

1 **Temporal Evolution of Cadmium, Copper and Lead Concentration in the**
2 **Venice Lagoon Water in relation with the Speciation and Dissolved/Particulate**
3 **Partition.**

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14
15 **Abstract**

16 In order to study the role of sediment re-suspension and deposition versus the role of organic
17 complexation, we investigated the speciation of cadmium (Cd), copper (Cu) and lead (Pb) in
18 samples collected in the Venice Lagoon during several campaigns from 1992 to 2006. The
19 increment in Cd and Pb concentration in the dissolved phases, observed in the central and
20 northern basins, can be linked to important alterations inside the lagoon caused by industrial
21 and urban factors. The study focuses on metal partition between dissolved and particulate
22 phases. The analyses carried out in different sites illustrate the complex role of organic
23 matter in the sedimentation process. While Cd concentration in sediments can be correlated
24 with organic matter, no such correlation can be established in the case of Pb, whose
25 particulate concentration is related only to the dissolved concentration. In the case of Cu, the
26 role of organic complexation remains unclear.

27
28 *Keywords: Lagoon, Metals, Sediment, Chemical speciation*

29
30 **Introduction**

31 The Venice Lagoon is the largest Italian lagoon and is densely inhabited. Since the 13th
32 century, it has been subjected to substantial human-caused changes, mainly in order to
33 maintain certain hydraulic characteristics and to stop the silting up. Industrial and
34 agricultural activities, together with the population increase that marked the last century,
35 have caused serious problems of chemical pollution, considerably reducing the
36 environmental quality of the Venice Lagoon (Pavoni et al., 1987, Scarponi et al 1998,
37 Capodaglio et al 2005, Chapman et al. 2009). Studies to evaluate and quantify the lagoon's
38 environmental chemical contamination, which started more than 30 years ago, mainly
39 focused on the analysis of sediments and emphasized the presence of organic and inorganic

40 pollutants (Donazzolo et al., 1983; Donazzolo et al., 1984; Albani et al., 1989, Molinaroli et
41 al., 2013).

42 Previous attempts to evaluate pollutant dispersion were generally based on the
43 assumption that the phenomenon is largely controlled by sediment movement as a
44 consequence of tidal currents (Alberotanza et al., 1987; Basu and Molinaroli, 1994).
45 Although these studies showed a general agreement with the distribution of pollutants in
46 bottom sediments, they also highlighted a few anomalies. An in-depth distribution of
47 pollutants may be described taking into account the processes affecting their partitioning
48 between water/atmosphere and sediment/water interfaces and the influence of the chemical-
49 physical parameters (Martin et al., 1994, Millward, 1995),

50 Studies carried out on the lagoon sediments showed that their toxicity was not correlated
51 to the total content of pollutants but to their speciation (Scarponi et al., 1998); consequently,
52 the differentiation between the forms in which components are present (Iyer and Sarin, 1992;
53 Achterberg and Van Den Berg, 1997) is fundamental.

54 Benthic fluxes of trace elements studied in the Venice Lagoon (Turetta et al., 2005)
55 were prevalently controlled by chemical and diffusive processes, whilst benthic fluxes of
56 organic pollutants tended to be remobilized from the sediments by re-suspension and partly
57 trapped as particulate matter in the microlayer at the water/atmosphere interface (Manodori
58 et al., 2006; 2007).

59 Improvements in sampling procedures, sample treatments and analytical techniques
60 enabled the reliable quantification of pollutants and the speciation study of trace elements
61 (Martin et al., 1994; Capodaglio et al., 1996; Cescon et al., 1996) to evaluate their bio-
62 available fraction (Pavoni et al., 1998; Scarponi et al., 1998).

63 Furthermore, the concentration of elements in the dissolved phase, especially for Pb, Cu, Cd
64 and Chromium (Cr), may be a function of the geographical area and tide level (Martin et al.,
65 1994; Cescon et al., 1996). The increase in re-suspension in lagoon waters since 1994, due to
66 the reduction of macroalgal coverage, which was combined with a significant decrease in
67 organic carbon (OC), and to the mechanical dredges used for harvesting the invasive Manila
68 clam (*Ruditapes philippinarum*) (Sfriso et al., 2005) got the sediments mix down to 30 cm
69 (Pranovi et al. 2003; 2004). Resuspension phenomena and increased navigation in the lagoon
70 contributed to the net loss (erosion) of sediments observed.

71 The modeled contaminant transport from the industrial area of the Venice Lagoon
72 (Sommerfreund et al., 2010) highlighted that the resuspension and the erosion of the
73 sediments, together with the present industrial discharges and the tributary sources, are an

74 important source of pollutants to the entire lagoon,. However, the model did not take into
75 account the effects of the significant decrease of organic matter observed in the sediment.

76 In this paper, we will study the spatial distribution of cadmium (Cd), copper (Cu) and
77 lead (Pb) and their temporal evolution from 1992 to 2006 in different sites of the Venice
78 Lagoon. The study focuses on the metal speciation and the metal partition between dissolved
79 and particulate phases, in order to evaluate the mobility and the partition of Cd, Cu and Pb in
80 the transition and lagoon water ecosystems.

81 As shown in fig. 1, in order to study the temporal evolution of trace element speciation in the
82 Venice Lagoon, sub-surface waters were sampled across several sites and in different years
83 (from 1992 to 2006). In more detail, in July 1992, six sub-surface water samples were
84 collected in six different sites; in October 1992, twelve sub-surface water samples were
85 collected at the San Marco dock (Punta della Salute, every two hours); in 1994, from March
86 to the end of June, twelve sub-surface water samples were collected at Sacca Sessola: in
87 1997, from March to the end of September, nineteen samples were collected of the island of
88 San Giorgio in Alga; finally, in 2005-2006, ten sub-surface water samples were collected at
89 Campalto and at Sacca Sessola. In 2001 and 2002-03, in relation with the two benthic
90 chamber experiments carried out in Tresse and Campalto (Turetta et al., 2005), trace metal
91 speciation was also studied in sub-surface water samples; in relation with the sampling of
92 microlayer in the Venice Lagoon, trace metal speciation was investigated in eight samples of
93 sub-surface water collected at Sacca Sessola and Murano in 2001-2003 (Manodori et al.,
94 2006) and on nine sub-surface samples collected at Mazzorbo in 2005-2006 (Manodori et al.,
95 2007). All the samples were collected under neap tidal conditions, except for those sampled
96 in October 1992, which were collected under spring tidal conditions in order to evaluate the
97 possible variability of the trace metal concentrations as a function of tide level. Furthermore,
98 in 2005-2006, in order to assess the OC concentration, campaign surface sediment samples
99 were collected at Campalto and Sacca Sessola.

