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1 **Diagnosis of trace metal contamination in sediments: the example of Ensenada and El**
2 **Sauzal, two harbors in Baja California, Mexico**

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4 by

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23

24 **Abstract**

25

26 Total metal concentrations in sediments from within Ensenada and El Sauzal harbors are
27 generally higher than at the mouths. Grain-size analyses suggested that this enrichment could
28 be due to the presence of fine-grained sediments in the inner part of the harbors rather than to
29 anthropogenic perturbations. The $(\text{Me}/\text{Al})_{\text{sample}}$ ratios for Pb, Co, Ni and Fe were significantly
30 higher for Ensenada Harbor relative to El Sauzal Harbor, whereas the ratios for Cd, Mn, Zn and
31 Cu were statistically equivalent for both harbors. Calculated enrichment factors [$\text{EF}_{\text{Me}} =$
32 $(\text{Me}/\text{Al})_{\text{sample}}/(\text{Me}/\text{Al})_{\text{shale}}$] indicated that the metals showing slight enrichment were those
33 associated with anthropogenic contamination (Pb, Zn), or probably related to primary productivity
34 in the water column (Cd, Co). The levels of most of the metals were not greatly enriched, a
35 consideration that is of the utmost importance when contamination issues are at stake.

36

37 **Keywords:** enrichment factor, geochemistry, grain size, metals, sediment pollution, trace
38 elements, Baja California.

39 1. Introduction

40

41 Harbors are enclosed and low-energy water bodies where fine-grained sediment tends to
42 accumulate. They are also prone to receive significant metal inputs from marinas, boat hull
43 maintenance, wholesale fish markets, shipping activities, sacrificial anodes, and industrial, storm
44 and urban discharges. Once in the water column, metals are quickly adsorbed onto particulates
45 and eventually removed to bottom sediments (de Groot et al., 1982; Santschi et al., 1984; Blake
46 et al., 2004), thus producing conspicuous trace metal enrichments. Moreover, trace metal
47 enrichments in sediments produced by normal harbor activities can be further enhanced by the
48 larger surface area of the finer sediments that are naturally deposited in these areas of minimum
49 hydrodynamic energy. It is therefore important to measure the extent of metal enrichment in
50 harbor sediments since they can act as point sources of contamination during dredging
51 operations or any other activity by which contaminated sediments can be transported out of the
52 harbors and into neighboring bays or open ocean areas.

53 Ensenada and El Sauzal harbors are the main harbors on the Pacific coast of northern
54 Mexico. They are located in Todos Santos Bay (Figure 1) and plans are well underway to
55 modernize both harbors by increasing their extension and container handling capacity, especially
56 in the case of El Sauzal Harbor, whose area will be increased approximately ten times.
57 Additionally, Ensenada Harbor has a cruise terminal capable of handling at least two cruise ships
58 simultaneously. All this expansion work and increase in shipping traffic are associated with
59 dredging activities that may produce a net export of metals out of the harbors. Hence,
60 understanding the relative contributions of the different trace metals is necessary in order to
61 assess the impact of future developments in these harbors and their surrounding waters, and to
62 develop effective strategies to protect them and other harbors elsewhere.

63 In this paper we will try to answer the following specific questions: Are sediments from
64 Ensenada and El Sauzal harbors enriched in trace metals (Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn)? If
65 so, to what extent and with which metals? Which harbor presents the highest metal
66 enrichments? If present, are these trace metal enrichments anthropogenically derived? To

67 answer these questions, trace element levels (normalized with Al) will be compared with those
68 reported for other sediments from the Southern California Bight and with average shale values of
69 sedimentary rocks to evaluate the extent of anthropogenic perturbations in the sediments of these
70 two important Mexican harbors. Additionally, pollution load indexes (Tomlinson et al., 1980;
71 Angulo, 1996) and geoaccumulation indexes (Müller, 1979) will be calculated for both harbors.
72 Finally, total concentrations will be compared with the U.S. NOAA's sediment quality guidelines
73 (as proposed by Long et al., 1995) to estimate the possible consequences of the metal levels
74 analyzed in this study to the local biota. Because of the absence of similar studies in the region,
75 this paper will also provide baseline data for future research on anthropogenic impacts in the
76 region.

77

78 **2. Materials and methods**

79 *2.1. Study area*

80

81 Ensenada and El Sauzal harbors are situated in Todos Santos Bay, which is located in
82 the northwestern part of the Baja California Peninsula, Mexico (Figure 1a), 100 km south of the
83 US-Mexico border (31° 40', 31° 56' N; 116° 36', 116° 50' W). This 240-km² bay is limited to the
84 south by Punta Banda, to the north by Punta San Miguel, to the southwest by two small islands
85 located near the mouth of the bay, and to the northeast by the city of Ensenada (around 400,000
86 inhabitants). According to Pavía (2004), the climate of the region is Mediterranean, with scarce
87 rainfall (annual average of 250 mm) that occurs mainly during the winter (average of 200 mm).
88 The regional surface circulation pattern is produced by a predominant northwest component of
89 the wind and surface currents have been reported to average 15 cm s⁻¹ and 5 cm s⁻¹ during
90 summer and winter, respectively (Alvarez-Sánchez et al., 1988). This wind-driven circulation
91 pattern promotes the transport of water from the adjacent Pacific Ocean towards the inner bay,
92 generating a cell circulation system (dotted arrows; Figure 1b). Part of this flow is directed toward
93 Ensenada harbor and the other part toward Punta Banda, in the southwestern part of the bay

94 (Figure 1b). Upwelling is intense all year round, but especially in spring and summer (Gonzalez-
95 Morales and Gaxiola-Castro, 1991).

96 Ensenada Harbor, an international marine terminal, was built in 1956 and covers an area
97 of 1.95 km² (i.e., approximately 13 times bigger than El Sauzal Harbor). The mouth of the harbor
98 is formed by a 1,640-m-long rock breakwater that is connected to the coast and by a 855-m-long
99 jetty (El Gallo; Figure 1d). Water depths range from 1.5 to 11 m, with the deepest parts located
100 adjacent to the loading and terminal docks and the main navigation channel. In addition to the
101 presence of fine-grained sediments (approximately 80% <62.5 μm), this harbor tends to
102 accumulate metals due to inputs from (a) a wholesale fish market, (b) marine vessels normally
103 docked in the port and marina areas, (c) urban runoff discharged through Arroyo Ensenada
104 (Figure 1d) during the winter rains, and (d) vessel repair and maintenance activities
105 (liberation of antifouling paint, sand blasting operations) within the port zone.

106 El Sauzal Harbor, built in the mid-1980s and located 10 km north of Ensenada in the
107 town of El Sauzal de Rodriguez (approximately 7,500 inhabitants), has an area of 0.15 km²
108 (Flores-Vidal et al., 2005) and a 100-m-wide mouth formed by two breakwaters that are 500 m
109 and 250 m long (Figure 1c). Water depths range from 1 to 9 m, with maximum depth occurring in
110 the main navigation channel (Flores-Vidal et al., 2005). Inputs to this harbor are essentially from
111 fishery companies dedicated to extraction, processing and production activities, as well as from
112 blood and organic wastes discharged by docked fishing boats, and from the powder generated
113 during the unloading of cement from large boats or vessels.

114

115 *2.2. Field and laboratory methods*

116

117 Sediment samples from Ensenada Harbor were obtained from one core (core 0E)
118 collected at approximately 6 m water depth on November 2, 1998 (Carreón-Martínez et al., 2001).
119 This core was collected within the dredged channel, close to Arroyo Ensenada and in front of the
120 cruise terminal, which was still not constructed at that time. Six more cores (cores 1E to 6E) were
121 collected on January 8, 2002 at water depths of approximately 9 m (Figure 1d) and beneath the

122 docks, considered the areas least affected by sediment resuspension and dredging. Sediments
123 had a hydrogen sulfide smell, were black along the length of the cores and did not show any
124 oxidized portion close to the sediment-water interface. Cores from El Sauzal Harbor were
125 collected on September 29, 2004 (cores 1S to 4S) at water depths ranging from 6 to 9 m (Figure
126 1c). A polycarbonate plastic core liner (7.2 cm internal diameter, 60 cm in length) was introduced
127 into the sediment, retrieved and capped underwater by a diver who transferred it to a boat. Once
128 on board, the core liner was capped with a plastic cap, sealed with electrical tape and transported
129 to shore, where it was extruded and sliced every 1 cm with a plastic spatula. Each section was
130 then transferred to a 50-mL centrifuge polypropylene tube and stored at -20°C for further
131 laboratory analysis. Only core 0E was sliced in a glove bag under nitrogen atmosphere to avoid
132 precipitation of the reduced Fe and Mn dissolved in the anoxic portion of the interstitial water.
133 The 10-13 cm sediment depths of core 2S consisted almost entirely of fish scales.

134 All laboratory materials were washed with phosphate-free soap, rinsed three times with
135 distilled water and left for 24 hours in a 5% HCl solution. The material was then rinsed three
136 times with deionized water (Milli-Q grade) and left semi-closed to dry at room temperature. Total
137 metal concentrations were obtained after complete digestion of 0.5 g of sediment in Teflon
138 beakers with concentrated HNO_3 , HClO_4 and HF (Carignan and Tessier, 1988). Trace metal
139 concentrations were measured by atomic absorption spectrometry (Thermo Jarrel Ash model
140 Smith Hieltje 12 or Varian model SpectrAA 220 Fast Sequential). Certified Reference Material
141 (CRM) Beaufort Chemistry Standard Sediment (BCSS-1; National Research Council of Canada)
142 was used to ascertain the accuracy and precision of the total extraction procedure. Recovery
143 percentages of the BCSS-1 CRM ranged from 90% for Cd to 104% for Cu (Table 1). Blanks were
144 routinely run and analyzed in the same manner as the samples. Limits of detection for the
145 different trace metals, calculated as three times the standard deviation of the procedural blanks,
146 were (in $\mu\text{mol g}^{-1}$): 2.4 (Al), 0.0076 (Cd), 0.026 (Co), 0.024 (Cu), 0.014 (Fe), 0.0047 (Mn), 0.11
147 (Ni), 0.035 (Pb), 0.013 (Zn). In this paper, and for practical purposes, all metals associated with
148 sediments will be designated as trace metals, regardless of their concentration level. Percentage
149 of sediment grain size $<62.5 \mu\text{m}$ (%GS) was measured using a Horiba laser scattering particle

150 size distribution analyzer model LA-910, with size interval of 0.02-1000 μm . The analytical
151 efficiency of the particle analyzer was determined with 0.9- μm sieved polystyrene spheres (CRM
152 NIST 8010D and NIST 1690). Organic carbon (org-C) concentrations in the sediments were
153 estimated using the loss on ignition (LOI) method (550 $^{\circ}\text{C}$ for 5 h). These measurements were
154 transformed to org-C concentrations through a calibration curve (org-C % = $(0.206 \pm 0.010) \cdot \text{LOI}$;
155 $r^2 = 0.929$, $p < 0.001$, $n = 33$) using org-C values from Todos Santos Bay sediments measured by
156 a LECO model CHNS-932 elemental analyzer. Due to the lack of available samples, org-C and
157 grain size were not measured in core 0E.

158 To reduce the complexity within the similarity matrix, the dataset (including metal
159 concentrations, org-C content and %GS) was transformed into a simpler factor matrix by principal
160 components analysis (PCA). For both Ensenada and El Sauzal harbors, the PCA was calculated
161 based on the correlation matrix of the standardized data using the SYSTAT 8.0 statistical
162 package. For this analysis, eigenvalues > 1 were considered significant and, in addition, the
163 orthogonal varimax rotation was chosen for factor rotation.

