (sandy-silts). No direct relationship was found
267 between metal content in sediments and grain size. Only concentrations measured at C4

268 site were significantly different (t-test: t values ranged from 19.13 for Co to 70.0 for Cu,
269 p value: < 0.001, DF: 4, n: 5) from the rest of the samples, exhibiting lower metal
270 contents. This station was also characterised by the highest content of shells and other
271 carbonated structures (Ca: 8 – 26%) with lower metal binding capacity. Cobalt, Fe and
272 Ni concentrations in the surface sediments of Maó Harbour were similar to those
273 reported for other Mediterranean bays (Table 3). Sediments were particularly enriched
274 in Cu, Pb and Zn with measured concentrations of up to 28 – 75%, 42 – 95% and 12 –
275 48%, higher than in other Mediterranean areas (Table 3).

276

277 *3.3 Sources of metals in Maó Harbour waters*

278 Several trace metal sources can be identified in the harbour waters. Diversions from
279 urban drainage systems, and groundwater discharges through the porous limestone
280 substrate along the southern coast of the harbour could represent a source of metals for
281 the harbour. A stream located in the innermost part of the harbour is the most important
282 source of freshwater runoff, though the evacuation through the city storm-water
283 drainage system could be also significant during the heaviest rainfall events. Median
284 concentrations of metals in the stream were higher than those measured in the inner
285 harbour waters, suggesting an influence of this stream on overall metal budgets (Co: 4.4
286 \pm 3.2 nM, Cd: 0.2 \pm 0.2, Cu: 53.9 \pm 7.1 nM, Fe: 677 \pm 375 nM, Mo: 37.5 \pm 29.5 nM, Ni:
287 62.4 \pm 2.1 nM, Pb: 1.9 \pm 0.2 nM, and Zn: 70.9 \pm 8.5 nM). Table 4 shows the estimated
288 annual metal fluxes from the stream considering a drainage area of $2.8 \cdot 10^7$ m², an
289 impervious area of $5.0 \cdot 10^5$ m², an average precipitation of 563 mm y⁻¹ and a calculated
290 flow of $3 \cdot 10^6$ m³ y⁻¹. Since differences of Mo and Cd with offshore waters were not
291 significant they were not included in the different fluxes estimations.

292 Atmospheric deposition could be also an important source of trace metals in this region
293 (e.g. Jordi et al., 2012). Direct atmospheric metal fluxes in Maó Harbour can be
294 calculated from reported atmospheric fluxes (mol km⁻² y⁻¹) in the NW Mediterranean
295 Sea (Cd: 1.9 - 8.0, Co: 0.3 - 2.2, Cu: 13 - 20, Fe: 575 - 2525, Ni: 6.8 - 8.0, Pb: 4.6 - 9.0,
296 and Zn: 11 - 1150; Guieu et al., 1997) considering the water body surface area (~ 2.3
297 km²; Table 4). Additionally, it has been demonstrated that submarine groundwater
298 discharge (SGD) may deliver a substantial amount of trace metals into the sea, and in
299 some areas represents a major source of these compounds to coastal ecosystems

300 (Windom et al. 2006; Beck et al. 2007; Rodellas et al. 2014; Tovar-Sánchez et al., 2014;
301 Trezzi et al., 2016). Here, we differentiate between fresh groundwater input, which is
302 the only SGD fraction supplying external input of water, and metals to the harbour, and
303 seawater recirculation through sediments. In order to evaluate the influence of fresh
304 groundwater discharge, we measured the concentrations of metals in 8 wells located
305 around the harbour (Average \pm SDV; Cd: 0.1 ± 0.3 nM, Co: 4.2 ± 3.5 nM, Cu: 53 ± 23
306 nM, Fe: 460 ± 280 nM, Mo: 15 ± 9 nM, Ni: 54 ± 41 nM, Pb: 6 ± 8 nM and Zn: $190 \pm$
307 310 nM; Fig S1). The flux of metals supplied by fresh groundwater discharge was
308 calculated by multiplying the concentrations measured in the wells by the estimated
309 annual terrestrial groundwater flow into Maó Harbour ($3.3 \cdot 10^6$ m³ y⁻¹) (depicted from
310 island-scale hydrographic budget calculations (DGRH, 2013) and assuming a drainage
311 area of 27.9 km². The resulting fresh groundwater flow represents some 7% of total
312 SGD measured by Rodellas et al. (2015a) in Maó Harbour using Ra isotopes, suggesting
313 that > 90% is recirculated seawater, which, is consistent with reports from other
314 Mediterranean areas (Rodellas et al., 2015b). Thus, the seawater recirculation, through
315 harbour sediments can also contribute to the transfer of metals from sediments into the
316 water column, and thus it is included as benthic fluxes.

317 Input of metals from sediments can occur by diffusion, bioirrigation, desorption,
318 resuspension of sediments, and seawater recirculation (also referred to as pore-water
319 transfer) driven by pressure gradients mainly forced by seiches, tides, waves, bottom
320 currents, benthic organisms, storms, or density-driven convection. Additionally, intense
321 sediment resuspension occurs in the Harbour as the result of the navigation of deep-
322 draft vessels (Fig. S2). This mainly occurs in the shallow areas of the inner basin where
323 the vessels manoeuvre, and where the bottom sediments have been affected by
324 progressive contamination (Garcia-Orellana et al., 2011).

325 In order to evaluate the importance of each metal source, as well as to try and
326 understand the role of sediments in the input of metals in the water column, several
327 approaches can be taken. Trace metal input from sediments into the water column is
328 usually evaluated performing laboratory experiments (Kalnejais et al., 2010; Durán et
329 al., 2012), measuring in-situ fluxes at the water-sediment interface (Viollier et al., 2003)
330 or monitoring continuously concentrations of trace metals in the water column
331 (Superville et al., 2014), among others. Here, metal fluxes from sediments into water