100 The procedure adopted for collecting all the samples was the same. In order to minimize
101 contamination, the sampling apparatus and all the containers and materials were acid-cleaned,
102 appropriately rinsed and conditioned following previously reported procedures (Scarponi et
103 al., 1996b) in a clean chemistry laboratory (Class 100) at the Environmental Science
104 Department of the Ca' Foscari University of Venice, where the handling, treatment, and
105 analysis of the samples were carried out, as well. After being collected with a Teflon pump
106 and stored in a 50 l polyethylene tank, water samples were filtered through a suitable
107 filtering apparatus (Sartorius, SM 16540, with acid-clean cellulose nitrate membrane filters

108 0.45 μm pore, Sartorius, SM 11306, 142 mm diameter). The filtered samples were collected
109 directly in 2 l FEP bottles and stored at $-20\text{ }^{\circ}\text{C}$ until analysis.

110 Total OC concentration was established by applying a Shimadzu TOC SSM-5000A
111 analyzer directly on the sediment sample. A portion of the dried sample was treated with
112 HCl 2,5N and heated at 120°C for 30 minutes to remove inorganic carbon.
113 The analyzer operated through the high-temperature conversion to carbon dioxide of all
114 carbon in the treated sample. The carbon dioxide was quantified by infrared detection, and
115 the results were reported as mg C on g of dried-weight.

116 To assess the total dissolved concentration of cadmium (C_{Cd}), lead (C_{Pb}) and copper (C_{Cu})
117 in the samples collected up to 1994, the filtered samples were previously irradiated with a
118 high-intensity UV lamp and then acid-digested (HCl Ultrapure 30%, Merck or Romil); the
119 treated samples were then analyzed by Differential Pulse Anodic Stripping Voltammetry
120 (DPASV) with a Multipolarograph Analyzer EG&G mod. 384 B. Details of the analytical
121 method are described elsewhere (Capodaglio, 1989; Capodaglio, 1991; Capodaglio, 1994,
122 Scarponi et al., 1996). For the samples collected after 1994, the analysis of total metal
123 concentrations was performed by Inductively Coupled Plasma Sector Field Mass
124 Spectrometry (ICP-SFMS, ElementThermoquest, Bremen, Germany), following the method
125 developed by Turetta et al. (2004). To assess the total concentration of Cu, Cd and Pb in
126 particulate matter, samples were previously mineralized by microwave acid digestion
127 following the analytical procedures described by Frache et al. (2001).

128 The metal complexation in the dissolved phase was analyzed by DPASV, following a
129 procedure described elsewhere (Capodaglio 1989, Capodaglio 1991, Capodaglio 1994,
130 Scarponi et al., 1996). The study of complexation of each metal was carried out individually
131 on separate aliquots of untreated and freshly unfrozen water samples.

132 The procedure involves the titration of ligands by the metal of interest; the labile metal
133 concentration $[M']$ was determined by the peak current after each addition, and the
134 organically complexed metal concentration ($C_{\text{M}} - [M']$) was determined by the mass balance.
135 The metal complexation was estimated in terms of ligand concentration and conditional
136 stability constants by plotting the ratio $[M']/(C_{\text{M}} - [M'])$ versus $[M']$ (Scarponi et al., 1996).

137 The plot of $[M']/(C_{\text{M}} - [M'])$ versus $[M']$ for Pb took a linear shape, indicating the
138 presence of one single class of ligands complexing this element. The concentration and the
139 relative conditional stability constant can be calculated by the slope and the intercept of the
140 straight line obtained by a procedure of linear regression.

141 The plot of $[M']/(C_M-[M'])$ versus $[M']$, obtained to study the speciation of Cp and Cu,
142 take a curved shape, indicating that these metals are complexed by more than one class of
143 ligands. In particular, the model of two classes of ligands showed the best fit with the
144 experimental titration data, and the parameters relative to the complexation were obtained by
145 a nonlinear fitting procedure using the Marquart-Levenberg algorithm.

146 Details about the evaluation of the initial values for the parameters and the function used
147 in the fitting procedure are reported elsewhere (Capodaglio et al., 1994; Scarponi et al.,
148 1996).

149 $[M']$ for samples with values below the detection limit were evaluated through
150 equilibrium calculations using the ligand concentrations and the conditional stability
151 constants obtained by titration. Calculations were performed with a MINEQL+ program
152 (Schecher and McAvoy, 1998); these values are reported in brackets. The same program was
153 used to evaluate metal distribution between the different chemical forms when the metals
154 were complexed by two classes of ligands.

155 The results of the total dissolved concentrations of the metals studied are expressed as
156 the average of at least three measurements; in case of uncertainty, the complexing capacity
157 (namely the concentration of the ligands) and the conditional stability constants are
158 expressed as the average of at least two measurements.

159 The accuracy of the method for the determination of total dissolved metal concentration
160 was periodically checked by repeat analysis of the certified seawater reference materials
161 NASS-3 or NASS-5 (National Research Council of Canada). To express the precision and
162 reproducibility of the assay for total dissolved metal concentration, the relative standard
163 deviation (RSD) was calculated.

164 For the speciation parameters, namely the ASV labile fraction of the studied metal, the
165 concentration of the ligands and the conditional stability constants, the calculated RSD
166 ranged between 10% and 15% for the first two and between 15% and 20% for the last
167 parameter.

168 Data of tide level and salinity for all the campaigns are reported in table 1. The total
169 concentration and speciation results in dissolved phase for Cd, Cu and Pb are reported
170 respectively in tables 2, 3 and 4. The metal concentration in particulate matter is reported in
171 table 5. The OC concentration in the superficial sediment was of 7.1 mg g^{-1} .

172 In July 1992, excluding the sample from Marghera, the average value of C_{Cd} was
173 $0.13 \pm 0.05 \text{ nM}$, in good agreement with the values determined in the northern Venice Lagoon
174 (Martin et al., 1994) and in the Adriatic sea (Zago et al., 2002). The C_{Cd} in the sample

175 collected in Marghera was remarkably higher (1.1 M) and consistent with one of the sources
176 of trace metals in the lagoon, namely the industrial area of Porto Marghera. It was also in
177 agreement with pollution dynamics in the lagoon waters (Donazzolo et al., 1984;
178 Alberotanza et al., 1987).

179 In October 1992, sub-surface waters were collected to evaluate whether the tidal
180 circulation might affect the trace metal concentration. As shown in fig. 2 the C_{Cd} ranged
181 between 0.06 and 0.19 nM, and the highest concentration was observed in low tide
182 conditions, namely when water flows from the inner areas of the lagoon to the lagoon inlet,
183 showing a negative correlation with the tide level ($r=-0.70$). The C_{Cd} in samples collected in
184 the Adriatic Sea and at the mouth of tributary rivers (Silone channel and Dese river) were in
185 agreement with the results of Martin et al. (1994), who studied the Silone channel/Adriatic
186 Sea interface and observed an increase in the C_{Cd} towards the Adriatic Sea, underlining the
187 relevance of the presence of OC in these waters. Nevertheless, our data indicated a local
188 source in the central lagoon, which, according to Martin, was not supposed to affect the
189 water composition in the northern lagoon.

190 In 1994, the C_{Cd} at Sacca Sessola, a site located along the water flow from the industrial
191 area and the Lido port mouth, ranged between 0.21 and 0.88 nM, with an average
192 concentration higher than the one observed in July 1992.