164

165 **3. Results and discussion**

166 *3.1. Trace metal distributions*

167

168 Trace metal profiles for both Ensenada and El Sauzal harbors showed no substantial
169 changes in concentration with sediment depth (Figures 2 and 3), except for Cu and Zn in core 1E,
170 in which peaks of maximum concentration ($229 \mu\text{mol g}^{-1}$ and $30 \mu\text{mol g}^{-1}$, respectively; Figures 2c
171 and 2i) were observed at a depth of 5.5 cm for both elements. The concentration of Cu was also
172 high in the first 6 cm of core 4E ($2.66 \pm 0.49 \mu\text{mol g}^{-1}$), while Cd concentrations increased with
173 depth (maximum value = $0.018 \mu\text{mol g}^{-1}$ at 19.5 cm) in the first 20 cm of core 0E. Significant
174 trace metal enrichments close to the sediment-water interface are absent in both harbors, further
175 proof that the cores were anoxic up to the sediment-water interface. The lack of significant
176 features in all trace metal profiles is probably a consequence of the absence of the oxic layer
177 (and probably the anoxic non-sulfidic layer as well) and of the homogeneity of the %GS (Figure

178 2j). Bioturbation can be discarded as the cause since all the cores were anoxic-sulfidic up to the
179 sediment-water interface.

180 Overall, trace metals in Ensenada Harbor showed a wide range of average
181 concentrations (Table 2), the lowest corresponding to Cd (overall average $32 \pm 16 \text{ nmol g}^{-1}$) and
182 the highest to Al (overall average $3.81 \pm 0.75 \text{ mmol g}^{-1}$). On average, core 1E showed the
183 highest values for Cu ($15 \pm 40 \text{ } \mu\text{mol g}^{-1}$), Fe ($1.33 \pm 0.16 \text{ mmol g}^{-1}$), Mn ($12.7 \pm 2.5 \text{ } \mu\text{mol g}^{-1}$) and
184 Zn ($5.8 \pm 4.5 \text{ } \mu\text{mol g}^{-1}$); core 0E for Co ($1.79 \pm 0.45 \text{ } \mu\text{mol g}^{-1}$) and Ni ($2.136 \pm 0.046 \text{ } \mu\text{mol g}^{-1}$);
185 core 2E for Cd ($50.6 \pm 2.5 \text{ nmol g}^{-1}$) and Al ($4.94 \pm 0.25 \text{ mmol g}^{-1}$); and core 6E for Pb (371 ± 14)
186 (Table 2). Metals (Co, Cu, Ni, Zn, Fe and, to a certain extent, Al, Mn and Cd) and org-C generally
187 decreased in concentration from the inner part of Ensenada Harbor to its mouth (Figure 4). This
188 result is not unexpected since the inner portion of the harbor shows finer grain size (Figure 4),
189 more shipping activity and less hydrodynamic energy than the outer parts. In this harbor, the
190 deepest areas range from 8 to 12 m and the shallower parts from 2 to 6 m. Cores 3E, 4E and 5E
191 were taken just at the edge of the deep main channel and thus presented higher sand
192 composition but also low metal concentrations (Figure 4). Sediments located at the mouth of the
193 harbor presented low %GS (reflecting a high level of hydrodynamic energy) and, consequently,
194 high sand contents that diluted trace metal concentrations. Core 0E, however, usually presented
195 anomalous concentrations when compared with the other cores from Ensenada Harbor (Figure
196 4); for example, it had considerably higher median concentrations of Co, Fe and Ni, and lower
197 median concentrations of Cd and Pb relative to the other cores. This anomalous behavior can be
198 attributed to the location of the core, which was collected inside the dredged channel and close to
199 the mouth of Arroyo Ensenada. Sediment resuspension produced by continuous shipping traffic,
200 repeated dredgings (which can alter the distribution of some key components of sediments, like
201 nutrients and carbon; Nayar et al., 2007) and occasional particulate and dissolved contributions
202 from the seasonal stream have evidently altered the distribution and levels of trace metals in core
203 0E. These alterations are more noticeable for Cd, Co, Fe, Mn, Pb and Zn, as reflected in the
204 variability (spread) of their concentrations (Figures 2a,b,d,f,h and i, respectively) and by the
205 increase in length of the box plots shown in Figure 4.

206 Average metal concentrations in El Sauzal Harbor (Table 2) were consistently high in
207 cores 2S ($\text{Cd} = 28.2 \pm 1.5 \text{ nmol/g}$, $\text{Cu} = 1.24 \pm 0.13 \text{ } \mu\text{mol g}^{-1}$, $\text{Ni} = 0.476 \pm 0.017 \text{ } \mu\text{mol g}^{-1}$, $\text{Pb} =$
208 $183 \pm 18 \text{ nmol g}^{-1}$, $\text{Zn} = 4.75 \pm 0.70 \text{ } \mu\text{mol g}^{-1}$) and 3S ($\text{Al} = 2.81 \pm 0.24 \text{ mmol g}^{-1}$, $\text{Co} = 0.495 \pm$
209 $0.037 \text{ } \mu\text{mol g}^{-1}$, $\text{Fe} = 0.668 \pm 0.085 \text{ mmol g}^{-1}$, $\text{Mn} = 7.6 \pm 1.1 \text{ } \mu\text{mol g}^{-1}$). As in Ensenada Harbor,
210 trace metal enrichments close to the sediment-water interface are conspicuously absent for
211 practically all metals, suggesting that the cores were anoxic up to the sediment-water interface.
212 Median concentration values were consistently high in cores 2S, 3S and 4S from the inner
213 stations and low in core 1S from the harbor mouth, a reflection of the coarser grain size that
214 characterizes this last core (Figure 4). The bathymetry for this harbor (Flores-Vidal et al., 2005)
215 shows that cores 3S and 4S were located at approximately 9 m depth (*i.e.*, the deepest inner
216 area), whereas cores 1S and 2S were collected at water depths of approximately 6 m. Judging
217 from the grain size composition, station 1S was located where the hydrodynamic energy was higher.

218 Figure 4 shows that total concentrations of Cd, Co, Fe, Mn, Ni and Pb are generally lower
219 in El Sauzal Harbor than in Ensenada Harbor. These results probably cannot be ascribed to
220 differences in org-C concentrations for Ensenada ($1.50 \pm 0.38 \text{ mmol g}^{-1}$; $n = 139$) and El Sauzal
221 ($1.78 \pm 0.97 \text{ mmol g}^{-1}$; $n = 74$) harbors, since statistically both have similar average org-C levels
222 ($p = 0.142$, Mann-Whitney rank sum test). The metal concentration results may suggest that
223 Ensenada Harbor, which is approximately 30 years older than El Sauzal Harbor, tentatively has
224 had more time to accumulate trace metal contaminants in its sediments. Alternatively, the
225 sediments of both harbors may have, on average, different particulate sizes. A Mann-Whitney
226 rank sum test of the %GS indicated that the average fraction $<62.5 \text{ } \mu\text{m}$ from Ensenada Harbor
227 ($80 \pm 18\%$, $n = 182$) was significantly higher ($p \leq 0.001$) than the one measured for El Sauzal (73
228 $\pm 14\%$, $n = 74$). The differences in %GS distribution between the two harbors are also noticeable
229 in Figure 5, in which plots of metal concentrations versus %GS are displayed. This figure shows
230 that the sediments from El Sauzal (closed symbols) form distinctly different groups for Co, Fe, Ni,
231 Mn, Pb and Cd, which tend to cluster in the lower portion of the concentration range and
232 generally below the concentrations measured in Ensenada Harbor (open symbols). One of the
233 most important factors controlling the natural distribution of trace metals in sediments is the

234 variation in grain size (Cauwet, 1987; Grant, 1990; Ergin, 1995; Lin et al., 2002). It is widely
235 accepted that metals are enriched in the fine (<62.5 μm) fraction of sediments (Gibbs, 1977;
236 Helmke et al., 1977; de Groot et al., 1982; Förstner, 1982; Cauwet, 1987; Horowitz et al., 1989;
237 Zhang et al., 2002) and that metals exhibit positive linear correlations with the fine-grained sizes
238 (de Groot et al., 1982; Ackermann et al., 1983; Ergin, 1995; Meador et al., 1998; Charlesworth
239 and Service, 2000; Zhang et al., 2002). Although grain size analysis is not suitable for
240 differentiating natural baseline versus anthropogenic enrichments of trace elements, such an
241 analysis may help to account for the natural diluting effect of sand.

242

243 *3.2. Trace metals and grain size*

244

245 The size-class distribution in sediments is intimately related to the hydrodynamics of the
246 systems. Hence, comprehension of this process in combination with coastal topography can help
247 to understand the behavior of sediments in terms of flocculation, adsorption or precipitation.
248 Based on textural parameters, Pérez-Higuera and Chee-Barragán (1984) inferred the existence
249 of a southward dominant transport in the littoral zone of Todos Santos Bay. In the case of
250 Ensenada Harbor, the water flow across the mouth produced by the tide effect is considered to
251 be the main hydrodynamic forcing in the movement of particulate material, sediments and
252 pollutants (Coronado-Méndez et al., 2003). The high sand contents (and low metal
253 concentrations) are just a reflection of the high level of hydrodynamic energy at both harbor
254 mouths.

255 Figure 5 suggests that for sediments showing similar %GS, the metal concentrations
256 measured in Ensenada and El Sauzal harbors were higher than those measured at the Point
257 Loma Ocean Outfall (PLOO) discharge point and its surroundings, off San Diego Bay (City of San
258 Diego, 2005). This is surprising, considering that sediments from the PLOO area have been
259 found to be contaminated with a number of trace metals (Sb, As, Ba, Be, Cd, Cr, Cu, Fe, Pb, Mn,
260 Hg, Ni; City of San Diego, 2005). Furthermore, data reported for the Southern California Bight
261 (SCB; Schiff, 2000) show that average Cu, Ni and Zn values for the whole SCB (3,420.3 km^2)

262 follow the same trends as the ones observed for Ensenada and El Sauzal harbors (Figures
263 5c,f,h). Only Cd and Pb (Figures 5a, g) exhibited a differential behavior, with average SCB
264 concentrations well below the ones observed for Ensenada and El Sauzal sediments (Co, Fe and
265 Mn were not measured by Schiff, 2000). Similar results (Figure 5) were obtained for the average
266 values of Santa Monica Bay (SMB, 457.4 km²), outfalls of publicly owned treatment works
267 (POTWs, 292.8 km²) and stormwater areas (STW, 81.1 km²), the latter located within 3 km of the
268 11 largest river and creek mouths draining directly into the SCB (Schiff, 2000). Pristine
269 sediments from Strangford and Carlingford loughs (Charlesworth and Service, 2000), as well as
270 from anthropogenically impacted regions of Mexico (Mazatlan Harbor: contaminated with oil,
271 sewage and industrial discharges; Osuna-López et al., 1986) and Europe (Belfast Lough:
272 domestic and industrial inputs from the city of Belfast; Charlesworth and Service, 2000) follow
273 trends similar to the ones observed for Ensenada and El Sauzal sediments (Figure 5). Only Ni
274 and, to a certain extent, Zn in the Belfast samples show higher concentrations than those
275 measured for sediments with similar %GS. Hence, apparently the grain size:metal relationship is
276 not a useful indicator of trace metal enrichment: sediments with similar %GS, but far more
277 contaminated by sewage effluents and industrial inputs (*e.g.*, San Diego-PLOO, Los Angeles-
278 SMB, Belfast) than our study area have metal concentrations that are generally below or at the
279 same level as the ones measured in Ensenada and El Sauzal harbors (Figure 5).

280

281 3.3. Organic carbon

282

283 The concentrations of org-C in Ensenada Harbor showed considerable variation with
284 depth (except core 2E, Figure 2k), but without any noticeable trend. In contrast, El Sauzal Harbor
285 showed no substantial changes with depth, except core 2S. This core had the highest
286 concentrations of the four cores, probably because it was collected where docked fishing boats
287 wash their decks, discharging in the process blood and organic wastes into the water and
288 underlying sediment. The concentrations of org-C in core 2S were especially high between 8 and
289 13 cm (Figure 3k), probably reflecting past high inputs of organic wastes, whose degraded

290 remains are represented by the 10-13 cm sediment depth, consisting almost entirely of fish
291 scales. Additionally, this core showed anomalously high org-C concentrations with respect to the
292 %GS μm (Figure 5i), suggesting that anthropogenic contributions are considerable in the west
293 corner of the harbor (core 2S, Figure 1). There was a significant correlation between %GS and
294 org-C for both El Sauzal ($r = 0.54$, $p \leq 0.001$, $n = 74$) and Ensenada ($r = 0.71$, $p \leq 0.001$, $n = 139$)
295 harbors (Table 3); however, the correlation for El Sauzal increased substantially when core 2S
296 was eliminated ($r = 0.84$, $p \leq 0.001$, $n = 61$; data not shown), further supporting the contention of
297 the anthropogenic origin of the sedimentary org-C.