332 column were evaluated through a mass balance of the studied compounds (i.e.
333 comparing major sources and sinks of the metals analysed, where the only unknown is
334 the input from sediments). In order to obtain a conservative estimate, the fluxes of
335 metals from sediments into the waters were estimated by calculating the difference
336 between the offshore export and the sum of fluxes of the major inputs (groundwater
337 discharge, atmospheric deposition and stream inputs) (Table 4). It is noteworthy that we
338 assume that major net output of trace metals from the harbour derive from the export to
339 the open sea (offshore exports), and therefore output related to the rapid (relative to
340 residence time) scavenge of dissolved trace metals by suspended particles, organic
341 matter and Fe- and Mn- hydroxides, and biological consumption were excluded from
342 the mass balance. Including the output would considerably increase the fluxes of trace
343 metals from sediments. The offshore metal export can be estimated from the excess
344 metal inventory in the harbour (i.e. the difference between the average concentrations in
345 the harbour (St 1-14) and the outer station (i.e. St 15) times the harbour volume (i.e.
346 $38.3 \cdot 10^6 \text{ m}^3$), divided by the residence time of dissolved compounds in harbour waters
347 (from 2 to 7 days, depending on the season Rodellas et al., 2015a) (Table 4). This
348 qualitative and conservative comparison allowed us to determine that the input from
349 sediments represent the main source in the Harbour, being 96% for Co, 99% for Cu,
350 80% for Fe, 92% for Ni, 99% for Pb and 98% for Zn of the total flux into the harbour
351 waters, and revealing the importance of the supply of trace metals from contaminated
352 bottom sediments.

353 Although several processes may be responsible for these metal fluxes from sediments
354 (e.g. diffusion, bioturbation, bioirrigation, pressure-induced advection), sediment
355 resuspension triggered by maritime traffic may represent the dominant mechanism,
356 when the frequency and magnitude of the resuspension events are taken into account.
357 Maó Harbour is an important mercantile centre and touristic destination where deep-
358 draft vessels are daily steaming along the harbour, especially during the summer season.
359 The shallowness of the inner part of the harbour (transit channel of 10 - 14 m depth) and
360 the draft of the vessels (6 to 9 m) produce the resuspension of significant amounts of
361 sediments (Fig. S2), which encourages the transfer of contaminants from the sediments
362 into the water column (Garcia-Orellana et al. 2011; Rodellas et al., 2015a). This
363 hypothesis has been recently tested by Rodellas et al. (2015a), identifying sediments in
364 the Maó Harbour as a major source of short-lived Ra isotopes (^{223}Ra and ^{224}Ra) into the

365 water column that are continuously produced in sediments by their parent disintegration
366 (^{227}Th and ^{228}Th , respectively). Resuspension events triggered by vessel docking
367 manoeuvres represented a significant contributor to the short-lived Ra budgets of the
368 water column. Indeed, concentrations of these short-lived Ra isotopes in waters
369 measured by Rodellas et al. (2015a), which were collected at the same stations and
370 concurrently with metal samples, are well correlated with metal concentrations in
371 harbour waters, except for Cd and Mo that have different sources, (coefficients of
372 determination, r^2 , ranging from 0.98 for Fe to 0.999 for Co, $p < 0.001$) (Fig. 5). These
373 correlations suggest that short-lived Ra isotopes and metals are supplied by the same
374 source, pointing to the relevance of sediments as a source of the trace metals found in
375 the water column, most likely through the resuspension events.

376 **4 Conclusions**

377 The results presented here show that Maó Harbour, a semi-enclosed ecosystem with
378 restricted exchange, exhibit a general onshore-offshore negative gradient of dissolved
379 metals parts during the four seasons. Contaminated sediments represent the main source
380 of the Co, Cu, Fe, Ni, Pb and Zn found in the water column, most likely as the result of
381 their resuspension driven by maritime traffic. As a consequence of metal contamination
382 in the sediment, and the continuous transfer with the water column, the levels of Cu and
383 Pb in Maó Harbour are considerably higher than the values reported for the sediment
384 and waters of other Mediterranean areas. The effect of the input of trace metals from
385 these anthropogenic sources on the ecological functioning of the Maó Harbour deserves
386 further analysis.

387

388 **Acknowledgments**

389 This work was financed by the *Ministerio de Economía y Competitividad* (MINECO)
390 grants EHRE (CTM2009-08270) and GRADIENTS (CTM2012-39476-C02-01). M.C.
391 Martínez-Sotos's work was funded by a JAE-doc contract from CSIC. VR
392 acknowledges financial support from the European Union's FP7 (Marie Curie Actions
393 PCOFUND-GA-2013-609102), through the PRESTIGE programme coordinated by
394 Campus France. We are indebted to *Puertos del Estado* and *Autoritat Portuaria de*
395 *Balears* for support during sampling and providing meteorological data. Thanks also to

396 Ana Massanet, Itziar Alvarez for their collaboration in the development of the
397 experimental and labs part of this research. We would like to gratefully acknowledge
398 the OBSAM, Estación de Investigación Jaume Ferrer (IEO), Joan Moranta (IEO),
399 Museu Militar de Menorca, Grupo CLH and Bodegues Ferré for their collaboration. The
400 authors also want to thank the support of the Generalitat de Catalunya to MERS (2014
401 SGR-1356). This research is a contribution to the ANR @RAction chair (ANR-14-
402 ACHN-0007-01) and Labex OT-Med (ANR-11-LABEX-0061) funded by the
403 “Investissements d’Avenir” programme through the A*MIDEX project (ANR-11-
404 IDEX-0001-02) of the French National Research Agency (ANR).