193 As reported in table 2 and in fig. 3, the C_{Cd} at Sacca Sessola showed a further variability
194 in the following years (2001-2006). These values were in agreement with the data collected
195 in other sites of the lagoon, namely S.Giorgio in Alga, Campalto, Tresse and Murano (from
196 1997 to 2006, table 2). Compared to the data collected in 1992 near the Dese site, the
197 average C_{Cd} at Mazzorbo showed a relevant increase in 2005-2006. These data were close to
198 those observed at the industrial area of Marghera and were in good agreement with the
199 modeling results of J.K. Sommerfreund et al. (2010), which suggest a net enrichment of
200 contaminants in the water column via re-suspension of upper sediments in the central basin
201 (including the industrial and urban areas) and a subsequent transport towards the northern
202 basin. According to the source apportionment and the contaminant fate analyses proposed by
203 J.K. Sommerfreund et al. (2010), the contaminant loadings that originated in the central
204 basin may circulate in the northern and central basins, but may not reach the far southern
205 basin (where the main source of contaminants are tributary rivers); only a small portion of
206 contaminants from the central basin (where industrial discharges and re-suspension of
207 sediment occur) may reach the Chioggia inlet.

208 No evident temporal trend was observed for speciation data, and the concentration of labile
209 cadmium ($[Cd^*]$) changed with the sampling site. The labile fraction ranged from 0% to 97%
210 of the total dissolved metal concentration, with an average value of 30%.

211 In many water samples, Cd was complexed by two classes of organic ligands: the first
212 class of ligands (L_1) is stronger than the second class of ligands L_2 (for the concentration of
213 the first class of ligands C_{L1} and the concentration of the second class of ligands C_{L2} , see
214 table 2. The mean concentration of the first class of ligands (C_{L1}) was 0.47 nM with a mean
215 conditional stability constant ($\log K'_1$, in logarithmic form) of 11.6; the mean concentration
216 of the second class of ligands (C_{L2}) was 2.5 nM; and the mean of the logarithm of the
217 conditional stability ($\log K'_2$) constant was 8.9. The speciation was strongly variable as a
218 function of space and time, as shown by the speciation data of October 1992 and 1994 (see
219 table 2). The speciation of dissolved Cd in the lagoon water, evaluated with the program
220 MINEQL+ (Schecher and McAvoy, 1998), was composed on average of 24% labile (ionic
221 and inorganic) forms, 47% complexed with the stronger ligands and 28% complexed with
222 the weaker ligands. The mean speciation values during the tide cycle (October 1992) were
223 16% (SD=9), 66% (SD=11) and 18% (SD=7) for $[Cd^*]$, $[CdL1]$ and $[CdL2]$ respectively; the
224 mean speciation values during the spring-summer 1994 study were 33% (SD=14), 30%
225 (SD=18) and 38% (SD=16) for $[Cd^*]$, $[CdL1]$ and $[CdL2]$.

226 In water samples collected in the northern lagoon, Martin et al. (1995) distinguished the
227 dissolved organic carbon (DOC) in completely dissolved and colloidal compounds of OC;
228 the results showed that 34% of dissolved Cd was bound up with colloidal carbon and only
229 66% is truly dissolved, containing both inorganic and dissolved organic forms of Cd.
230 Although the technique and procedure used in this study could not discriminate colloidal
231 ligands from dissolved ligands, the hypothesis is that if both classes of DOC were able to
232 complex metals, the two classes of ligands detected in our study might be equivalent to the
233 truly dissolved organic compounds and colloidal compounds determined by Martin et al.

234 According to the data for particulate Cd, reported in table 5, the concentration of
235 particulate Cd increased after the sampling campaigns of 1992 and 1994. The partition
236 coefficient between the particulate and dissolved phases, K_d , varied considerably depending
237 on the different parts of the lagoon, ranging from 1000 (in the Adriatic Sea) to 80000 (inside
238 the Venice urban area). This difference was also determined by the sampling time. For
239 instance, in 1994, the K_d ranged between 900 and 22000; despite these high values, the
240 dominant physical form of Cd was generally the dissolved one, due to the low amount of
241 suspended matter (the mean particulate concentration was 13.2 mg/l (SD 3.6)). Depending

242 on the sampling site, the concentration of particulate Cd varied; for instance, in the samples
243 of the urban area of Venice, particulate Cd concentration was 60% of the total, while in the
244 samples of the Tresse Canal it was about 40% of the total. However, on average, particulate
245 Cd concentration was about 16% of the total and the dissolved concentration accounted for
246 most of the total Cd concentration.

247 In particular, in the samples from 1994, the concentrations of particulate Cd and
248 dissolved Cd were not correlated; nevertheless, the concentration of particulate Cd was
249 positively correlated to C_{L1} ($r=0.71$) and negatively correlated to $[Cd']$ ($r=-0.67$) (see fig. 4).
250 These results underlined firstly that the Cd speciation was influenced by the geochemical
251 reactivity of the element, and, secondly, that organic compounds (ligands) have an essential
252 role in the partition process. Our results did not seem in good agreement with the findings of
253 Martin et al. (1995), who observed a positive correlation between the completely dissolved
254 organic compounds (which may be analogous to the L_2 class identified by our technique) and
255 the concentration of particulate Cd. It is worth remembering that the truly dissolved organic
256 matter and the colloidal organic matter might differently affect the partition equilibrium.
257 Moreover, the organic matter in the area studied by Martin et al. and in the areas investigated
258 in the present study could be very different in terms of composition and origin. Finally, the
259 salinity gradient in the Silone channel in the area studied by Martin et al. could sensitively
260 affect the heterogeneous equilibrium of the organic matter and Cd.

261 C_{Cu} varied depending on the sampling site and sampling time, but without showing any
262 clear temporal trend, in agreement with its geochemical behavior, which is characterized by
263 a lesser mobility in the re-suspension processes from sediments (Bruland, 1992). Although
264 the observed C_{Cu} results were similar (e.g., 8.2 nM at Sacca Sessola in July 1992 and 9.8 nM
265 in July 1994), the total concentration of particulate Cu (see table 5) was significantly higher
266 and showed a large variability (e.g., 6.8 $\mu\text{g/g}$ at Sacca Sessola in July 1992 and 31.6 $\mu\text{g/g}$ in
267 July 1994).

268 According to the data obtained during the campaign of October 1992, whose aim was to
269 investigate the variability in function of the tide levels, the C_{Cu} showed a similar trend to that
270 of C_{Cd} (see fig. 5), with higher concentrations at low spring tide, when the lagoon waters
271 flowed from the inner areas towards the port mouths.

272 The particularly high C_{Cu} observed in 2003 at Campalto and at Sacca Sessola might depend
273 on tidal conditions or on an increase in C_{Cu} concentration in the nearby industrial area of
274 Porto Marghera.