298

299 *3.4. Correlations between the different sediment components*

300

301 Results of the PCA analysis (Table 4) show that two components explained 79.9% and
302 81.4% of the total variance for Ensenada and El Sauzal, respectively. In the case of Ensenada, a
303 firmly related group (PC1) was formed by Al, Cd, Co, Fe, Mn, Ni, Pb and %GS (loadings >0.63),
304 while the second group (PC2) was formed by Cu, Zn and org-C (loadings >0.75). For El Sauzal
305 Harbor, Cd, Cu, Zn and org-C (loadings >0.89) constituted the first group (PC1), and Al, Co, Fe,
306 Mn and %GS the second (PC2; loadings >0.76). The strong correlation among Cu, Zn, Cd and
307 org-C found for both harbors reflects the complex nature of organic matter as well as the
308 importance of the role played by the diagenetic reactions driven by its degradation, which, in turn,
309 regulates the behavior of these reactive metals. The strong association among Al, Fe, Mn, Co
310 and %GS suggests that the concentrations of these metals are strongly controlled by the
311 sediment grain size of these two Mexican harbors. The PCA results are essentially in agreement
312 with the Pearson correlation coefficient matrix (Table 3), which probably indicates the association
313 of Cd, Cu and Zn with organic matter and the existence of a strong lithogenous component (Al,
314 Fe and %GS) controlling the distribution of trace metals in sediments.

315

316 *3.5. Enrichment factors*

317

318 Another approach by which trace element enrichments can be evaluated consists of the
319 geochemical normalization of metal concentrations with a conservative element. This approach
320 is based on the assumption that there are certain elements that represent proxies for the clay
321 mineral concentration (Kersten and Smedes, 2002). Geochemical normalization has several
322 advantages. For example, it compensates for the mineralogical as well as the natural grain size
323 variability of trace element concentrations in sediment (Loring, 1991; Birch, 2003). Aluminum has
324 been widely used as a normalizing agent for evaluating metal concentrations in estuarine and
325 coastal sediments (*e.g.*, Goldberg et al., 1979; Schropp et al., 1990; Summers et al., 1996;
326 Weisberg et al., 2004). Some of the main advantages of using Al as a geochemical normalizer
327 are its high natural concentration (second most abundant metal in the Earth's crust), minimal
328 anthropogenic contamination, it is a structural element of clays, and the metal to Al proportions in
329 the crust are relatively constant (Schropp et al., 1990; Summers et al., 1996). Although Fe has
330 also been used to normalize metal concentrations (*e.g.*, Schiff and Weisberg, 1999), Al is a better
331 agent because it is more strongly associated with the aluminosilicate matrix (one of the most
332 important metal-bearing phases of sediments). In contrast, Fe can be significantly affected by
333 diagenetic processes (redistribution, anthropogenically induced formation of Fe sulfides and Fe
334 oxides; Summers et al., 1996), which can distort total Fe concentrations (Loring, 1991).

335 Metal/aluminum (Me/Al) ratios for both Ensenada and El Sauzal harbors increase in the
336 following order: $Cd/Al < Pb/Al < Ni/Al \approx Co/Al \approx Cu/Al < Zn/Al < Mn/Al \ll Fe/Al$ (Figure 6). The
337 Me/Al ratios of Pb, Co, Ni and Fe were significantly higher for Ensenada Harbor relative to El
338 Sauzal Harbor, whereas the ratios for Cd, Mn, Zn and Cu were statistically equivalent for both
339 harbors. Hence, geochemical normalization suggests that metal concentrations in sediments
340 from El Sauzal show some similarities with those from Ensenada Harbor, but that the latter
341 sediments are more enriched in some elements. Proximity to a larger urban settlement (City of
342 Ensenada) may explain the higher Pb/Al ratio for Ensenada; however, explaining the higher
343 values for the other three metal ratios is more difficult. It can be hypothesized that the presence
344 of more intense reducing conditions and greater flushing times (due to its smaller size) in El
345 Sauzal Harbor may explain the deficiency in Fe, Pb, Co, Ni and, to a certain extent, Mn. Fishing

346 boats are routinely cleaned inside this harbor and blood and organic waste end up accumulating
 347 in the sediments. For example, the last 6 cm (7–13 cm interval) of core 2S were almost entirely
 348 made up of fish scales, an indirect indication of the magnitude of organic matter contribution to
 349 the sediments. All this waste could conceivably drive the sediment redox conditions toward a
 350 reducing condition, which is probably not so intense in Ensenada Harbor due to the absence of
 351 this type of wastes. Fe and Mn are dynamic participants in the redox cycle and their more active
 352 reductive dissolution in the El Sauzal sediments with subsequent diffusion to the water column,
 353 coupled with a rapid flushing out of this harbor may explain the differences between Fe/Al and
 354 Mn/Al in El Sauzal and Ensenada sediments. However, since the reaction of Mn with oxygen is
 355 several orders of magnitude slower than that for reduced Fe (Jørgensen and Boudreau, 2001),
 356 Mn will be preferentially lost to the water column due to its slower oxidation kinetics of
 357 precipitation. Cobalt enrichment could be associated with primary productivity since this element
 358 is associated with vitamin B12 (cobalamin), an essential component for the growth of many
 359 phytoplankton species (Okbami and Sañudo-Wilhelmy, 2004). Furthermore, high
 360 concentrations of dissolved B12 are generally found in shallow harbors and bays with limited
 361 flushing (Okbami and Sañudo-Wilhelmy, 2004), characteristics that should favor the
 362 accumulation of Co in Ensenada Harbor.

363 It is generally accepted that for the calculation of metal enrichments it is preferable to use
 364 regional pre-industrial background concentrations. However, since no such information was
 365 available for the study area, the values of Turekian and Wedepohl (1961) and Li and
 366 Schoonmaker (2005) for the average composition of shale were used instead. The enrichment
 367 factor (EF_{Me}) was simply calculated as:

368

$$369 \quad EF_{Me} = \left(\frac{(Me/Al)_{\text{sample}}}{(Me/Al)_{\text{shale}}} \right) \quad (1)$$

370

371 If $EF_{Me} > 1$, the metal concentration in the sample is enriched relative to the average shale values
 372 and, maybe, anthropogenically impacted. If $EF_{Me} < 1$, then the metal is impoverished relative to

373 the average shale values and, probably, subjected to a diagenetic process that reduces its
374 concentration in the sample. Finally, if $EF_{Me} = 1$, then the metal concentration has the same
375 value as the reference value (normalized with Al). The results of this exercise are shown in
376 Figure 7, where each core from Ensenada and El Sauzal harbors was plotted against the
377 corresponding EF_{Me} value. Values ranged from 0.41 (EF_{Cu} , core 5E) to 13 (EF_{Cu} , core 1E), and
378 from 0.36 (EF_{Ni} , core 4S) to 12 (EF_{Cd} , core 2S). Based on the EF_{Me} values, the elements were
379 arbitrarily divided into four groups: (1) those highly enriched ($EF_{Me} > 2.5$) in the harbor sediments,
380 represented solely by Cd (average EF_{Me} value of 10 ± 3); (2) those slightly enriched ($1.5 > EF_{Me} >$
381 2.5), represented by Zn, Co and Pb (average EF_{Me} values of 1.7 ± 0.9 , 2.1 ± 0.9 and 2.3 ± 0.5 ,
382 respectively); (3) those neither enriched nor impoverished ($0.6 > EF_{Me} > 1.5$), represented
383 (excluding core 1E) by Fe and Cu (average EF_{Me} values of 0.9 ± 0.2 and 1.2 ± 0.6 , respectively);
384 and (4) those slightly impoverished ($EF_{Me} < 0.6$), represented by Mn and Ni (average EF_{Me} values
385 of 0.50 ± 0.06 and 0.6 ± 0.3 , respectively).

386 The high EF_{Me} values of Cd may be a consequence of the Cd-enriched plankton (10 to 20
387 ppm; Martin and Broenkow, 1975) found in Baja California waters, which probably transfer this
388 element to the sediments after their death and subsequent sedimentation. Additional Cd
389 enrichment in the sediments can be produced by upwelling processes (Segovia-Zavala et al.,
390 1998; Muñoz-Barbosa et al., 2004), which are common off the northwest coast of Baja California
391 during spring and summer (Alvarez-Borrego and Alvarez-Borrego, 1982). The metals showing
392 slight enrichment were those generally associated with anthropogenic contamination (Pb, Zn), or
393 probably related to primary productivity and its relationship with vitamin B12, as was previously
394 discussed for Co. However, it is surprising that Cu was among the metals neither enriched nor
395 impoverished, since granular copper mine tailings were routinely employed to sandblast ships in
396 a dry dock facility located adjacent to Ensenada Harbor. It is highly probable that the high
397 enrichment value ($EF_{Cu} = 13$) obtained for core 1E (Figure 7) was due to the use of this
398 sandblasting tailing. Impoverishment of Mn and Ni can be the result of the slow kinetics of
399 precipitation of the former (Jørgensen and Boudreau, 2001), and the known association of the
400 latter with Mn oxides (Murray, 1975; Sclater et al., 1976; Balistrieri and Murray, 1986; Tessier et

401 al., 1996; Kay et al., 2001; Trivedi and Axe, 2001), at least for the case of Ensenada Harbor,
 402 where a significant correlation was found between these two elements (Tables 3 and 4). Hence,
 403 Ni is probably released into the interstitial water upon reductive dissolution of the Mn oxides and,
 404 most likely, diffuses towards the sediment-water interface and is lost to the water column together
 405 with the dissolved Mn.

406 The average ratios of the Ensenada:El Sauzal enrichment factors (defined as
 407 $EF_{Me(Ensenada)}/EF_{Me(El\ Sauzal)}$) ranged from 0.63 ± 0.48 for Zn to 2.9 ± 12.4 for Cu (Table 5).
 408 According to these results, only Zn and Cd concentrations were higher in El Sauzal Harbor,
 409 whereas the rest of the metals were more concentrated in Ensenada Harbor, especially Cu with
 410 a ratio of 2.9 ± 12.4 . However, if the anomalously high EF_{Me} results for some of the cores are
 411 removed from the calculation of the average ratio (e.g., Cd and Ni without core 0E and Cu without
 412 core 1E), then the values are very close to unity for most of the metals (Table 5). Since a value
 413 of 1.0 would indicate that total metal concentrations in the sediments of both harbors are equal,
 414 these results suggest that Zn is the only metal whose concentrations are generally higher in El
 415 Sauzal, while Co is higher in Ensenada (0.63 ± 0.48 and 1.7 ± 0.8 , respectively; Table 5).
 416 Furthermore, the EF_{Me} values calculated from reported concentrations of pristine (Strangford and
 417 Carlingford loughs; Charlesworth and Service, 2000) and anthropogenically impacted areas
 418 (Belfast Lough and PLOO; Charlesworth and Service, 2000; City of San Diego, 2005) were
 419 approximately equal or generally higher for Cu, Fe, Mn, Ni, Pb and Zn than the values measured
 420 for Ensenada and El Sauzal harbors (Figure 7).

421

422 3.6. Pollution Load Index

423

424 The pollution load index (PLI) for a given core or zone is calculated from the
 425 contamination factors (CF_{Me} = concentration in sediment/base value for that metal) of each of its
 426 constituent samples, according to the following equation (Tomlinson et al., 1980):

427

$$428 \quad PLI = (CF_{Cd} \times CF_{Co} \times CF_{Cu} \times CF_{Ni} \times CF_{Pb} \times CF_{Zn})^{1/6} \quad (2)$$

429

430 where the metal base value represents its average concentration in shale (Turekian and
 431 Wedepohl, 1961; Li and Schoonmaker, 2005). According to Tomlinson et al. (1980), PLI values
 432 of zero, one, or larger than one suggest absence of baseline pollutants, presence of them, or
 433 progressive deterioration of sediment quality, respectively. Figure 8 shows that for Ensenada
 434 Harbor, the core closer to the value of baseline pollutants (1.24) was 5E (at the harbor mouth),
 435 whereas the innermost core 1E had the highest PLI value (4.29). The other cores showed values
 436 between 1.97 and 2.89, with an overall value for the zone of 2.47 (“Ens” black bar in Figure 8).
 437 The PLI values calculated for El Sauzal Harbor suggest that this zone is appreciably less
 438 impacted by metal pollutants than Ensenada, ranging from 1.01 (core 1S at the harbor mouth) to
 439 1.99 (core 2S), with a zonal value of 1.51 (“Sauz” black bar in Figure 8), equivalent to 61% of the
 440 overall value for Ensenada Harbor. Hence, as a rule, the cores collected at both harbor mouths
 441 had the lowest PLI values, whereas the inner cores had the highest values.