405

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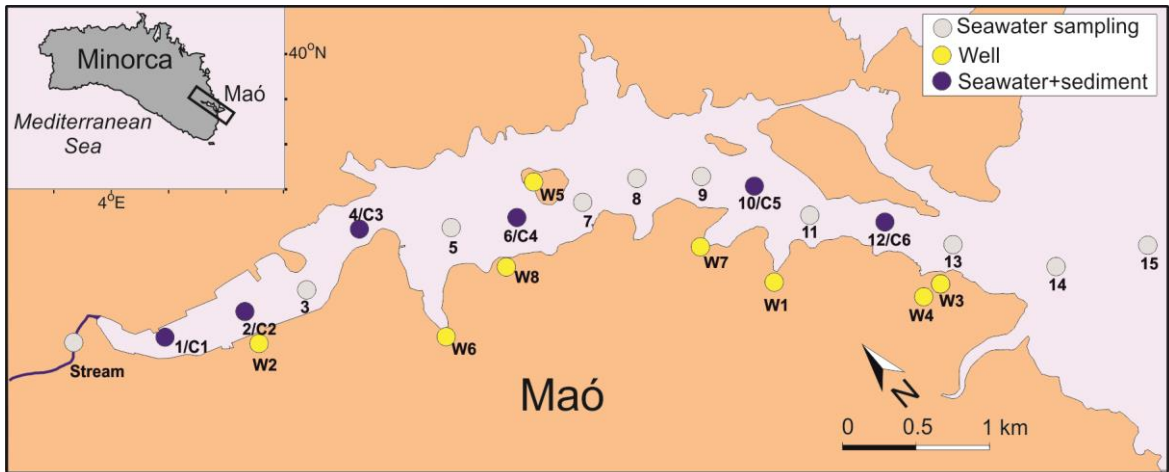
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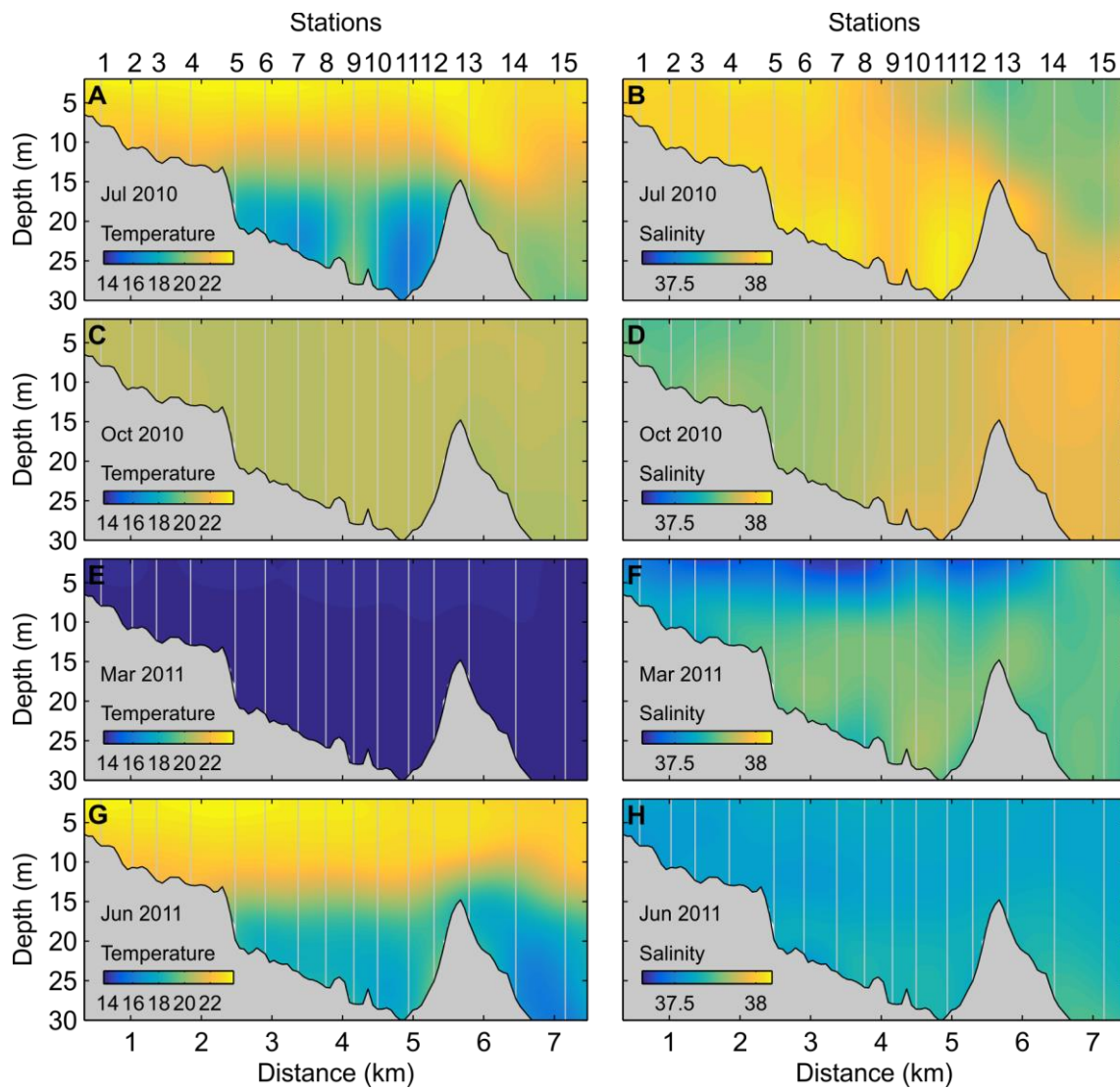
581 **Figures**



582

583 Fig. 1 Map showing the location of the study area in Minorca Island (North-Western
584 Mediterranean Sea), and the sampling stations of surface water (1 to 15), wells (W1 to
585 W8) and sediments (C1 to C6).

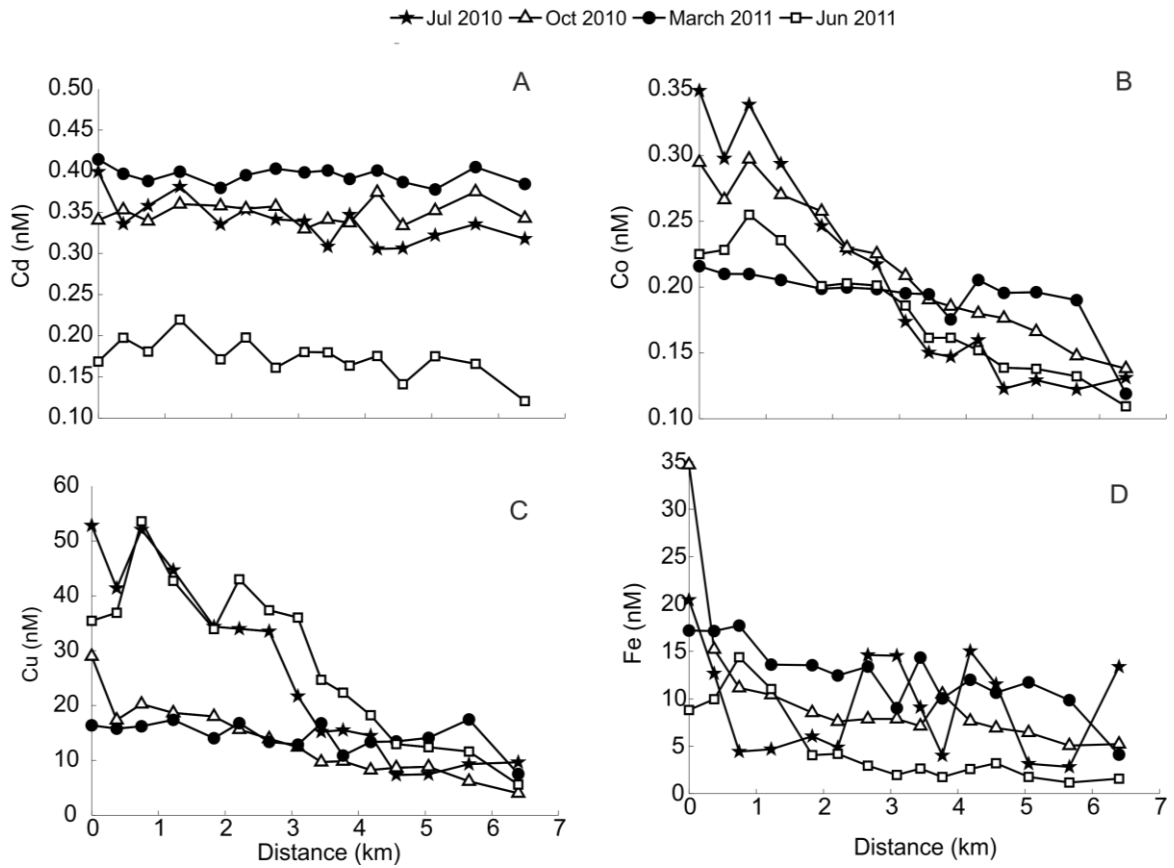
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588 Fig. 2 Temperature ($^{\circ}\text{C}$) and salinity along the Maó Harbour transect for the four
 589 conducted surveys. The x-axis indicates the distance from the inner shore of the port.