275 The concentration of labile copper ($[Cu']$) was often under the detection limit. Unlike Cd,
276 Cu is a micronutrient, but in the Venice Lagoon Cu is generally present in sub-surface waters
277 as a complex ($\geq 99\%$) and $[Cu']$ represented less than 1% of C_{Cu} .

278 Generally, Cu complexation in surface seawater and in coastal and estuarine environments is
279 characterized by multiple ligands (Bruland, 1992; Capodaglio et al., 1994; Scarponi et al.,
280 1995; Kozelka et al., 1997; Capodaglio et al., 1998; Kozelka and Bruland, 1998; Wells et al.,
281 1998; Buck and Bruland, 2005; Hirose, 2006). In surface ocean waters, Cu is complexed by
282 two classes of ligands (Coale and Bruland 1988, 90; Moffett et al., 1990; Capodaglio 1994;
283 Zago 2002); however, in estuary waters, three classes are frequently observed (Wells et al.,
284 1998; Muller, 1996). Two classes of ligands, L1 and L2, were determined by the technique
285 applied in our study; the concentration of the first class, L1, was about one order of
286 magnitude higher than the one observed in open sea areas (Coale and Bruland 1990, Moffett
287 et al., 1990, Capodaglio, 1994).

288 Throughout the campaigns (1992 to 2006), the complexing capacity of all the classes of
289 ligands binding Cu was high, with highly variable concentrations of ligands and stability
290 constants. Depending on the sampling sites and on the sampling year, the structure of the
291 organic matter to which the classes of ligands belonged was different.

292 At the Dese river outflow in June 1992 (see table 3) the concentration and stability
293 constant of the first and strongest class of ligands (C_{L1-Cu}) were similar to those of the second
294 class of ligands (C_{L2-Cu}) and to the stability constant of C_{L2-Cu} observed in other sampling
295 sites of the lagoon and in other sampling campaigns; on the other hand, the C_{L2-Cu} and its
296 stability constant observed at this site were very dissimilar. The hypothesis is that $L2-Cu$
297 observed the Dese river outflow in June 1992 might belong to organic matter with a different
298 composition, probably due to the fresh water flowing from the Dese river, while the $L1-Cu$
299 might correspond to the second class of ligands determined in the other sites of the lagoon. A
300 similar result was observed by Wells et al. in the Narragansett Bay: they detected three
301 classes of ligands; the third class of ligands prevalently consisted of colloidal matter (>8
302 kDa), showing a decrease moving away from the Providence River mouth, while the
303 strongest class of ligands was prevalent in the dissolved phase (Wells et al., 1998). From the
304 data collected in our study, Cu speciation in the Venice Lagoon (see table 3) seemed to be
305 controlled by the first class of ligands L1 (as shown in Wells et al. (1998)), which was not
306 influenced by the tidal conditions or salinity and was affected by local processes. In a study
307 carried out in open ocean waters (Coale and Bruland, 1988) a relation between strong
308 ligands complexing Cu and maxima of primary production was observed. Hence, the

309 hypothesis is that in the Venice Lagoon, the concentration of this class of ligands might be
310 related to the primary production occurring in the lagoon, depending on seasonal processes
311 and local characteristics. This hypothesis is supported by the fact that the Venice Lagoon is
312 characterized by high primary production (Sfriso et al., 1992; Sfriso and Pavoni, 1994).

313 As for samples collected under spring tidal conditions (October 1992), the L2-Cu is
314 negatively correlated with tide level, salinity and transmittance ($r=-0.81$, $r=-0.61$ and $r=-0.79$,
315 respectively). Thus, the origin of L2-Cu may be related to terrigenous macromolecular organic
316 matter or to sedimentary organic matter re-suspended and transported during the ebb tide.
317 Studies carried out in oceanic areas (Coale and Bruland, 1988; Coale and Bruland, 1990;
318 Moffett et al., 1990) confirm the refractory nature of this organic matter, distributed
319 homogeneously along the water column. These characteristics may be found in organic
320 matter subjected to degradation processes at sediment level.

321 Samples collected in Sacca Sessola during spring/summer 1994 showed a good correlation
322 ($r=0.71$) between the concentration of particulate Cu and C_{L1-Cu} (fig. 6); however, the
323 partition coefficient, K_p , did not show any correlation with C_{L1-Cu} . Thus, this correlation
324 might be actually misleading due to the co-variability of C_{Cu} , which affects the particulate
325 composition and the concentration of L1-Cu.

326 Our data on Cu speciation were quite different from those of Martin et al. (1995); The
327 distribution of organic matter between the dissolved phase and the colloidal phase observed
328 by Martin and coworkers did not correspond to the distribution between the two classes of
329 ligands identified by the technique used in our studies. The ensuing hypothesis that there
330 might be two different speciation schemes is corroborated by Wells et al. (1998), and the
331 classes of ligands identified by ASV could be differentiated in accordance with the
332 molecular dimension separated by Cross Flow Filtration. Nevertheless, we cannot rule out
333 that the dissimilarities observed were due to differences in water composition in the two
334 areas, since the hydrological characteristics of the outflow of the Silone channel studied by
335 Martin et al. (1995) were more similar to those of the Dese site (Dese River mouth) than to
336 the other sites studied.

337 The C_{Pb} assessed in all the samples ranged between 0.09 nM and 2.6 nM; any change
338 observed was a function of the sampling site, the tidal condition and the season. The total
339 concentration of particulate Pb ranged between 2.3 ug/g and 106 ug/g (see table 5).

340 In particular, in July 1992 and in 1997, the samples collected at Marghera and at San
341 Giorgio in Alga respectively showed the maximum C_{Pb} (see table 4).

342 In agreement with what was observed for C_{Cd} and C_{Cu} , in October 1992, C_{Pb} was
343 negatively correlated to tidal conditions ($r=-0.81$), salinity ($r=-0.59$) and transmittance ($r=-$
344 0.64).

345 In many of the samples, C_{Pb} was in agreement with the concentrations observed by Martin
346 et al. in the northern lagoon (Martin et al., 1994; Martin et al., 1995), and with those
347 observed in coastal, bay and estuary waters of different geographical areas (Muller, 1996;
348 Kozelka et al., 1997; Kozelka and Bruland, 1998; Wells et al., 1998).

349 The particulate concentration of Pb ranged between 77% and 83% and these results were
350 in agreement with those obtained in one subsequent experiment: the fractions of particulate
351 Pb in Marghera and Dese sites were 93 and 89% respectively (Pellizzato F. 1999). Our
352 results were also in agreement with those obtained by Muller (Muller, 1996) in the coastal
353 areas of southern England, while Martin et al. (1995) showed a lower contribution of
354 particulate Pb to the total content (52%.)

355 In a study on Pb speciation in the San Francisco Bay, Kozelka et al (1998) pointed out
356 that the particulate fraction of Pb may represent the dominant form of Pb in coastal waters:
357 they reported that 98% of Pb was in particulate form.

358 As regards the speciation study, Pb was complexed by one class of ligands (C_{L-Pb}),
359 whose concentration ranges between 0.1 nM to 4.0. The mean value for the logarithms of
360 conditional stability constant was 9.7 (see table 4).