442

443 3.7. Geoaccumulation index

444

445 The geoaccumulation index (I_{geo}), introduced by Müller (1981), has been used to
 446 quantitatively measure metal pollution in aquatic sediments (e.g., Santos Bermejo et al., 2003),
 447 based on a pollution intensity classification (I_{geo} class) that consists of 7 grades or classes (0 to 6,
 448 Table 6), the highest grade reflecting a 100-fold enrichment above baseline values. The I_{geo} can
 449 be calculated using the equation (Müller, 1979):

450

$$451 \quad I_{geo} = \log_2 \frac{[Me]_{studied\ area}}{1.5 [Me]_{baseline}} \quad (3)$$

452

453 where $[Me]_{baseline}$ represents the metal concentration in average shales taken from Turekian and
 454 Wedepohl (1961) and Li and Schoonmaker (2005), with a “1.5” factor included because of
 455 possible variations in the background data due to lithogenic effects (Salomons and Förstner,

456 1984). Results from this exercise indicated that 79.3% (Ensenada Harbor) and 86.1% (El Sauzal
457 Harbor) of the elements belonged to I_{geo} classes 0 and 1 (unpolluted to moderately polluted), with
458 only 6.3% (Ensenada Harbor only) positioned in I_{geo} class 4 (0% for El Sauzal Harbor; Table 6).
459 The only element that consistently ranked high in the I_{geo} classes (3 or 4), for both harbors and all
460 cores (except 0E), was Cd (Table 6). It is clear that Ensenada has more metals in the “polluted”
461 I_{geo} classes (2 to 6; Table 6) than El Sauzal (20.6% vs. 13.9%, respectively). None of the
462 analyzed elements were positioned in the last two, more polluted classes (5 and 6).

463

464 *3.8. Sediment quality guidelines*

465

466 Comparison of our total concentrations with the NOAA's sediment quality guidelines
467 (Long et al., 1995) can be used to evaluate the possible biological consequences of the levels of
468 metals in Ensenada and El Sauzal harbors. Long et al. (1995) matched biological and chemical
469 data compiled from numerous modeling, laboratory, and field studies performed in marine and
470 estuarine sediments. Using these data, effects range-low (ERL: lower 10th percentile of the
471 effects data) and range-median (ERM: the median, or 50th percentile, of the effects data)
472 guideline values were determined for a number of metals (Table 7: guideline values available only
473 for Cd, Cu, Ni, Pb and Zn). These two guideline values (ERL and ERM) delineate three
474 concentration ranges (<ERL, ERL-ERM, >ERM) for a particular metal. Hence, concentrations
475 below the ERL value will represent a minimal-effects range, a range intended to estimate
476 conditions in which biological effects would be rarely observed. Concentrations equal to and
477 above the ERL, but below the ERM, will represent a possible-effects range within which effects
478 would occasionally occur. Finally, concentrations equivalent to and above the ERM value will
479 represent a probable-effects range within which effects would frequently occur (Long et al., 1995).
480 Table 7 shows that there is a considerable difference between the two harbors in the allocation of
481 Cu, Ni and Pb levels among the different concentrations ranges. In El Sauzal Harbor (n = 74), Cu
482 was distributed between the <ERL (29.7%) and ERL-ERM (70.3%) ranges, whereas in Ensenada
483 Harbor (n = 147), it occurred between the <ERL (10.4%), ERL-ERM (75.3%) and >ERM (14.3%)

484 ranges (Table 7). In El Sauzal, Ni was also distributed between the <ERL and ERL-ERM ranges
485 (17.6 and 82.4%, respectively), whereas in Ensenada it was between the ERL-ERM and >ERM
486 ranges (47.8 and 52.2%, respectively) (Table 7). Finally, Pb was distributed only between the
487 first two concentration ranges in both harbors, though the proportion of this metal in the <ERL
488 range was only 14.3% in Ensenada Harbor, but 98.6% in El Sauzal Harbor (Table 7). The rest of
489 the metals (Cd and Zn) showed similar behaviors in their distribution ranges (Table 7).

490

491 **4. Conclusions**

492

493 Despite the high total metal concentrations measured in the sediments of Ensenada and
494 El Sauzal harbors, their Al-normalized values generally correspond to what would be expected
495 from their aluminosilicate content. Results from EF_{Me} , PLI, I_{geo} and effects range (Figures 7 and
496 8, and Tables 6 and 7, respectively) clearly demonstrate that the inner parts of both harbors
497 contain higher levels of metals relative to the outer parts (with cores 1E and 2S generally the
498 most enriched), and that Ensenada is the more trace metal-enriched harbor of the two. In terms
499 of particular elements, Cd ranked among the most enriched in both harbors (*e.g.*, Figure 7,
500 Tables 6 and 7); however, Cu and Ni in Ensenada and, to a much lesser extent, Zn in both
501 harbors, are the metals that can potentially cause adverse effects to local living resources.
502 Overall, PLI values for both harbors were reasonable (≤ 2.47), with an important percentage (79.3-
503 86.1%) of the analyzed metals belonging to I_{geo} classes 0 and 1 (unpolluted to moderately
504 polluted). Hence, despite the apparently high total trace element concentrations measured in
505 both Mexican harbors, the levels of most of the metals are not greatly enriched in these
506 sediments and do not represent a threat to the local biota, a consideration that is of the utmost
507 importance when contamination issues are at stake.

508

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510

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515

516

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665 **Figure legends**

666

667

668 **Figure 1.** Location of Ensenada and El Sauzal harbors. The circulation pattern shown in (b) was
669 taken from Peña-Manjarrez et al. (2005).

670

671 **Figure 2.** Profiles of total trace metal concentrations (on a dry weight basis), percentage of grain
672 size <62.5 μm (%GS) and organic carbon (org-C) for each of the seven cores collected in
673 Ensenada Harbor. Gray symbols represent concentrations below the detection limit.

674

675 **Figure 3.** Profiles of total trace metal concentrations (on a dry weight basis), percentage of grain
676 size <62.5 μm (%GS) and organic carbon (org-C) for each of the four cores collected in El Sauzal
677 Harbor.

678

679 **Figure 4.** Box plots of total trace metal concentrations, organic carbon (org-C) and percentage of
680 grain size <62.5 μm (%GS) for each one of the sediment cores collected in Ensenada and El
681 Sauzal harbors (open and gray boxes, respectively). Cd concentrations below the detection limit
682 in core 0E were not considered for the calculation of basic statistics. In this figure, the boundary
683 of the box closest to zero indicates the 25th percentile, a line within the box marks the median,
684 and the boundary of the box farthest from zero indicates the 75th percentile. Bars above and
685 below the box indicate the 90th and 10th percentiles, respectively.

686

687 **Figure 5.** Plots of percentage of grain size <62.5 μm (%GS) vs. metal concentration and organic
688 carbon (org-C) for sediment cores collected in Ensenada and El Sauzal harbors. Concentrations
689 (\pm one standard deviation) reported for Point Loma Ocean Outfall (PLOO; City of San Diego,
690 2005), Mazatlan Harbor (MH; Osuna-López et al., 1986), northern Irish coastal sediments (NICS;
691 Charlesworth and Service, 2000), Southern California Bight (SCB), Santa Monica Bay (SMB),

692 outfalls of publicly owned treatment works (POTWs) and stormwater areas (STW) (Schiff, 2000),
693 are also included for comparison purposes

694

695 **Figure 6.** Box plots and average values (\pm one standard deviation) of total metal (Me)
696 concentrations and Me/Al ratios for sediments collected in Ensenada and El Sauzal harbors.
697 Metals were arranged in increasing order of average values of Ensenada Harbor. Note the log
698 scales in the y-axes.

699

700 **Figure 7.** Enrichment factors, $EF_{Me} = (Me/Al)_{sample}/(Me/Al)_{shale}$, for each one of the sediment
701 cores collected in Ensenada (E) and El Sauzal (S) harbors (black and gray bars, respectively).
702 The average composition of shale was taken from Turekian and Wedepohl (1961) and Li and
703 Schoonmaker (2005). Concentrations (\pm one standard deviation) reported for Point Loma Ocean
704 Outfall (PLOO; City of San Diego, 2005), Belfast Lough (B), and Strangford and Carlingford
705 loughs (S&C) (Charlesworth and Service, 2000) are also included for comparison purposes.
706 Dashed lines represent the value of 1.0 [$(Me/Al)_{sample} = (Me/Al)_{shale}$]. Error bars for E and S
707 harbors were calculated by error propagation analysis.

708

709 **Figure 8.** Pollution load index for each one of the sediment cores (gray bars) and for Ensenada
710 (Ens) and El Sauzal (Sauz) areas (black bars). PLI values of zero, one (dashed line), or larger
711 than one suggest absence of baseline pollutant, presence of them, or progressive deterioration of
712 sediment quality, respectively.