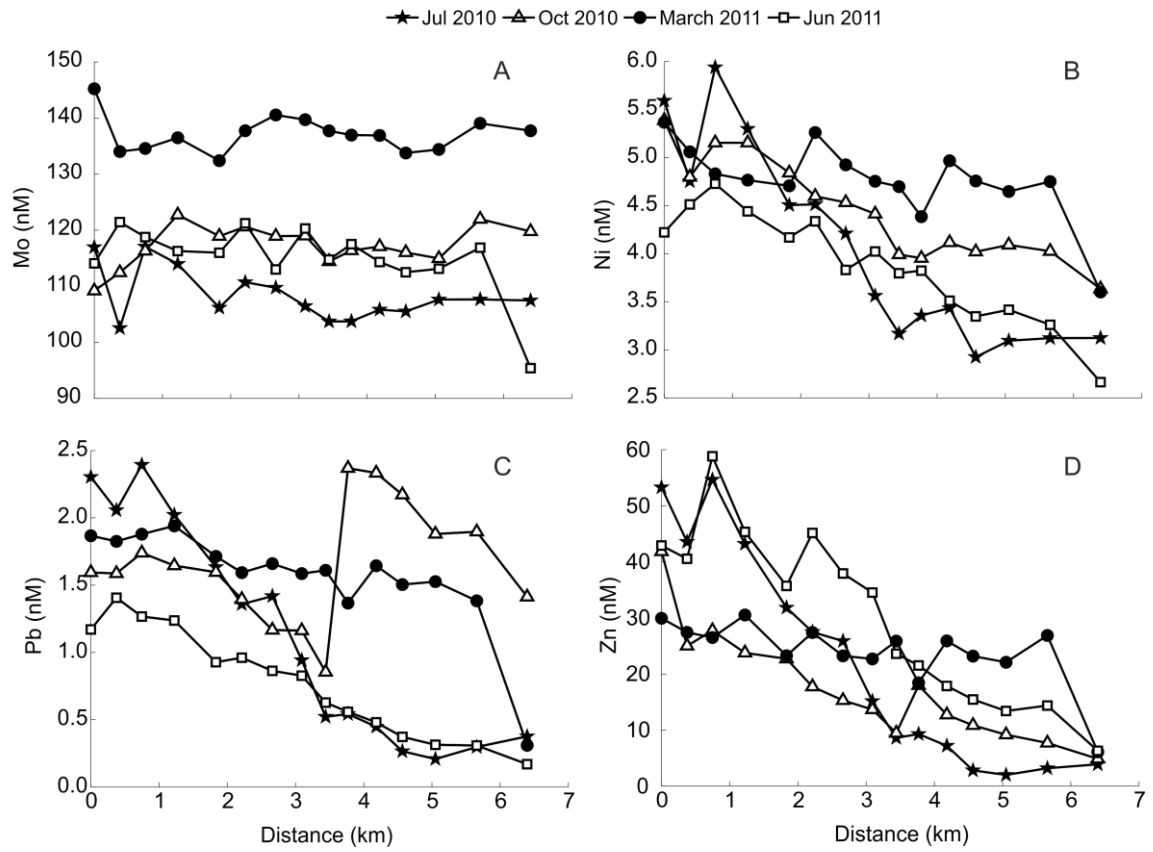
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592 Fig. 3. Trace metal concentrations along the Maó Harbour for all four surveys. (A) Cd;
 593 (B) Co; (C) Cu and (D) Fe. The x-axis indicates the distance from the inner shore of the
 594 port.