361 As observed for samples collected during October 1992 at Punta della Salute, C_{L-Pb} was
362 negatively correlated to the tidal conditions, and the salinity and average labile concentration
363 ($[Pb']$) accounted for 28% of C_{Pb} . According to several studies carried out in different coastal
364 areas, Pb was complexed by two classes of ligands: as regards ligand concentration and
365 conditional stability constant, our data were analogous to the strongest class of ligands
366 determined by Wells et al. in Narragansett Bay (1998), by Kozelka in San Francisco Bay
367 (1997) and by Muller in the coastal area of southern England (1996).

368 In our studies, the fact that more than one class of ligands for Pb was not recognized
369 might be due to the different analytical techniques employed or to the different
370 environmental characteristics of the sites under investigation.

371 Unlike what was observed for Cd and Cu, C_{L-Pb} did not show any evident relation with
372 particulate composition. The concentration of particulate Pb seemed definitely dependent
373 upon the total dissolved metal concentration, as shown in fig. 7; hence, compared to what
374 was observed for Cd and Cu, the sedimentation and the mobility of Pb in the waters of the
375 Venice Lagoon was significantly different.

376 The total concentration of the trace metals, both in the dissolved and particulate phases,
377 showed a great spatial variability throughout the years of our studies; the spatial variability
378 observed may be affected by the sampling season, since all the samples were collected under
379 neap tidal conditions (except those sampled in October 1992).

380 In all the samples, the salinity ranged between 28.2 psu and 35.6 psu. Possible variations
381 of ionic strength on the partition dissolved-particulate were quite limited. Nevertheless, the
382 total concentration of dissolved Cd and, to a lesser extent, [Cd'], which were assessed in the
383 samples of October 1992 was negatively correlated with the tidal conditions and with the
384 salinity. Hence, the freshwater entering the lagoon might efficiently control the total
385 dissolved concentration, giving rise to its dilution.

386 Changes in salinity, biological processes and other physical phenomena may greatly
387 influence the cycling, mobility and fate of trace metals in the Venice Lagoon. Many of these
388 processes may directly or indirectly involve organic matter in both dissolved and colloidal
389 forms.

390 According to our experiments, the metal complexation by organic ligands shifted the
391 heterogeneous equilibrium between dissolved/particulate metals toward the dissolved phase,
392 increasing the mobility of metals.

393 Compared to the processes which generally take place at interface areas, namely
394 transitional environments with a high salinity gradient, the results reported here highlight
395 that organic complexation may have an opposite effect: when the salinity variability is
396 limited, the role of organic matter in the sedimentation process is much more complex than
397 the simple desorption due to complexation.

398 The trends of trace metal concentrations observed in our study may be related not only
399 to sediment re-suspension, which may be influenced by the fishery stop, by boat traffic, etc.,
400 but also to the simultaneous decrease in the concentration of OC.

401 In conclusion, all the data collected and analyzed strongly suggest that the speciation of
402 trace elements is essential to evaluate the mobility, biogeochemical reactivity and interaction
403 of trace elements with components present in marine environments and especially in
404 complex systems such as transitional environments.

405

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409

410 **Contributors**

411 Elisa Morabito and Marta Radaelli conducted the experiments, analyzed the data and wrote
412 the manuscript.

413 Fabiana Corami contributed to the experimental part and revised the manuscript.

414 Clara Turetta and Giuseppa Toscano helped in the experimental part.

415 Gabriele Capodaglio conceived and designed the experiments.

416

417

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550 **Table 1**
 551 Geographic coordinates of sampling site, tide level, salinity for the samples collected from
 552 1992 to 2003.

	Geographic coordinates	Tide level (m)	Salinity (psu) 7-10 July 1992
<i>Marghera</i>	45°27'01.4''N 12°15'29.3''E	0.08	30.66
<i>Dese</i>	45°30'53.0''N 12°15'29.3''E	0.23	31.89
<i>Area urbana Venezia</i>	45°30'53.0''N 12°23'12.2''E	0.60	34.10
<i>Sacca Sessola</i>	45°24'32.1''N 12°18'39.5''E	0.32	33.57
<i>Chioggia</i>	45°14'32.1''N 12°15'35.5''E	0.11	32.04
<i>Mare adriatico</i>	45°15'51.3''N 12°22'06.7''E	0.31	35.60
28-29 Oct. 1992			
<i>Punta della Salute</i>	45°25'52.2''N 12°20'14.6''E		
min value		-0.05	29.61
max value		0.87	31.46
mean		0.48	30.60
std		0.27	0.57
22 Apr.- 24 Aug. 1994			
<i>Sacca Sessola</i>	45°24'32.1''N 12°18'39.5''E		
min value		-0.01	30.54
max value		0.60	34.35
mean		0.24	31.87
std		0.21	1.05
6 Mar.- 4 Sept. 1997			
<i>S. Giorgio in Alga</i>	45°25'32.9''N 12°17'30.7''E		
min value		-0.31	28.40
max value		0.52	32.10
mean		0.19	30.30
std		0.29	1.20
9 July 2001			
<i>Tresse</i>	45°26'36.5''N 12°17'08.4''E	0.53	32.00
23 July 2001			
<i>Campalto</i>	45°28'24.8''N 12°18'19.9''E	0.42	30.69
28 Oct. 2002			
<i>Tresse</i>	45°26'36.5''N 12°17'08.4''E	1.6	29.15
6 May 2003			
<i>Campalto</i>	45°28'24.8''N 12°18'19.9''E	0.75	28.22

553 **Table 2** Concentrations of total dissolved cadmium (C_{Cd}), labile cadmium ($[Cd']$), ligands
 554 (C_{L1} , C_{L2}) and stability constants expressed in logarithmic form ($\log K'_1$ $\log K'_2$) for samples
 555 collected from 1992 to 2006.