Figure 1

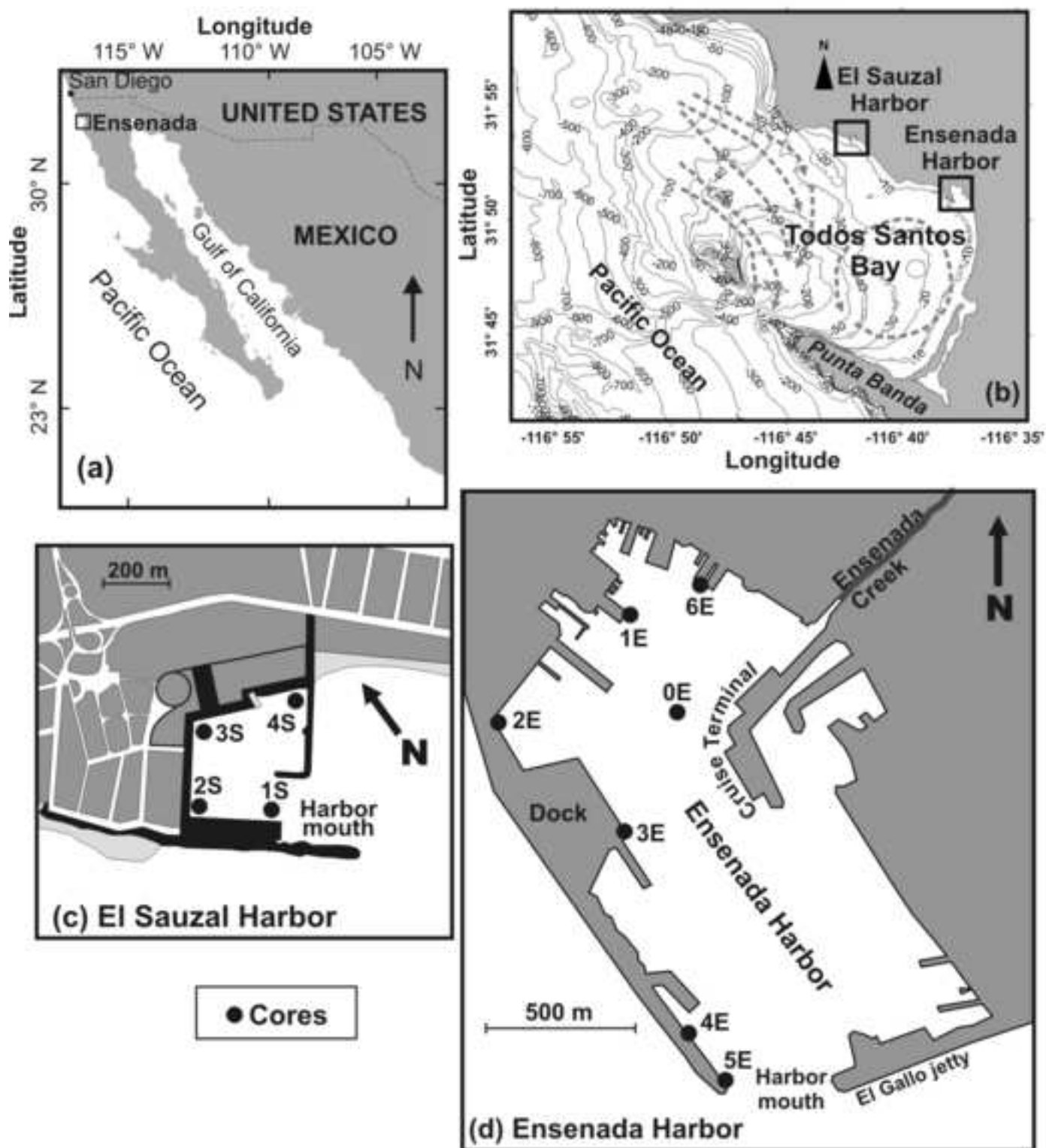


Figure 2a

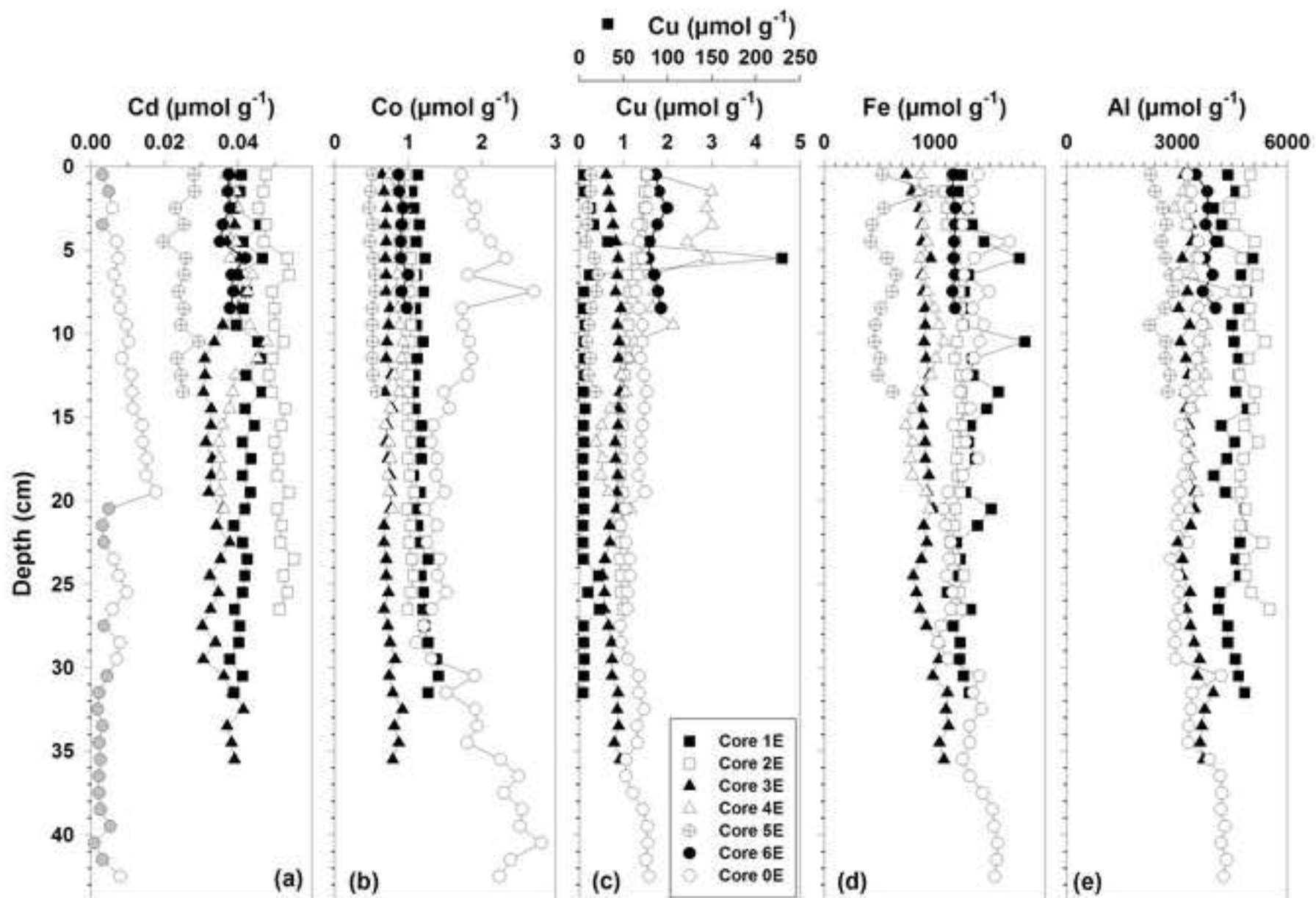


Figure 2b

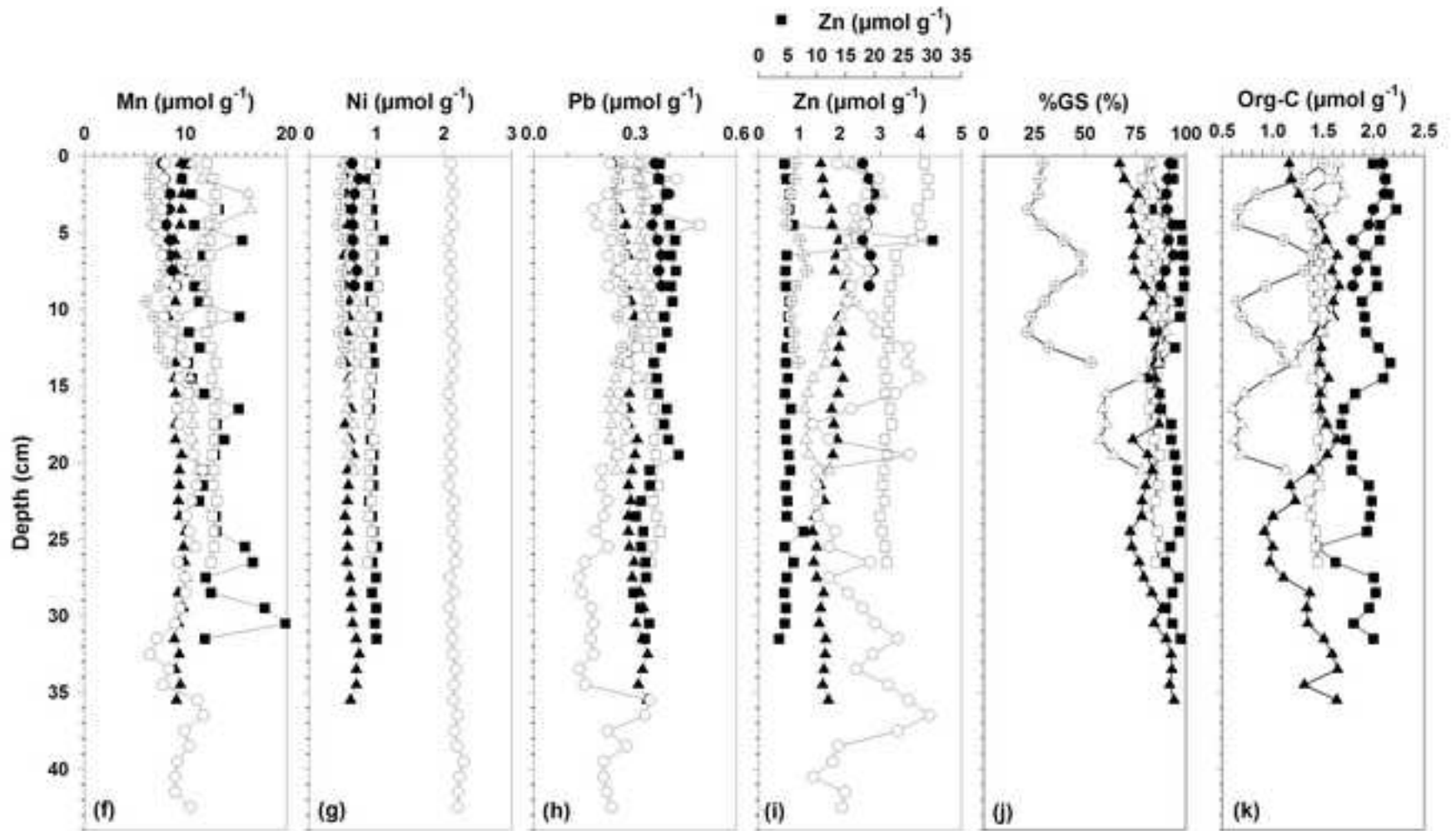


Figure 3a

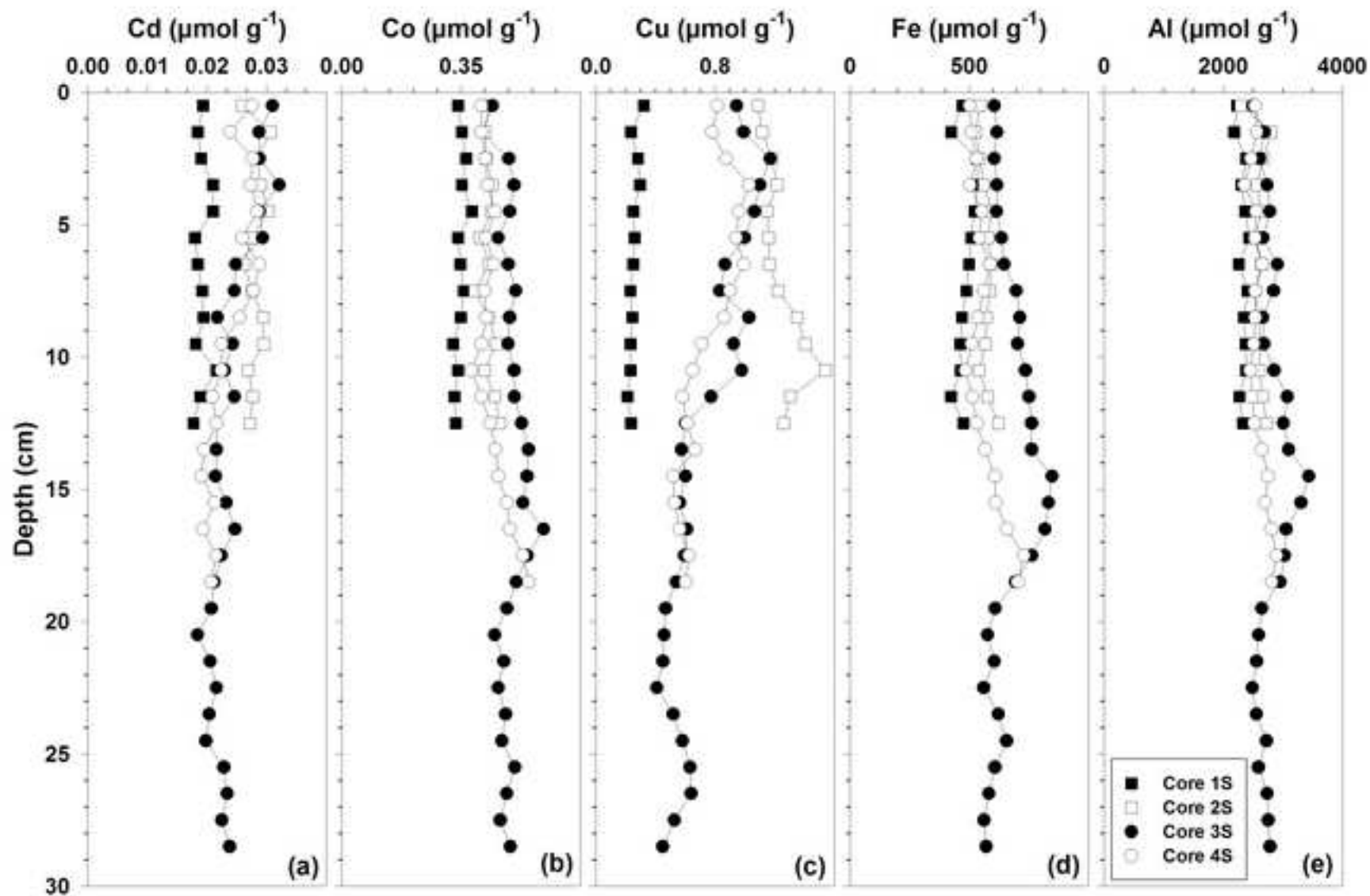


Figure 3b

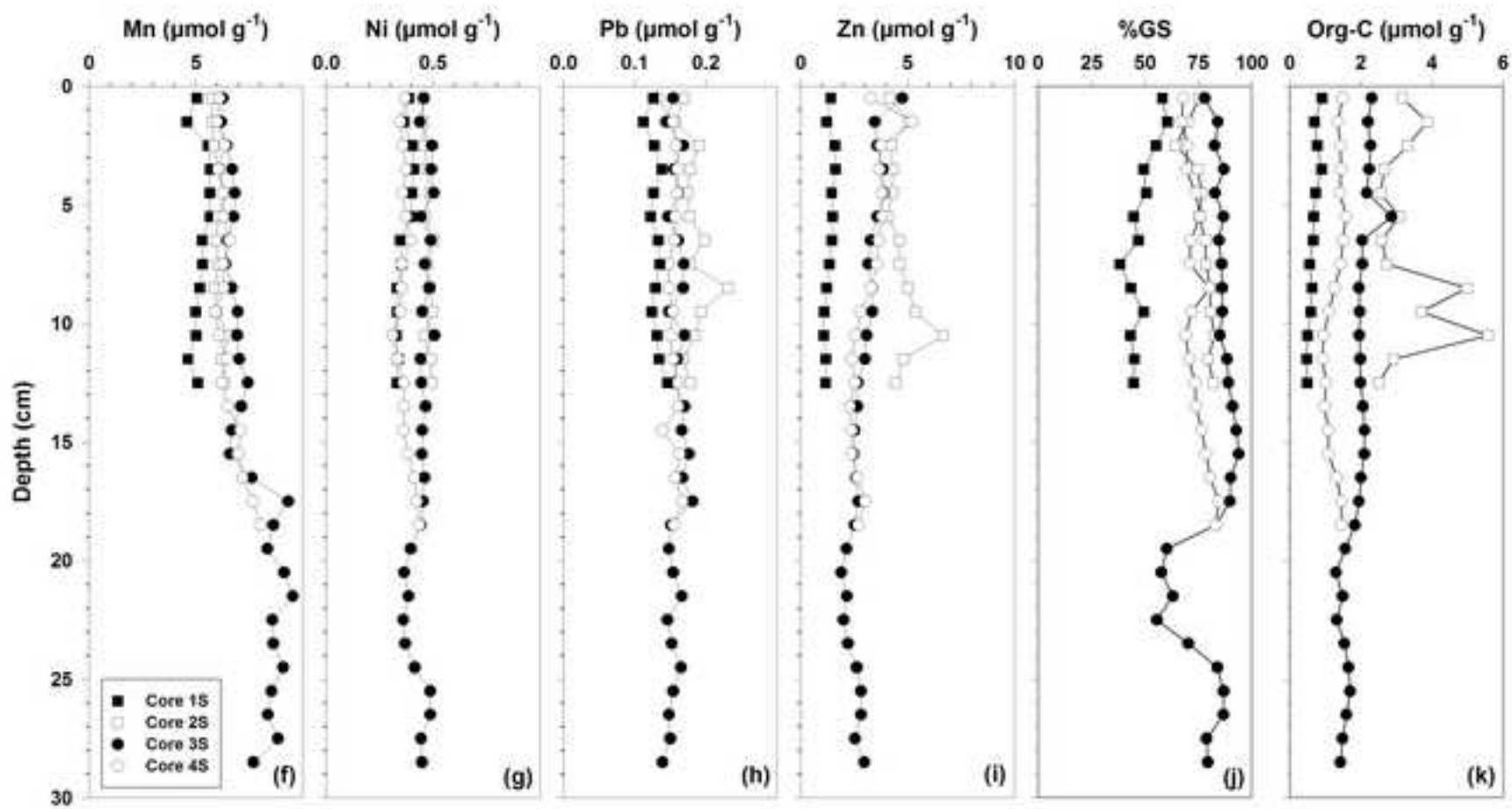


Figure 4

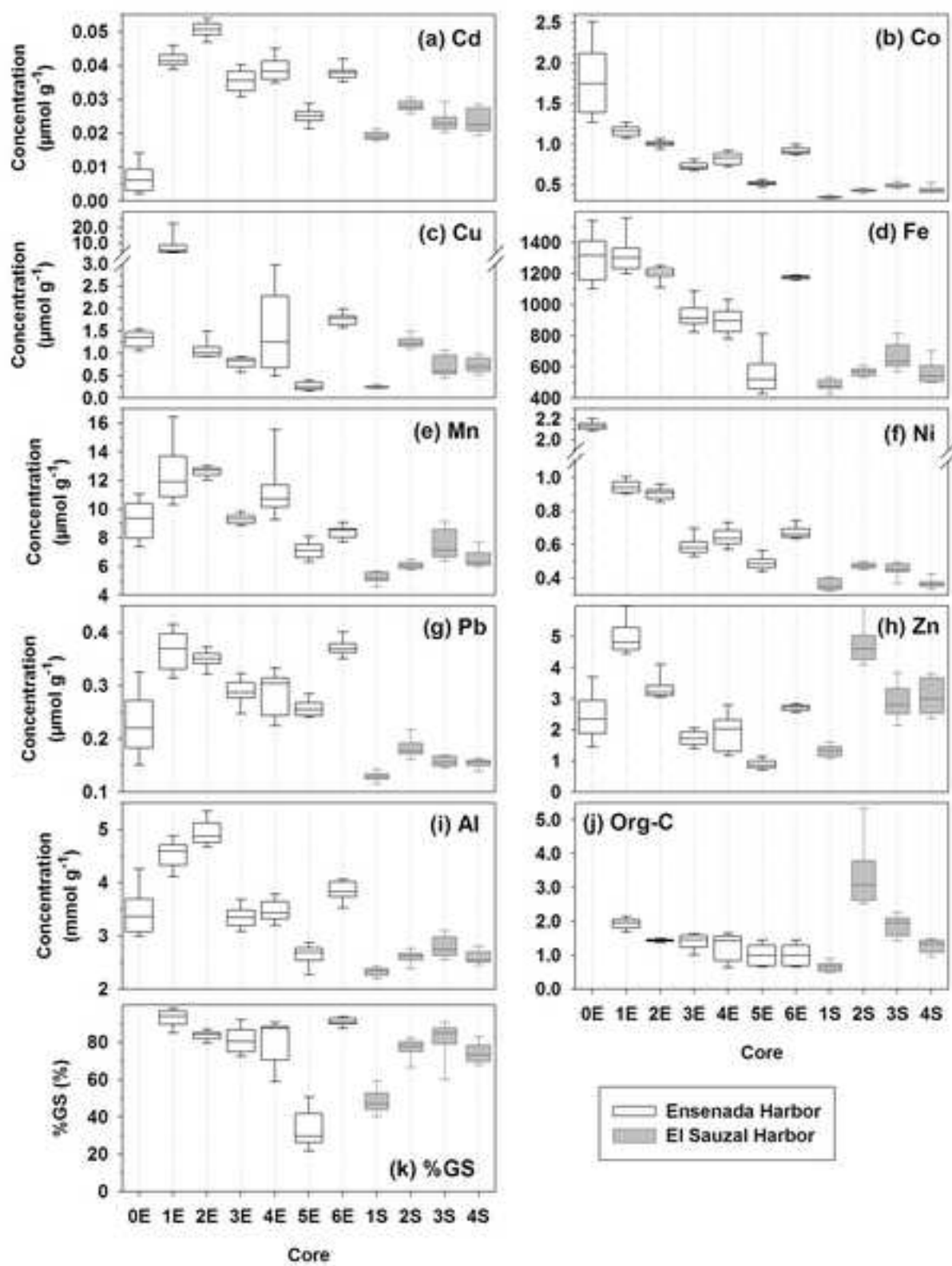


Figure 5

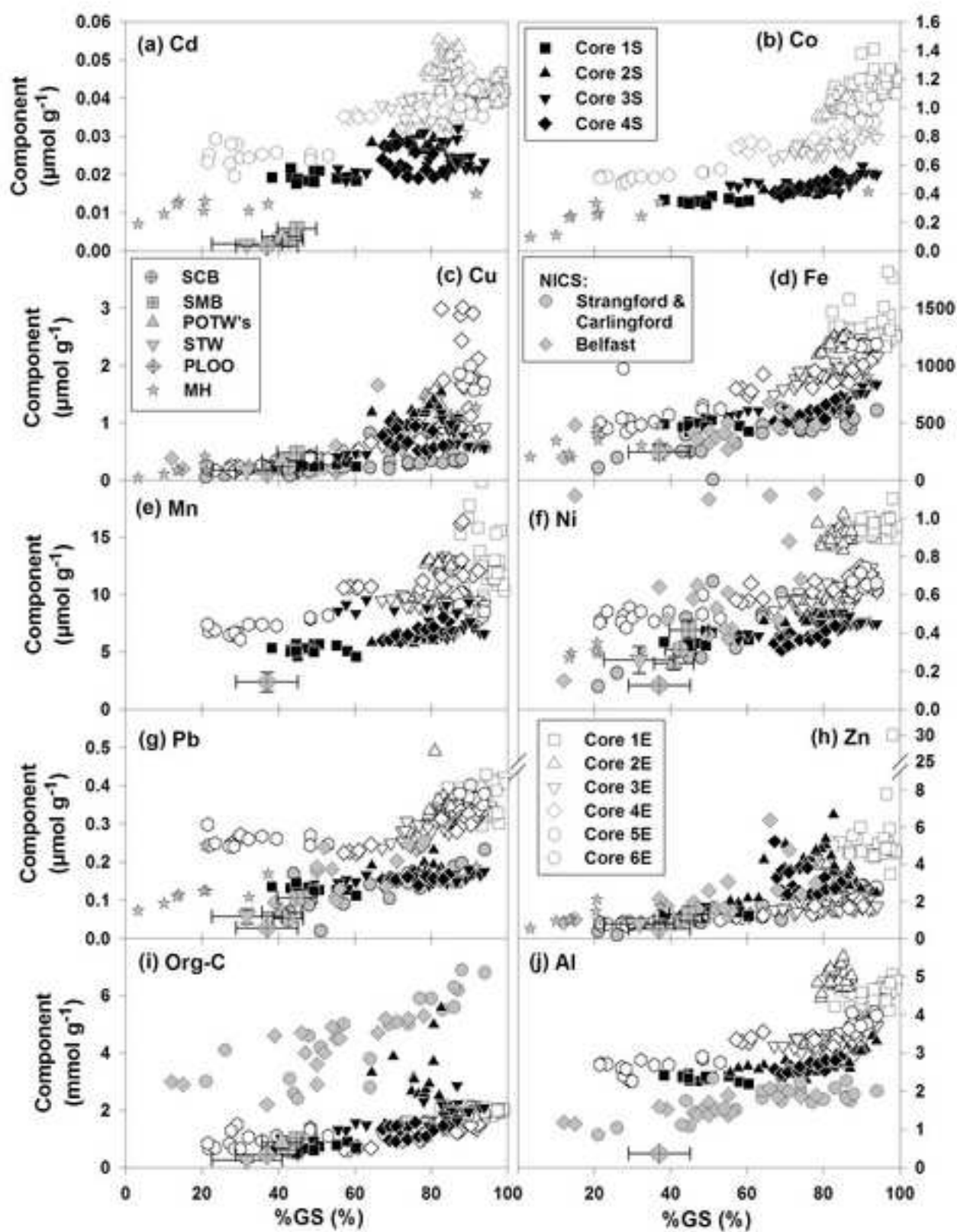


Figure 6

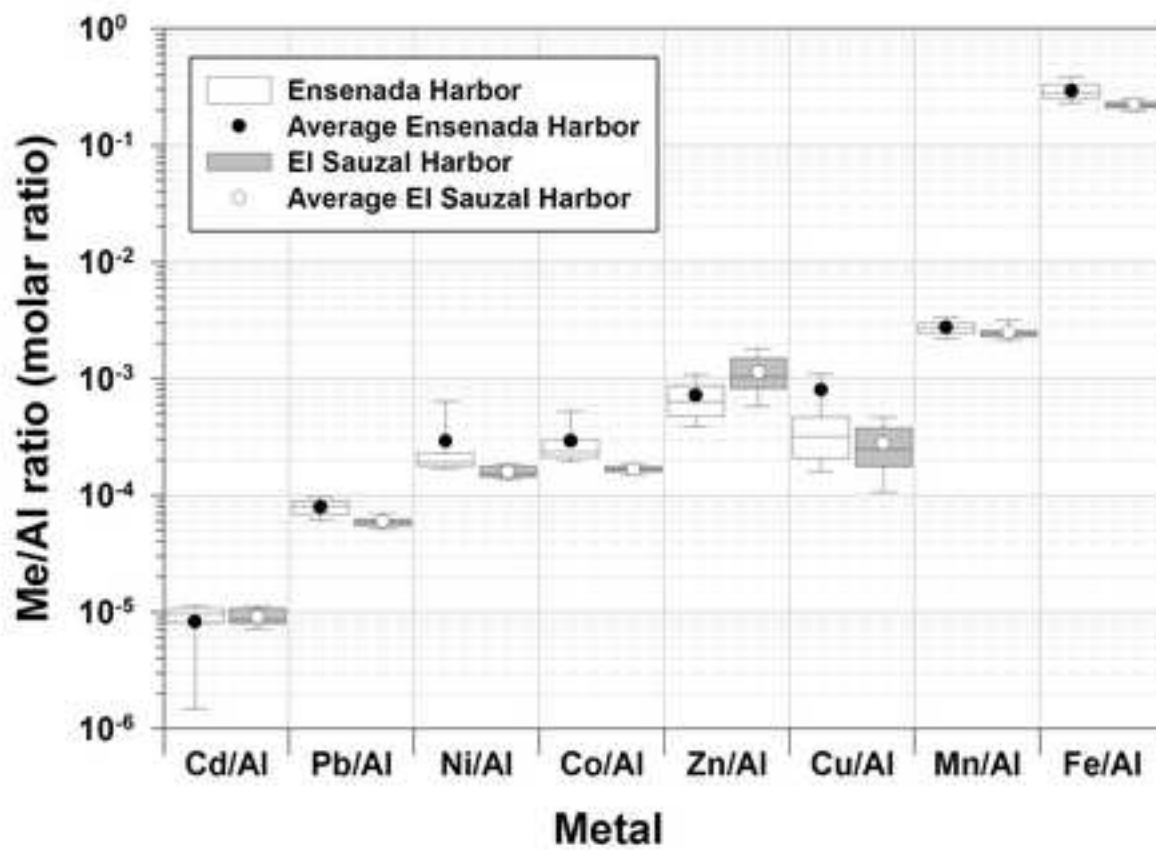


Figure 7

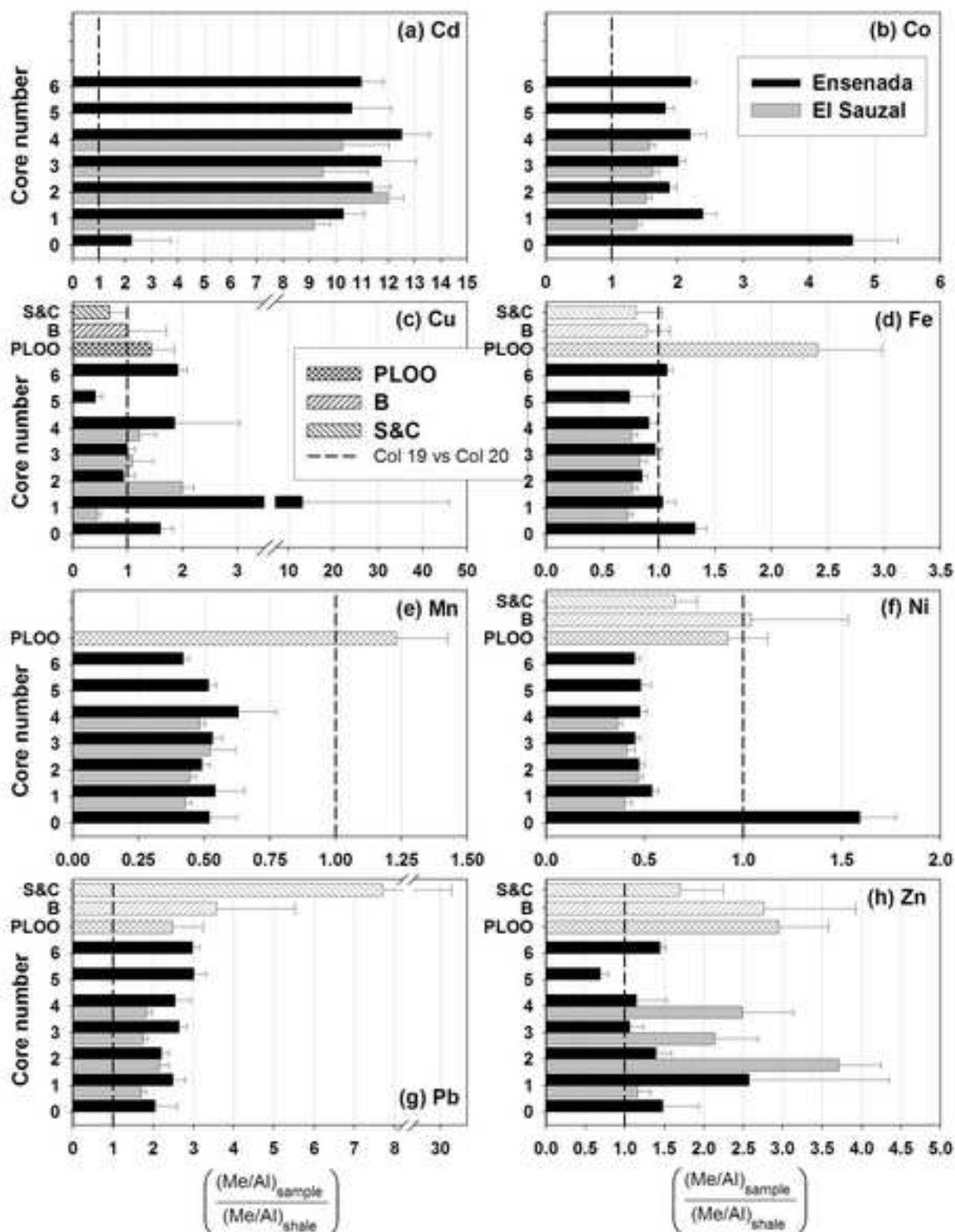


Figure 8