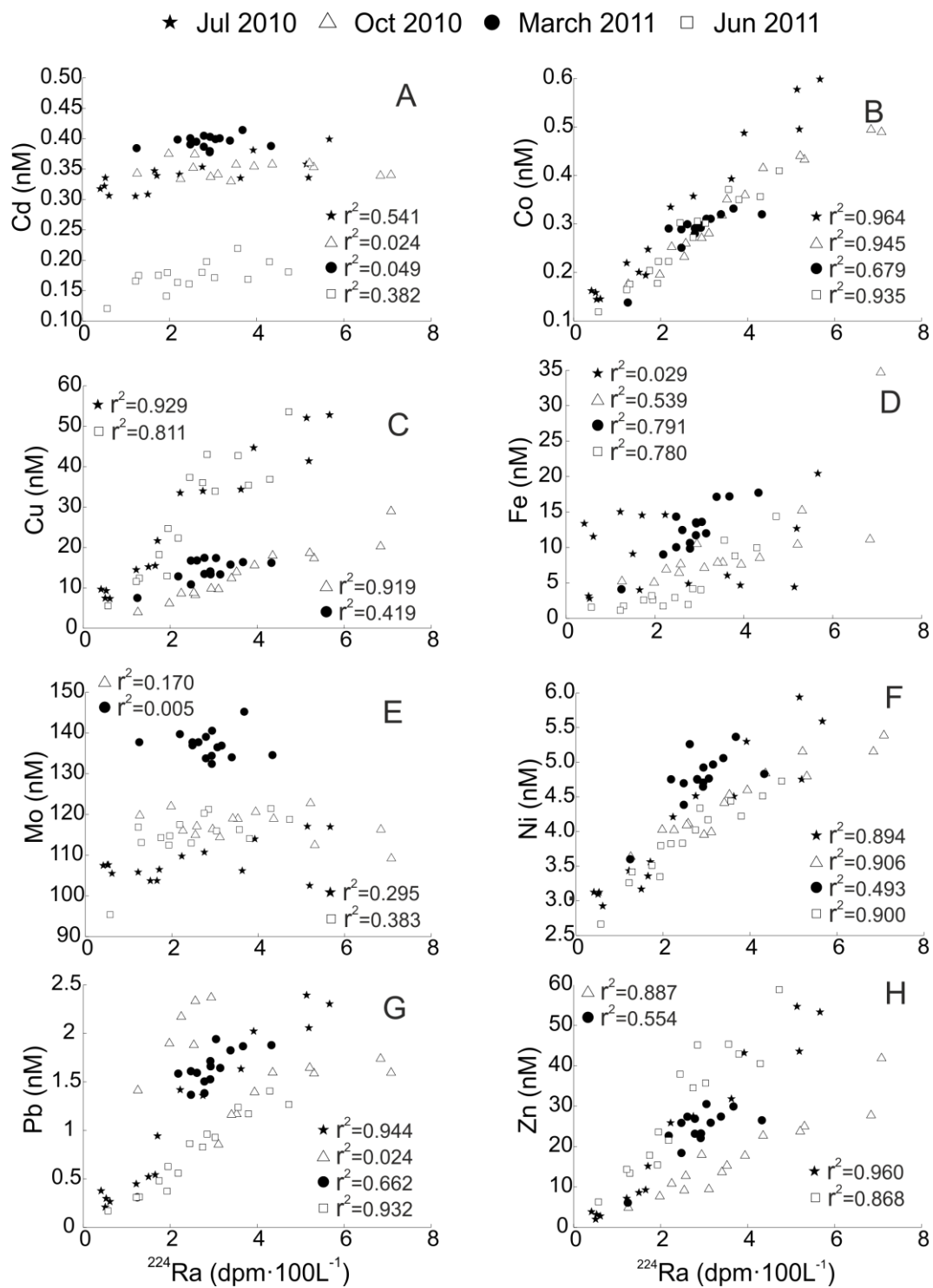
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597 Fig. 4 Trace metal concentrations along the Maó Harbour for all four surveys. (A) Mo;
 598 (B) Ni; (C) Pb and (D) Zn. The x-axis indicates the distance from the inner shore of the
 599 port.

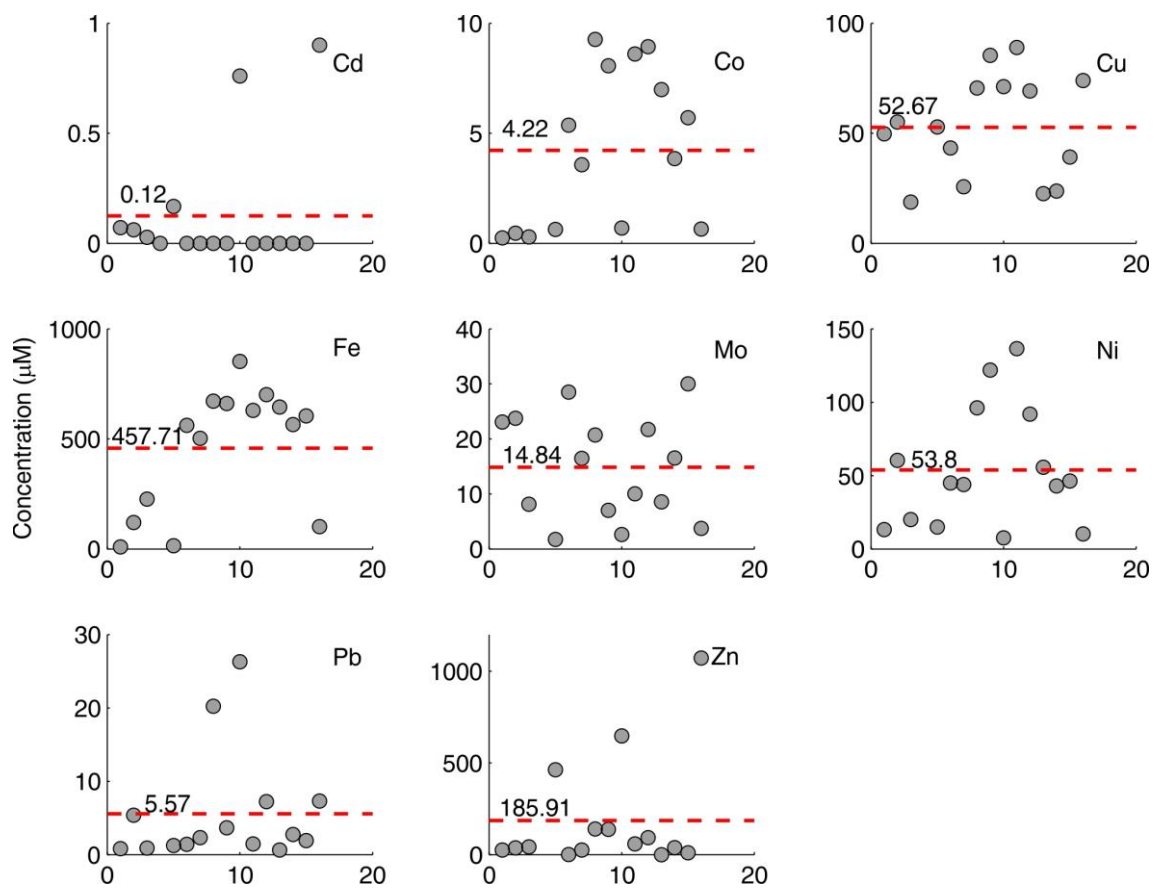
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602 Fig. 5 Scatter Plot of the concentrations between ^{224}Ra and trace metals. (A) Cd; Co (B);
 603 Cu; (C) Fe; (D); Mo; (E); Ni (F); Pb (G) and (H) Zn. r^2 values are the squared Pearson
 604 correlation coefficient.

605



606

607 Fig. S1 Concentration of trace metals in wells. Red and black dashed lines indicate
 608 mean values and first quartile, respectively.