	C_{Cd} (nM)	$[Cd']$ (nM)	C_{L1} (nM)	$\log K'_1$	C_{L2} (nM)	$\log K'_2$
July 1992						
<i>Marghera</i>	1.10	0.500			1.60	9.2
<i>Dese</i>	0.06	0.015	0.40	9.9	1.10	8.3
<i>Historic centre VE</i>	0.10	0.015			1.10	9.3
<i>Sacca Sessola</i>	0.18	0.078	0.14	9.8	1.10	8.9
<i>Chioggia</i>	0.14	0.016	0.29	10.7	1.50	8.8
<i>Mare adriatico</i>	0.15	0.014			2.80	8.7
Oct. 1992						
<i>Punta della Salute</i>						
min value	0.06	0.008	0.14	9.7	1.10	8.3
max value	0.19	0.038	0.37	11.0	4.20	9.2
mean	0.10	0.018	0.24	10.5	2.47	8.7
std	0.03	0.010	0.08	0.4	0.82	0.2
Campaign 1994						
<i>Sacca Sessola</i>						
min value	0.21	0.030	0.12	10.0	0.37	8.5
max value	0.88	0.300	0.63	16.0	2.41	9.8
mean	0.42	0.167	0.26	12.3	1.47	9.0
std	0.17	0.085	0.18	2.5	0.67	0.3
Campaign 1997						
<i>S. Giorgio in Alga</i>						
min value	0.34	0.000			0.14	8.0
max value	1.90	1.300			4.90	10.0
mean	0.78	0.373			1.73	8.8
std	0.37	0.309			1.26	0.5
Campaign 2001						
<i>Tresse</i>	0.37	0.080			1.35	9.6
<i>Campalto</i>	0.53	0.303			0.50	9.8
<i>Sacca Sessola</i>	1.02	0.130	0.71	15.5	2.85	8.1
<i>Murano</i>	0.88	0.150			1.85	9.4
Campaign 2002						
<i>Tresse</i>	1.0	0.13			1.96	9.8
<i>Sacca Sessola</i>	0.58	0.16			1.28	9.4
"	2.9	0.40			2.33	9.3
<i>Murano</i>	0.28	0.04			1.52	9.0
"	0.43	-	-	-	-	-
Campaign 2003						
<i>Campalto</i>	0.64	0.35			1.07	9.0
<i>Sacca Sessola</i>	0.75	0.33			3.05	9.3
<i>Murano</i>	0.38	0.12			1.83	8.9
"	1.1	0.16			1.30	10.1
Apr.-Oct. 2005						

<i>Sacca Sessola</i>						
min value	0.33	0.007	0.45	10.4	0.54	8.5
max value	1.54	0.052	2.10	14.6	3.96	9.3
mean	0.76	0.030	1.06	13.1	2.68	8.9
std	0.68	0.022	0.91	2.33	1.86	0.4
July-Aug. 2005						
<i>Mazzorbo</i>						
min value	0.04	0.007			0.28	8.2
max value	0.67	0.206			8.93	9.8
mean	0.33	0.045			4.62	8.7
std	0.26	0.079	0.53	10.7	3.51	0.6
Campaign 2006						
<i>Sacca Sessola</i>	0.38	0.05	0.31	14.3	3.52	8.8
"	1.27	0.06	3.32	9.7	4.10	8.6
<i>Campalto</i>	0.89	0.11	0.32	10.1	1.98	9.5
"	0.68	0.07	0.49	13.5	6.74	8.5
<i>Mazzorbo</i>						
min value	0.07	0.01			5.37	8.31
max value	0.49	0.03			16.19	9.20
mean	0.25	0.02			9.60	8.76
std	0.22	0.01			5.79	0.45

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558 **Table 3** Concentrations of total dissolved copper (C_{Cu}), labile copper ($[Cu']$), ligands (C_{L1} ,
559 C_{L2}) and stability constants expressed in logarithmic form ($\log K'_1$ $\log K'_2$) for samples
560 collected from 1992 to 2006.

	C_{Cu} (nM)	$[Cu']$ (nM)	C_{L1} (nM)	$\log K'_1$	C_{L2} (nM)	$\log K'_2$
July 92						
<i>Marghera</i>	14	0.63	11	15	71	7.7
<i>Dese</i>	6.9	udl	132	9	124	6.6
<i>Historic centre VE</i>	8.1	0.11	udl	--	121	8.0
<i>Sacca Sessola</i>	8.2	udl	20	15	107	7.9
<i>Chioggia</i>	7.5	udl	15	16	158	7.6
<i>Mare adriatico</i>	5.2	udl	17	11	94	7.8
Oct. 1992						
<i>Punta della Salute</i>						
min value	3.0	udl	0.10	11	51	8.1
max value	7.7	udl	31	16	144	8.7
mean	4.5	udl	12.8	14	77	8.4
std	1.6	udl	10.0	1	26	0.2
Campaign 1994						
<i>Sacca Sessola</i>						
min value	5.3	udl	5.1	10	35	8.4
max value	14.4	udl	24.6	17	169	9.4
mean	9.9	udl	14.2	14	99	8.9
std	3.2	udl	6.7	3	40	0.3

			Campaign 1997			
<i>S. Giorgio in Alga</i>						
min value	5.30	u.d.l.	10	11	15	7.5
max value	38.00	u.d.l.	61	14	229	8.4
mean	17.28	u.d.l.	25	13	88	7.9
std	7.63	u.d.l.	13	1	46	0.2
			Campaign 2001			
<i>Tresse</i>	9.50	u.d.l.	10	13	158	7.8
<i>Campalto</i>	26	0.01	-	-	80	8.2
<i>Sacca Sessola</i>	9.9	3.7	-	-	104	7.3
<i>Murano</i>	48	0.06	-	-	120	10
					115	8
			Campaign 2002			
<i>Tresse</i>	13	u.d.l.	4.1	16	122	9.8
<i>Sacca Sessola</i>	13	u.d.l.	-	-	134	8.0
"	8.3	u.d.l.	6.8	14	81	7.5
<i>Murano</i>	50	0.09	-	-	72	8.8
"	29	-	-	-	-	-
					96	8
			Campaign 2003			
<i>Campalto</i>	32	0.03	-	-	169	7.8
<i>Sacca Sessola</i>	31	u.d.l.	-	-	44	8.8
<i>Murano</i>	23	u.d.l.	3.89	16	120	8.0
"	13	0.17	-	-	71	8.0
	19	0.6	-	-	144	8.4
			April-Oct. 2005			
<i>Sacca Sessola</i>	7.4	1.10	7.9	9	29	8.6
	3.0	0.26	-	-	48	8.4
	5.9	0.04	53	9	33	8.9
<i>Campalto</i>	7.9	0.18	11	14	207	7.2
	5.6	u.d.l.	19	13	66	7.4
	6.8	0.22	17	15	48	6.4
			July-Aug. 2005			
<i>Mazzorbo</i>						
min value	4.7	0.10	1.8	9	36	6.8
max value	7.1	1.00	28	14	148	14
mean	5.7	0.51	19	11	81	8.5
std	0.87	0.46	11.7	3	45	2.7
			Campaign 2006			
<i>Sacca Sessola</i>	6.1	0.31	8.5	15	109	7.7
"	6.9	0.88	-	-	71	8.1
<i>Campalto</i>	4.5	0.41	6.3	14	207	7.6
"	9.3	0.64	12	10	23	7.5
<i>Mazzorbo</i>						
min value	5.2	0.10	2	10	117	7.2
max value	10.1	0.33	22	16	255	8.0

mean	7.0	0.24	12	14	180	7.6
std	2.3	0.10	10	3	58	0.3

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Table 4 Concentrations of total dissolved lead (C_{Pb}), labile lead ($[Pb']$), ligand (C_L) and stability constant expressed in logarithmic form ($\log K'$) for samples collected from 1992 to 1997.