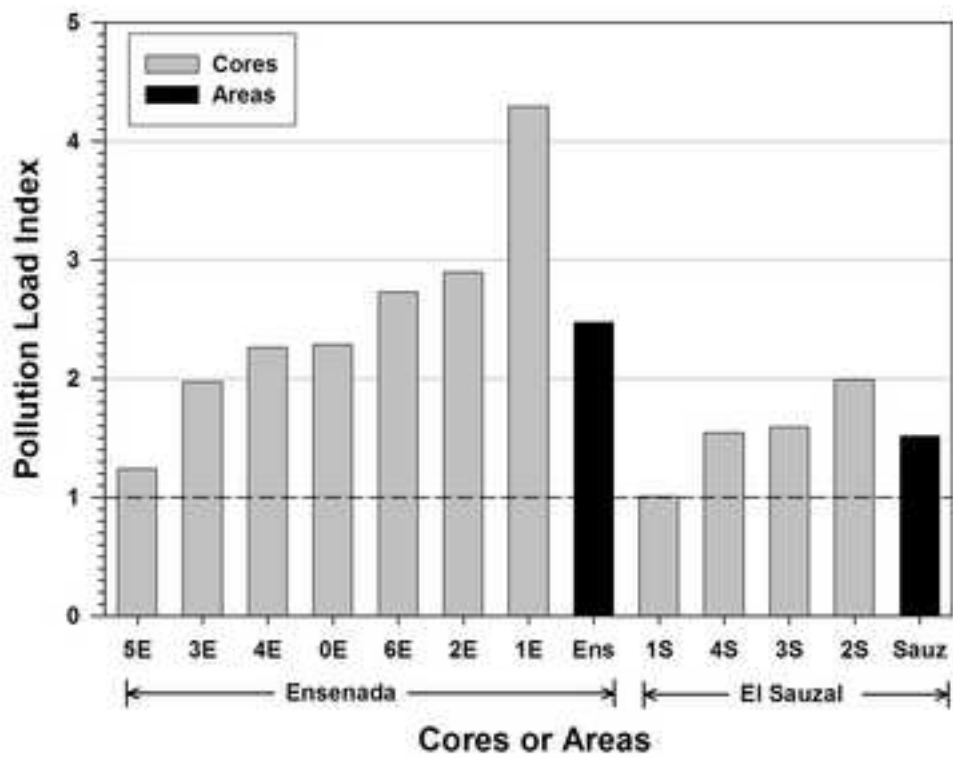


Table 1. Measured (n = 21) and certified concentrations (\pm two standard deviations), and percentages of recovery of Beaufort Chemistry Standard Sediment (BCSS-1; National Research Council of Canada).

Element	Measured concentration ($\mu\text{g g}^{-1}$)	Certified concentration ($\mu\text{g g}^{-1}$)	Percentage of recovery (%)
Al	$(6.5 \pm 1.0) \times 10^4$	$(6.3 \pm 0.2) \times 10^4$	103
Cd	0.23 ± 0.03	0.25 ± 0.04	90
Co	10.8 ± 0.2	11.4 ± 2.1	95
Cu	19.2 ± 0.7	18.5 ± 2.7	104
Fe	$(3.23 \pm 0.04) \times 10^4$	$(3.3 \pm 0.1) \times 10^4$	98
Mn	220 ± 10	229 ± 15	96
Ni	52.5 ± 0.3	55.3 ± 3.6	95
Pb	22.2 ± 1.8	22.7 ± 3.4	98
Zn	112 ± 5	119 ± 12	94

Table 2. Average total concentrations (Avg) and range of values for sediments from Ensenada (cores 0E to 6E) and El Sauzal (cores 1S to 4S) harbors. Numbers in parentheses refer to the number of samples. Cd concentrations below the detection limit in core 0E were not considered for the calculation of basic statistics.