609



610

611 Fig. S2 A deep-draft vessel manoeuvring in the inner basin of Maó Harbour, and
612 resuspending sediments.

Tables

Table 1 Range of dissolved metal concentrations in seawater from different areas of the Mediterranean Sea and Spanish coast. Numbers in parenthesis are average \pm standard deviation.

	Cd (nM)	Co (nM)	Cu (nM)	Fe (nM)	Mo (nM)	Ni (nM)	Pb (nM)	Zn (nM)
Ferrol ria ^a	0.09 - 0.10		6.7 - 9.2				0.20 - 0.30	17 - 24
Vigo ria ^b	0.02 - 0.10 (0.05 \pm 0.02)	0.30 - 1.6 (0.67 \pm 0.37)	1.1 - 5.3 (5.6 \pm 2.4)			1.7 - 7.8 (4.1 \pm 1.5)	0.08 - 0.25 (0.18 \pm 0.07)	7.4 - 19 (13 \pm 4)
Palma beach ^c			5.9 - 13	3.0 - 6.0	81 - 160	2.9 - 5.6	0.28 - 0.40	3.3 - 10
Cadiz bay ^d	(0.10 \pm 0.03)		(6.7 \pm 3.9)				(230 \pm 150)	(17 \pm 9)
Algeciras bay ^e	(0.2 \pm 0.1)		(17 \pm 8)				(14 \pm 2)	(130 \pm 60)
Majorca bays ^f	0.30 - 0.37	0.16 - 0.29	3.9 - 11	5.5 - 12	117 - 130	3.6 - 4.6	0.07 - 0.19	3.1 - 8.0
Majorca shelf water ^g	0.34 - 0.37	0.14 - 0.17	4.5 - 9.3	2.4 - 3.6	120 - 133	3.7 - 4.2	0.10 - 0.13	2.0 - 6.6
Western Mediterranean ^g	0.06 - 0.08	0.05 - 0.17	1.1 - 2.3	1.6 - 8.0	107 - 140			
Eastern Mediterranean ^g	0.07 - 0.09	0.08 - 0.14	1.4 - 1.9	1.9 - 6.1	115 - 1230			
Aegean Sea ^g	0.08 - 0.12	0.12 - 0.29	1.8 - 4.4	2.1 - 4.0	110 - 130			
Marmara Sea ^g	0.10 - 0.11	0.45 - 0.52	7.7 - 8.6	3.7 - 4.9	55 - 61			
Black Sea ^g	0.06 - 0.09	0.18 - 0.37	6 - 8.8	1.8 - 3.7	39 - 47			
Maó harbour ^h	0.1 - 0.4 (0.3 \pm 0.1)	0.1 - 0.6 (0.30 \pm 0.03)	2 - 54 (21 \pm 8)	1.2 - 35 (9.2 \pm 3.2)	95 - 150 (119 \pm 12)	2.7 - 5.9 (4.3 \pm 0.4)	0.2 - 2.4 (1.3 \pm 0.4)	2 - 59 (23 \pm 5)

^aCobelo-García et al. (2005); ^bSantos-Echeandia et al. (2009); ^cRodellas et al. (2014); ^d^eMorillo et al. (2008); ^fTovar-Sanchez et al. (2014a); ^gTovar-Sanchez et al. (2014b);

^hPresent study

Table 2 Average metal concentrations (Av) \pm standard deviation (SD) (n = 3) and grain-size in surficial sediments from Maó Harbour. Metal concentrations are expressed in $\mu\text{g g}^{-1}$, except Fe that is in % (dry weight).

Stations	Cd		Co		Cu		Fe		Mo		Ni		Pb		Zn		Grain size		
	Av	SD	Av	SD	Av	SD	Av	SD	Av	SD	Av	SD	Av	SD	Av	SD	< 63 μm (%)	> 63 μm (%)	
C1	nd	-	3.3	0.5	75.2	1.2	1	0	1.7	0.5	9.7	0.6	42.4	1.1	93.5	0.4	20	80	silty-sand
C2	nd	-	5.7	0.2	40.8	0.7	1.9	0	2.3	1.1	16.4	0.2	124	3	77.2	1.1	57	43	sandy-silt
C3	0.1	0.1	3.0	0.2	33	2	0.90	0	1.0	1.0	7.6	0.4	57	2	67	4	53	48	sandy-silt
C4	nd	-	0.85	0.14	2.1	0.2	0.2	0	1.1	0.6	1.4	0.6	14	2	17.1	0.8	23	77	silty-sand
C5	nd	-	4.5	0.4	48.0	0.6	1.6	0.1	2.6	1.0	16.2	0.3	93	6	91	2	35	65	silty-sand
C6	0.1	0.1	5.64	0.04	72	2	2.1	0.1	1.6	0.9	19.8	0.7	113	3	123	3	33	67	silty-sand

Table 3 Mean values \pm standard deviation (SD) of metal concentrations in surficial sediments of different areas of Mediterranean Sea. Concentrations are expressed in $\mu\text{g g}^{-1}$ (dry weight), except Fe (%).

Element	Gulf of Naples (Italy) ^a	Sfax Coast (Tunisia) ^b	Sardinia. Italy ^c	Corsica. France ^c	Toscana. Italy ^c	Ionian Sea. Southern Italy ^d	Maó Harbour ^e
Cd	0.57 \pm 0.62	5.9 \pm 0.5	0.07 \pm 0.03	0.03 \pm 0.00	0.40 \pm 0.10	-	0.09 \pm 0.00
Co	-	-	2.5 \pm 0.0	55 \pm 14	7 \pm 1	-	5 \pm 1
Cu	27 \pm 29	16 \pm 4	-	-	-	47 \pm 3	65 \pm 18
Fe	15 \pm 13	4.9 \pm 0.4	-	-	-	3.2 \pm 0.3	1.9 \pm 0.5
Mo	-	-	-	-	-	-	1.7 \pm 0.2
Ni	7 \pm 10	14 \pm 8	4 \pm 1	1 \pm 5	40 \pm 6	52 \pm 3	18 \pm 5
Pb	220 \pm 170	32 \pm 17	19 \pm 2	5 \pm 1	45 \pm 5	57 \pm 8	98 \pm 25
Zn	600 \pm 550	59 \pm 17	-	-	-	100 \pm 13	110 \pm 30

^aRomano et al., (2004); ^bGargouri et al., (2011); ^cLafabrie et al., (2007); ^dBuccolieri et al., (2006); ^ePresent study.