	C_{Pb} (nM)	$[Pb']$ (nM)	C_L (nM)	$\log K'$
July 92				
<i>Marghera</i>	1.4	0.27	1.40	10.2
<i>Dese</i>	0.53	0.08	1.20	9.6
<i>Historic centre VE</i>	0.70	0.18	1.50	9.3
<i>Sacca Sessola</i>	0.43	0.12	1.70	9.2
<i>Chioggia</i>	0.16	0.06	1.00	9.3
<i>Mare adriatico</i>	0.27	0.12	0.33	10
Oct. 1992				
<i>Punta della Salute</i>				
min value	0.22	0.05	0.49	8.90
max value	0.77	0.24	2.82	9.77
mean	0.40	0.11	1.33	9.43
std	0.18	0.05	0.69	0.28
Campaign 1994				
<i>Sacca Sessola</i>				
min value	0.09	0.01	0.21	10.05
max value	0.36	0.13	1.30	10.91
mean	0.21	0.07	0.82	10.54
std	0.08	0.03	0.32	0.30
Campaign 1997				
<i>S. Giorgio in Alga</i>				
min value	0.30	0.03	0.10	8.50
max value	2.60	0.47	4.00	11.00
mean	0.75	0.13	1.25	9.52
std	0.52	0.12	0.88	0.59

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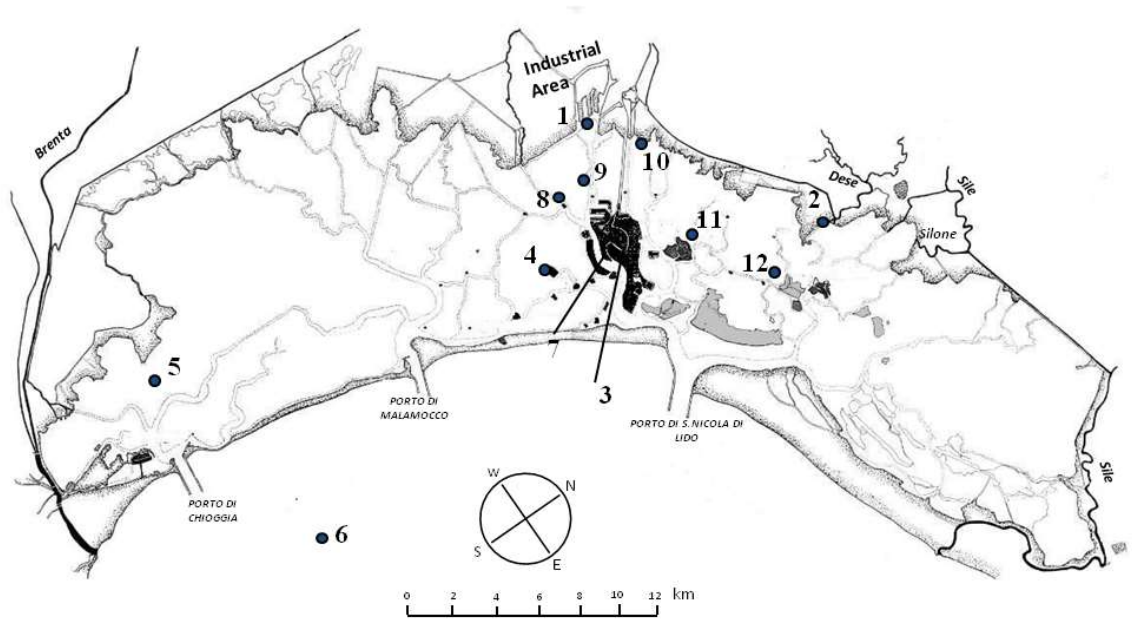
580 **Table 5** Concentration of metals (Cd, Cu and Pb) in particulate phase for samples collected
 581 from 1992 to 2003 and total particulate concentrations.

	Particulate (mg/l)	Cu (µg/g)	Cd (µg/g)	Pb (µg/g)
July 92				
<i>Marghera</i>	18	25	0.92	--
<i>Dese</i>	14	8.6	0.16	--
<i>Historic centre VE</i>	18	40	0.9	--
<i>Sacca Sessola</i>	16	6.8	0.21	--
<i>Chioggia</i>	8.3	4.3	0.07	--
<i>Mare adriatico</i>	12	0.34	0.02	--
Campaign 1994				
<i>Sacca Sessola</i>				
min value	8	21	0.03	2.3
max value	20	39	0.65	39.0
mean	13	32	0.30	16.9
std	4	6	0.20	11.7
Campaign 1997				
<i>S. Giorgio in Alga</i>				
min value	2.3	61.6	0.60	36.0
max value	26.7	103.6	2.23	106.0
mean	12.5	74.7	1.37	75.5
std	7.1	11.3	0.33	21.3
Campaign 2001				
<i>Tresse</i>	12	32.2		
Campaign 2002				
<i>Tresse</i>	29.9	63.2	2.61	78.9
Campaign 2003				
<i>Campalto</i>	30	31	1.06	35.3

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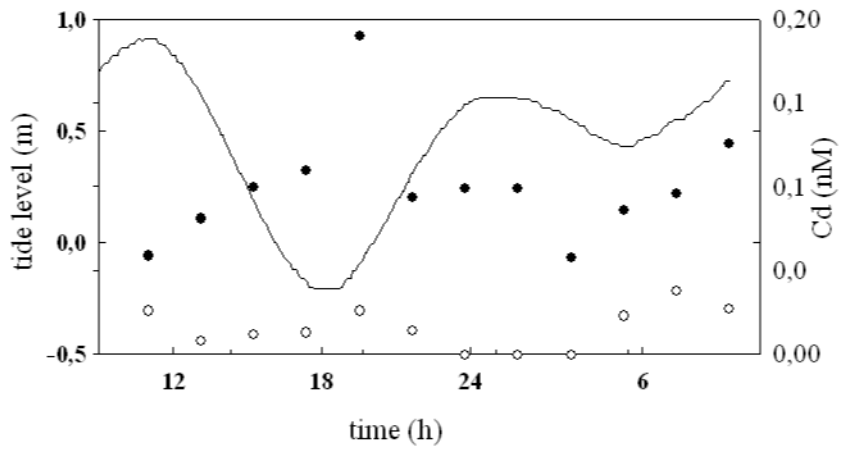
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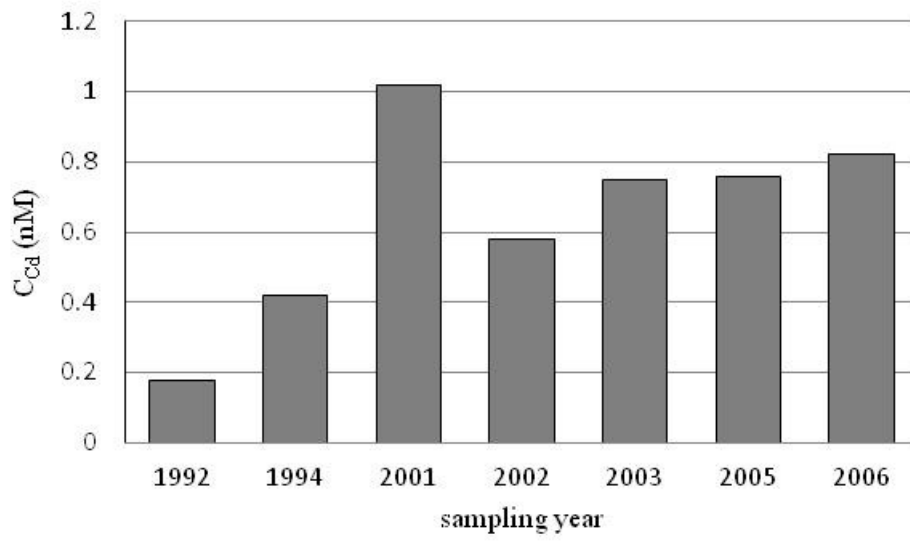
Figure 1. Map of the Lagoon with the sampling sites



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Figure 2. Tide level, total dissolved and labile cadmium concentration during October 1992 campaign.