	Al (mmol g ⁻¹)	Cd (nmol g ⁻¹)	Co (μmol g ⁻¹)	Cu (μmol g ⁻¹)	Fe (mmol g ⁻¹)	Mn (μmol g ⁻¹)	Ni (μmol g ⁻¹)	Pb (nmol g ⁻¹)	Zn (μmol g ⁻¹)
Avg 0E (43)	3.49 ± 0.47	6.8 ± 4.2	1.79 ± 0.45	1.32 ± 0.19	1.31 ± 0.16	9.3 ± 1.3	2.136 ± 0.046	231 ± 62	2.50 ± 0.78
Range 0E	2.84-4.56	<7.6-18	1.11-2.81	0.92-1.59	1.03-1.68	6.5-12	2.069-2.293	135-423	1.34-4.22
Avg 1E (32)	4.53 ± 0.28	41.8 ± 2.4	1.169 ± 0.085	15 ± 40	1.33 ± 0.16	12.7 ± 2.5	0.948 ± 0.044	366 ± 38	5.8 ± 4.5
Range 1E	3.99-5.07	37.7-46.6	1.052-1.411	4-229	1.11-1.82	10-20	0.892-1.10	295-429	3.5-30
Avg 2E (27)	4.94 ± 0.25	50.6 ± 2.5	1.006 ± 0.043	1.09 ± 0.21	1.200 ± 0.046	12.61 ± 0.35	0.907 ± 0.040	353 ± 32	3.36 ± 0.38
Range 2E	4.43-5.52	45.5-55.2	0.918-1.083	0.91-1.58	1.09-1.26	11.87-13.15	0.832-1.02	307-490	2.99-4.18
Avg 3E (36)	3.36 ± 0.22	35.3 ± 3.4	0.733 ± 0.059	0.79 ± 0.12	0.931 ± 0.089	9.28 ± 0.38	0.593 ± 0.054	288 ± 26	1.73 ± 0.23
Range 3E	3.00-3.99	30.2-41.4	0.637-0.919	0.53-0.94	0.742-0.126	8.27-10.0	0.518-0.744	233-337	1.33-2.17
Avg 4E (21)	3.46 ± 0.23	38.9 ± 3.7	0.823 ± 0.074	1.51 ± 0.90	0.900 ± 0.089	11.2 ± 1.9	0.645 ± 0.055	285 ± 40	1.92 ± 0.58
Range 4E	2.93-3.81	34.8-47.8	0.695-0.963	0.37-3.01	0.739-1.084	9.2-16.4	0.560-0.750	223-336	1.13-3.03
Avg 5E (14)	2.64 ± 0.20	25.0 ± 2.4	0.518 ± 0.028	0.262 ± 0.087	0.56 ± 0.14	7.12 ± 0.62	0.492 ± 0.042	257 ± 16	0.89 ± 0.14
Range 5E	2.26-2.90	19.6-29.3	0.470-0.574	0.148-0.418	0.42-0.97	6.14-8.19	0.428-0.600	241-298	0.70-1.2
Avg 6E (9)	3.84 ± 0.18	37.8 ± 2.0	0.918 ± 0.043	1.76 ± 0.13	1.175 ± 0.011	8.41 ± 0.41	0.671 ± 0.035	371 ± 14	2.72 ± 0.10
Range 6E	3.52-4.07	35.1-42.0	0.870-0.999	1.57-1.99	1.16-1.19	7.73-9.07	0.637-0.742	350-400	2.57-2.85
Overall Avg (182):	3.81 ± 0.75	32 ± 16	1.10 ± 0.48	3.5 ± 17.2	1.11 ± 0.26	10.4 ± 2.3	1.07 ± 0.62	299 ± 66	2.9 ± 2.4
Overall range:	2.26-5.52	<7.6-55	0.470-2.81	0.15-229	0.419-1.82	6.14-19.9	0.428-2.29	135-490	0.70-30
Avg 1S (13)	2.33 ± 0.08	19.2 ± 1.2	0.348 ± 0.015	0.251 ± 0.031	0.483 ± 0.036	5.21 ± 0.37	0.363 ± 0.032	129.5 ± 8.5	1.33 ± 0.19
Range 1S	2.18-2.44	17.7-21.6	0.327-0.382	0.210-0.320	0.423-0.536	4.58-5.68	0.327-0.411	112-146	1.08-1.62
Avg 2S (13)	2.61 ± 0.12	28.2 ± 1.5	0.431 ± 0.020	1.24 ± 0.13	0.570 ± 0.026	6.06 ± 0.24	0.476 ± 0.017	183 ± 18	4.75 ± 0.70
Range 2S	2.30-2.81	25.9-30.6	0.390-0.463	1.09-1.54	0.527-0.622	5.75-6.53	0.453-0.504	156-231	4.07-6.66
Avg 3S (29)	2.81 ± 0.24	23.8 ± 3.5	0.495 ± 0.037	0.72 ± 0.23	0.668 ± 0.085	7.6 ± 1.1	0.448 ± 0.041	158 ± 10	2.92 ± 0.64
Range 3S	2.49-3.44	18.4-32.1	0.409-0.592	0.41-1.2	0.561-0.848	6.2-9.6	0.361-0.507	139-181	1.90-4.75
Avg 4S (19)	2.60 ± 0.14	23.8 ± 3.4	0.444 ± 0.044	0.75 ± 0.17	0.565 ± 0.069	6.55 ± 0.59	0.370 ± 0.031	154 ± 82	3.15 ± 0.75
Range 4S	2.36-2.90	19.1-28.8	0.380-0.549	0.52-1.0	0.485-0.729	5.91-8.04	0.310-0.437	133-167	2.30-5.23
Overall Avg (74):	2.64 ± 0.24	23.8 ± 3.9	0.445 ± 0.062	0.74 ± 0.34	0.592 ± 0.095	6.6 ± 1.2	0.418 ± 0.057	157 ± 19	3.0 ± 1.2
Overall range:	2.18-3.44	17.7-32.1	0.327-0.592	0.21-1.5	0.423-0.848	4.6-9.6	0.310-0.507	112-231	1.1-6.7

Table 3. Pearson correlation matrix for the sedimentary geochemical data from Ensenada and El Sauzal harbors. Core 0E was not included in the analysis because the percentage of grain size <62.5 μm (%GS) and organic carbon (org-C) were not available. Cu and Zn concentrations at 5.5 cm depth in core 1E were also not considered because they represent outliers.

	Al	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn	%GS
El Sauzal Harbor (n = 70)										
Cd	0.14									
Co	0.85***	0.19								
Cu	0.20	0.87***	0.26							
Fe	0.90***	0.08	0.89***	0.17						
Mn	0.51***	-0.10	0.72***	-0.04	0.56***					
Ni	0.53***	0.53***	0.57***	0.63***	0.57***	0.24				
Pb	0.43***	0.52***	0.47***	0.74***	0.43***	0.21	0.61***			
Zn	0.21	0.84***	0.25	0.94***	0.14	0.00	0.57***	0.70***		
%GS	0.76***	0.45	0.83***	0.57***	0.77***	0.46***	0.68***	0.59***	0.55***	
Org-C	0.32	0.69***	0.31	0.84***	0.28	0.07	0.70***	0.77***	0.84***	0.54***
Ensenada Harbor (n = 120)										
Cd	0.85***									
Co	0.84***	0.71***								
Cu	0.31***	0.16	0.56***							
Fe	0.84***	0.74***	0.88***	0.46***						
Mn	0.66***	0.63***	0.77***	0.44***	0.60***					
Ni	0.92***	0.77***	0.93***	0.50***	0.86***	0.73***				
Pb	0.72***	0.60***	0.73***	0.36***	0.79***	0.43***	0.73***			
Zn	0.75***	0.57***	0.89***	0.74***	0.82***	0.67***	0.87***	0.72***		
%GS	0.63***	0.61***	0.75***	0.35***	0.79***	0.53***	0.62***	0.63***	0.62***	
Org-C	0.49***	0.37***	0.69***	0.50***	0.74***	0.30***	0.58***	0.69***	0.72***	0.71***

*** $p \leq 0.001$

Table 4. Results of PCA applied to sedimentary geochemical data gathered at Ensenada and El Sauzal harbors. Core 0E was not included in this analysis because the percentage of grain size <62.5 μm (%GS) and organic carbon (org-C) were not available. Cu and Zn concentrations at 5.5 cm depth in core 1E were also not considered because they represent outliers.

Harbor	Component	Eigenvalues	Explained variance (%)	Accumulated Variance (%)
Ensenada	1	5.40	49.1	49.1
Ensenada	2	3.39	30.8	79.9
El Sauzal	1	4.80	43.6	43.6
El Sauzal	2	4.16	37.8	81.4

Component loadings				
Geochemical factor	El Sauzal Harbor		Ensenada Harbor	
	PC1	PC2	PC1	PC2
Al	0.17	0.90	0.92	0.25
Cd	0.89	-0.03	0.94	0.04
Co	0.20	0.95	0.77	0.58
Cu	0.97	0.06	0.07	0.87
Fe	0.13	0.94	0.77	0.53
Mn	-0.11	0.76	0.71	0.28
Ni	0.66	0.50	0.83	0.45
Pb	0.75	0.36	0.64	0.50
Zn	0.95	0.05	0.58	0.75
%GS	0.52	0.76	0.63	0.48
Org-C	0.89	0.18	0.35	0.78

Table 5. Average ratios of Ensenada (n = 182) to El Sauzal (n = 74) enrichment factors ($EF_{Me(Ensenada)}/EF_{Me(El\ Sauzal)}$) for the different elements analyzed. The associated errors were calculated by error propagation analysis. For the special case of Cd, Ni and Cu, results are presented with and without some of the cores that showed anomalously elevated EF_{Me} values.

Element	$EF_{Me(Ensenada)}/EF_{Me(El\ Sauzal)}$ (molar ratio)	Propagated error
Zn	0.63	0.48
Cd	0.91	0.43
Cd (without core 0E)	1.1	0.2
Mn	1.1	0.3
Fe	1.3	0.3
Pb	1.3	0.3
Co	1.7	0.8
Ni	1.8	1.2
Ni (without core 0E)	1.2	0.2
Cu	2.9	12.4
Cu (without core 1E)	1.1	0.8

Table 6. Metals distributed according to their geoaccumulation index (I_{geo}). The I_{geo} classes (in parentheses) consist of 7 grades of pollution intensity (Santos Bermejo et al., 2003): 0 = unpolluted, 1 = unpolluted to moderately polluted, 2 = moderately polluted, 3 = moderately to strongly polluted, 4 = strongly polluted, 5 = strongly to very strongly polluted, and 6 = very strongly polluted.

Core	I_{geo} (I_{geo} class)						
	< 0 (0)	0-1 (1)	1-2 (2)	2-3 (3)	3-4 (4)	4-5 (5)	>5 (6)
0E	Al,Mn	Fe,Zn,Cu,Ni,Cd,Pb	Co	----	----	----	----
1E	Mn,Ni	Al,Fe	Co,Pb,Zn	Cu	Cd	----	----
2E	Mn,Ni,Fe	Cu,Al,Zn	Co,Pb	----	Cd	----	----
3E	Ni,Mn,Cu,Fe,Al,Zn	Co,Pb	----	----	Cd	----	----
4E	Ni,Mn,Fe,Al,Zn	Cu,Co,Pb	----	----	Cd	----	----
5E	Cu,Ni,Mn,Zn,Fe,Al	Co,Pb	----	Cd	----	----	----
6E	Mn,Ni,Cu,Fe,Zn,Al	Co,Pb	----	Cd	----	----	----
CP*	47.6 [30]	31.7 [20]	9.5 [6]	4.8 [3]	6.3 [4]	0	0
1S	Ni,Mn,Cu,Fe,Al,Zn,Co,Pb	----	----	Cd	----	----	----
2S	Mn,Ni,Fe,Al,Co	Cu,Pb	Zn	Cd	----	----	----
3S	Ni,Mn,Fe,Al,Cu	Co,Pb,Zn	----	Cd	----	----	----
4S	Ni,Mn,Fe,Al,Cu,Co	Pb,Zn	----	Cd	----	----	----
CP*	66.7 [24]	19.4 [7]	2.8 [1]	11.1 [4]	0	0	0
OP**	54.5 [54]	27.3 [27]	7.1 [7]	7.1 [7]	4.0 [4]	0	0

*Percentage for each I_{geo} class [number of metals]. **Overall percentage for each I_{geo} class [number of metals].

Table 7. Effects range-low (ERL) and range-median (ERM) guideline values for trace metals (on a dry weight basis) and percent incidence of sediment concentration values in concentration ranges defined by the two guideline values.

Harbor	Element	ERL ($\mu\text{mol/g}$)	ERM ($\mu\text{mol/g}$)	Percent (ratios) incidence for each concentration range ^b		
		Guidelines ^a		<ERL	ERL-ERM	>ERM
Ensenada	Cd	0.011	0.085	19.2 (35/182)	80.8 (147/182)	0.0 (0/182)
El Sauzal	Cd	0.011	0.085	0.0 (0/74)	100 (74/74)	0.0 (0/74)
Ensenada	Cu	0.54	4.25	10.4 (19/182)	75.3 (137/182)	14.3 (26/182)
El Sauzal	Cu	0.54	4.25	29.7 (22/74)	70.3 (52/74)	0.0 (0/74)
Ensenada	Ni	0.225	1.05	0.0 (0/182)	47.8 (87/182)	52.2 (95/182)
El Sauzal	Ni	0.225	1.05	17.6 (13/74)	82.4 (61/74)	0.0 (0/74)
Ensenada	Pb	0.356	0.879	14.3 (26/182)	85.7 (156/182)	0.0 (0/182)
El Sauzal	Pb	0.356	0.879	98.6 (73/74)	1.4 (1/74)	0.0 (0/74)
Ensenada	Zn	2.29	6.27	47.3 (86/182)	51.6 (94/182)	1.1 (2/182)
El Sauzal	Zn	2.29	6.27	24.3 (18/74)	74.3 (55/74)	1.4 (1/74)

^aTaken from Long et al. (1995); ^bPercentage and number of data entries within each concentration range divided by the total number of entries for all ranges.