Table 4 Average annual flows in mol y⁻¹ of the different metal sources to the Maó Harbour. Numbers in parenthesis are the contribution in percentages of the total flow.

	Co		Cu		Fe		Ni		Pb		Zn	
Groundwater	13 ± 11	(2)	160 ± 70	(0.3)	1,400 ± 900	(6)	160 ± 130	(3.7)	17 ± 23	(0.6)	600 ± 900	(0.7)
Stream waters	13 ± 12	(2)	160 ± 80	(0.3)	2,000 ± 1,500	(9)	180 ± 90	(4.1)	6 ± 3	(0.2)	210 ± 110	(0.3)
Atmospheric deposition ^a	1	(0)	10	(0)	1,200	(5)	4	(0.1)	4	(0.1)	550	(0.7)
Sediments	620 ± 16	(96)	59,500 ± 100	(99.4)	18,600 ± 1,700	(80)	4,000 ± 160	(92.0)	3,000 ± 20	(99.1)	76,000 ± 33,000	(98.3)
Export offshore	650		60,000		23,200		4,400		3,000		78,000	

^aMaximum value from Guieu et al., 1997.

Table S1 Concentration of trace metals (nM) in seawater samples and the stream collected during July 2010, October 2011, March 2010 and June 2011. nm.: not measured. < LOD.: below the limit of detection.

Campaign	Station	Cd	Co	Cu	Fe	Mo	Ni	Pb	Zn
July 2010	St1	0.40	0.60	52.8	20.4	117	5.6	2.3	53.3
	St2	0.34	0.50	41.4	12.7	103	4.8	2.1	43.6
	St3	0.36	0.58	52.1	4.4	117	5.9	2.4	54.6
	St4	0.38	0.49	44.7	4.7	114	5.3	2.0	43.2
	St5	0.34	0.39	34.4	6.0	106	4.5	1.6	31.8
	St6	0.35	0.36	34.0	4.9	111	4.5	1.4	27.5
	St7	0.34	0.33	33.5	14.6	110	4.2	1.4	25.9
	St8	0.34	0.25	21.7	14.5	106	3.6	0.9	15.2
	St9	0.31	0.20	15.2	9.1	104	3.2	0.5	8.6
	St10	0.35	0.19	15.5	4.0	104	3.4	0.5	9.3
	St11	0.31	0.22	14.5	15.0	106	3.4	0.4	7.2
	St12	0.31	0.15	7.3	11.5	106	2.9	0.3	2.8
	St13	0.32	0.16	7.5	3.1	108	3.1	0.2	2.0
	St14	0.34	0.14	9.3	2.8	108	3.1	0.3	3.2
	St15	0.32	0.16	9.6	13.4	107	3.1	0.4	3.9
	Stream	nm	nm	nm	nm	nm	nm	nm	nm
October 2010	St1	0.34	0.49	29.0	34.7	109	5.4	1.6	41.8
	St2	0.35	0.43	17.3	15.2	112	4.8	1.6	25.0
	St3	0.34	0.49	20.3	11.1	116	5.2	1.7	27.7
	St4	0.36	0.44	18.7	10.4	123	5.2	1.6	23.8
	St5	0.36	0.42	18.0	8.5	119	4.8	1.6	22.7
	St6	0.35	0.36	15.6	7.6	121	4.6	1.4	17.7
	St7	0.36	0.35	13.9	7.9	119	4.5	1.2	15.3
	St8	0.33	0.32	12.4	7.9	119	4.4	1.2	13.7
	St9	0.34	0.28	9.7	7.1	114	4.0	0.9	9.5
	St10	0.34	0.27	9.8	10.5	116	4.0	2.4	18.0
	St11	0.37	0.26	8.2	7.6	117	4.1	2.3	12.7
	St12	0.33	0.25	8.6	6.9	116	4.0	2.2	10.8
	St13	0.35	0.23	8.8	6.4	115	4.1	1.9	9.2
	St14	0.38	0.20	6.2	5.1	122	4.0	1.9	7.7
	St15	0.34	0.18	4.0	5.2	120	3.6	1.4	4.9
	Stream	< LOD	7.62	60.9	1051.6	8	64.6	1.8	62.4
March 2011	St1	0.41	0.33	16.4	17.2	145	5.4	1.9	29.9
	St2	0.40	0.32	15.8	17.1	134	5.1	1.8	27.4
	St3	0.39	0.32	16.2	17.7	135	4.8	1.9	26.5
	St4	0.40	0.31	17.4	13.6	136	4.8	1.9	30.5
	St5	0.38	0.30	14.0	13.5	132	4.7	1.7	23.2
	St6	0.40	0.30	16.8	12.5	138	5.3	1.6	27.4
	St7	0.40	0.30	13.4	13.4	141	4.9	1.7	23.2
	St8	0.40	0.29	12.9	9.0	140	4.8	1.6	22.7
	St9	0.40	0.29	16.8	14.3	138	4.7	1.6	25.9
	St10	0.39	0.25	10.9	10.0	137	4.4	1.4	18.4
	St11	0.40	0.31	13.4	12.0	137	5.0	1.6	25.9
	St12	0.39	0.29	13.4	10.6	134	4.8	1.5	23.2
	St13	0.38	0.29	14.1	11.7	134	4.6	1.5	22.1
	St14	0.40	0.28	17.4	9.8	139	4.7	1.4	26.9
	St15	0.38	0.14	7.5	4.1	138	3.6	0.3	6.1
	Stream	0.31	1.20	46.8	302.4	67	60.3	2.1	79.4

Campaign	Station	Cd	Co	Cu	Fe	Mo	Ni	Pb	Zn
June 2011	St1	0.17	0.35	35.4	8.8	114.1	4.2	1.2	42.9
	St2	0.20	0.36	36.9	10.0	121.4	4.5	1.4	40.5
	St3	0.18	0.41	53.6	14.4	118.8	4.7	1.3	58.8
	St4	0.22	0.37	42.7	11.0	116.3	4.4	1.2	45.3
	St5	0.17	0.30	33.9	4.1	116.0	4.2	0.9	35.7
	St6	0.20	0.31	43.0	4.2	121.2	4.3	1.0	45.1
	St7	0.16	0.30	37.4	2.9	113.0	3.8	0.9	37.9
	St8	0.18	0.27	36.0	2.0	120.3	4.0	0.8	34.5
	St9	0.18	0.22	24.7	2.6	114.8	3.8	0.6	23.6
	St10	0.16	0.22	22.3	1.7	117.5	3.8	0.6	21.5
	St11	0.18	0.20	18.2	2.6	114.3	3.5	0.5	17.9
	St12	0.14	0.18	13.0	3.2	112.5	3.3	0.4	15.5
	St13	0.18	0.18	12.4	1.8	113.1	3.4	0.3	13.4
	St14	0.17	0.16	11.6	1.2	116.9	3.3	0.3	14.4
	St15	0.12	0.12	5.6	1.6	95.4	2.7	0.2	6.3
	Stream	nm	nm	nm	nm	nm	nm	nm	nm