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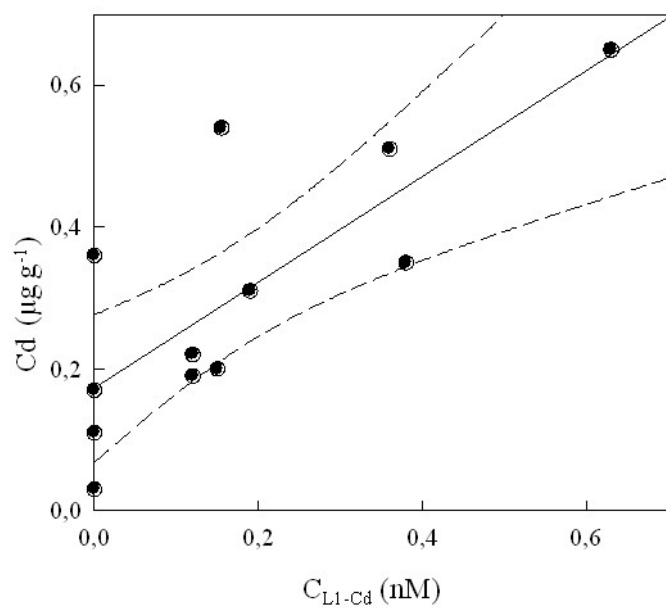


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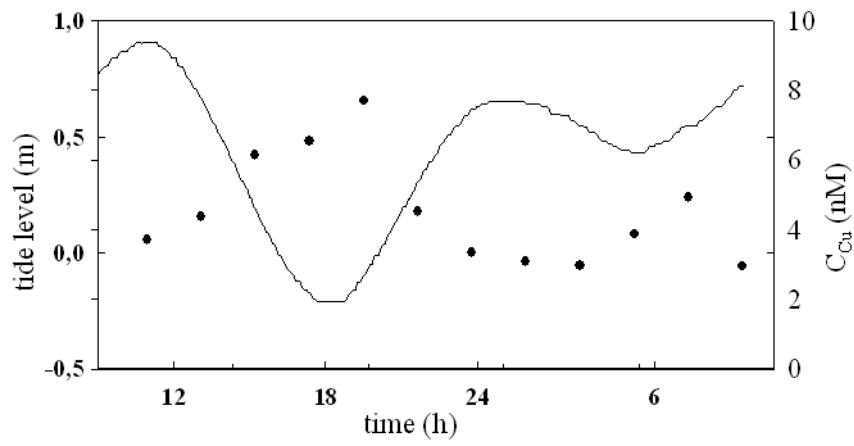
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Figure 3. Trend of dissolved cadmium concentration. C_{Cd} , at Sacca Sessola.

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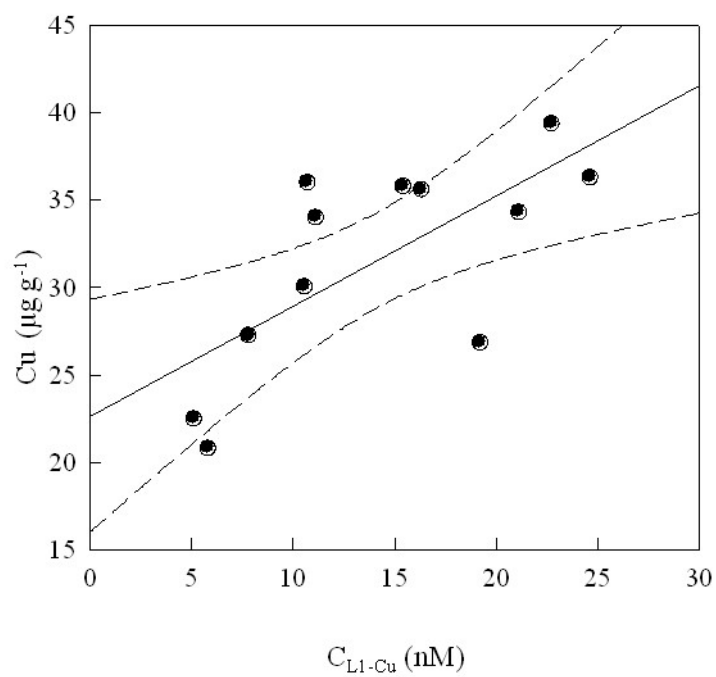


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 597 Figure 4. Particulate cadmium concentration and concentration of the stronger class of
 598 ligands.
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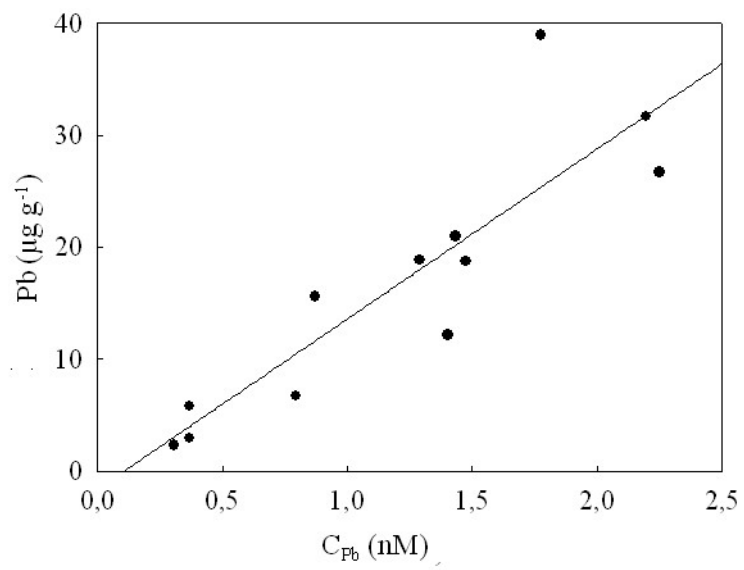
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Figure 5. Tide level and total dissolved copper concentration during October 1992 campaign.



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Figure 6. Particulate copper concentration and concentration of the stronger class of ligands.



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Figure 7. Particulate lead concentration and total dissolved lead concentration.