Campaign	Station	Cd	Co	Cu	Fe	Mo	Ni	Pb	Zn
July 2010	St1	0.40	0.60	52.8	20.4	117.0	5.6	2.3	53.3
	St2	0.34	0.50	41.4	12.7	102.5	4.8	2.1	43.6
	St3	0.36	0.58	52.1	4.4	117.1	5.9	2.4	54.6
	St4	0.38	0.49	44.7	4.7	114.0	5.3	2.0	43.2
	St5	0.34	0.39	34.4	6.0	106.2	4.5	1.6	31.8
	St6	0.35	0.36	34.0	4.9	110.7	4.5	1.4	27.5
	St7	0.34	0.33	33.5	14.6	109.7	4.2	1.4	25.9
	St8	0.34	0.25	21.7	14.5	106.5	3.6	0.9	15.2
	St9	0.31	0.20	15.2	9.1	103.7	3.2	0.5	8.6
	St10	0.35	0.19	15.5	4.0	103.7	3.4	0.5	9.3
	St11	0.31	0.22	14.5	15.0	105.8	3.4	0.4	7.2
	St12	0.31	0.15	7.3	11.5	105.5	2.9	0.3	2.8
	St13	0.32	0.16	7.5	3.1	107.6	3.1	0.2	2.0
	St14	0.34	0.14	9.3	2.8	107.7	3.1	0.3	3.2
	St15	0.32	0.16	9.6	13.4	107.5	3.1	0.4	3.9
		Sream	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
October 2010	St1	0.34	0.49	29.0	34.7	109.2	5.4	1.6	41.8
	St2	0.35	0.43	17.3	15.2	112.5	4.8	1.6	25.0
	St3	0.34	0.49	20.3	11.1	116.3	5.2	1.7	27.7
	St4	0.36	0.44	18.7	10.4	122.7	5.2	1.6	23.8
	St5	0.36	0.42	18.0	8.5	118.9	4.8	1.6	22.7
	St6	0.35	0.36	15.6	7.6	120.6	4.6	1.4	17.7
	St7	0.36	0.35	13.9	7.9	118.9	4.5	1.2	15.3
	St8	0.33	0.32	12.4	7.9	119.0	4.4	1.2	13.7
	St9	0.34	0.28	9.7	7.1	114.4	4.0	0.9	9.5
	St10	0.34	0.27	9.8	10.5	116.4	4.0	2.4	18.0
	St11	0.37	0.26	8.2	7.6	117.1	4.1	2.3	12.7
	St12	0.33	0.25	8.6	6.9	116.0	4.0	2.2	10.8
	St13	0.35	0.23	8.8	6.4	114.9	4.1	1.9	9.2
	St14	0.38	0.20	6.2	5.1	122.0	4.0	1.9	7.7
	St15	0.34	0.18	4.0	5.2	119.8	3.6	1.4	4.9
		Stream	<LOD	7.62	60.9	1051.6	8.1	64.6	1.8
March 2011	St1	0.41	0.33	16.4	17.2	145.2	5.4	1.9	29.9
	St2	0.40	0.32	15.8	17.1	134.0	5.1	1.8	27.4
	St3	0.39	0.32	16.2	17.7	134.6	4.8	1.9	26.5
	St4	0.40	0.31	17.4	13.6	136.5	4.8	1.9	30.5
	St5	0.38	0.30	14.0	13.5	132.4	4.7	1.7	23.2
	St6	0.40	0.30	16.8	12.5	137.7	5.3	1.6	27.4
	St7	0.40	0.30	13.4	13.4	140.5	4.9	1.7	23.2
	St8	0.40	0.29	12.9	9.0	139.7	4.8	1.6	22.7
	St9	0.40	0.29	16.8	14.3	137.7	4.7	1.6	25.9
	St10	0.39	0.25	10.9	10.0	137.0	4.4	1.4	18.4
	St11	0.40	0.31	13.4	12.0	136.9	5.0	1.6	25.9
	St12	0.39	0.29	13.4	10.6	133.8	4.8	1.5	23.2
	St13	0.38	0.29	14.1	11.7	134.4	4.6	1.5	22.1
	St14	0.40	0.28	17.4	9.8	139.0	4.7	1.4	26.9
	St15	0.38	0.14	7.5	4.1	137.7	3.6	0.3	6.1
		Stream	0.31	1.20	46.8	302.4	67.0	60.3	2.1

Table S1. Continued

Campaign	Station	Cd	Co	Cu	Fe	Mo	Ni	Pb	Zn
June 2011	St1	0.17	0.35	35.4	8.8	114.1	4.2	1.2	42.9
	St2	0.20	0.36	36.9	10.0	121.4	4.5	1.4	40.5
	St3	0.18	0.41	53.6	14.4	118.8	4.7	1.3	58.8
	St4	0.22	0.37	42.7	11.0	116.3	4.4	1.2	45.3
	St5	0.17	0.30	33.9	4.1	116.0	4.2	0.9	35.7
	St6	0.20	0.31	43.0	4.2	121.2	4.3	1.0	45.1
	St7	0.16	0.30	37.4	2.9	113.0	3.8	0.9	37.9
	St8	0.18	0.27	36.0	2.0	120.3	4.0	0.8	34.5
	St9	0.18	0.22	24.7	2.6	114.8	3.8	0.6	23.6
	St10	0.16	0.22	22.3	1.7	117.5	3.8	0.6	21.5
	St11	0.18	0.20	18.2	2.6	114.3	3.5	0.5	17.9
	St12	0.14	0.18	13.0	3.2	112.5	3.3	0.4	15.5
	St13	0.18	0.18	12.4	1.8	113.1	3.4	0.3	13.4
	St14	0.17	0.16	11.6	1.2	116.9	3.3	0.3	14.4
	St15	0.12	0.12	5.6	1.6	95.4	2.7	0.2	6.3
	Stream	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.