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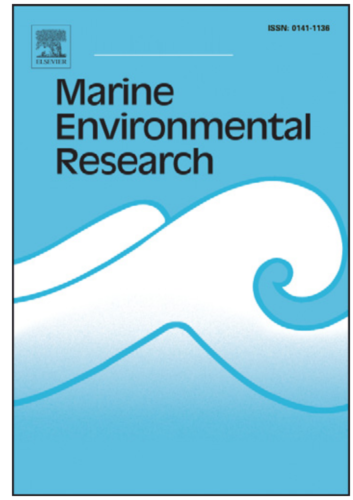
Accepted Manuscript



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PII: S0141-1136(08)00162-1
DOI: 10.1016/j.marenvres.2008.05.008
Reference: MERE 3260

To appear in: *Marine Environmental Research*

Received Date: 8 May 2007
Revised Date: 1 May 2008
Accepted Date: 15 May 2008

Please cite this article as: Huerta-Diaz, M.A., Delgadillo-Hinojosa, F., Hernández-Ayón, M., Segovia-Zavala, J.A., García-Esquivel, Z., López-Zárate, H., Siqueiros-Valencia, A., Galindo-Bect, S., Diagnosis of trace metal contamination in sediments: the example of Ensenada and El Sauzal, two harbors in Baja California, Mexico, *Marine Environmental Research* (2008), doi: 10.1016/j.marenvres.2008.05.008

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

by

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Abstract

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

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

1. **Introduction**

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

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

In this paper we will try to answer the following specific questions: Are sediments from Ensenada and El Sauzal harbors enriched in trace metals (Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn)? If so, to what extent and with which metals? Which harbor presents the highest metal enrichments? If present, are these trace metal enrichments anthropogenically derived? To answer these questions, trace element levels (normalized with Al) will be compared with those reported for other sediments from the Southern California Bight and with average shale values of sedimentary rocks to evaluate the extent of anthropogenic perturbations in the sediments of these two important Mexican harbors. Additionally, pollution load indexes (Tomlinson et al., 1980; Angulo, 1996) and geoaccumulation indexes (Müller, 1979) will be calculated for both harbors. Finally, total concentrations will be compared with the U.S. NOAA's sediment quality guidelines (as proposed by Long et al., 1995) to estimate the possible consequences of the metal levels analyzed in this study to the local biota. Because of the absence of similar studies in the region, this paper will also provide baseline data for future research on anthropogenic impacts in the region.

2. Materials and methods

2.1. Study area

Ensenada and El Sauzal harbors are situated in Todos Santos Bay, which is located in the northwestern part of the Baja California Peninsula, Mexico (Figure 1a), 100 km south of the US-Mexico border (31º 40’, 31º 56’ N; 116º 36’, 116º 50’ W). This 240-km^2 bay is limited to the south by Punta Banda, to the north by Punta San Miguel, to the southwest by two small islands located near the mouth of the bay, and to the northeast by the city of Ensenada (around 400,000 inhabitants). According to Pavía (2004), the climate of the region is Mediterranean, with scarce rainfall (annual average of 250 mm) that occurs mainly during the winter (average of 200 mm). The regional surface circulation pattern is produced by a predominant northwest component of the wind and surface currents have been reported to average 15 cm s^{-1} and 5 cm s^{-1} during summer and winter, respectively (Alvarez-Sánchez et al., 1988). This wind-driven circulation pattern promotes the transport of water from the adjacent Pacific Ocean towards the inner bay, generating a cell circulation system (dotted arrows; Figure 1b). Part of this flow is directed toward Ensenada harbor and the other part toward Punta Banda, in the southwestern part of the bay

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

Ensenada Harbor, an international marine terminal, was built in 1956 and covers an area of 1.95 km^2 (i.e., approximately 13 times bigger than El Sauzal Harbor). The mouth of the harbor is formed by a 1,640-m-long rock breakwater that is connected to the coast and by a 855-m-long jetty (El Gallo; Figure 1d). Water depths range from 1.5 to 11 m, with the deepest parts located adjacent to the loading and terminal docks and the main navigation channel. In addition to the presence of fine-grained sediments (approximately 80% <62.5 μm), this harbor tends to accumulate metals due to inputs from (a) a wholesale fish market, (b) marine vessels normally docked in the port and marina areas, (c) urban runoff discharged through Arroyo Ensenada (Figure 1d) during the winter rains, and (d) vessel reparation and maintenance activities (liberation of antifouling paint, sand blasting operations) within the port zone.

El Sauzal Harbor, built in the mid-1980s and located 10 km north of Ensenada in the town of El Sauzal de Rodriguez (approximately 7,500 inhabitants), has an area of 0.15 km^2 (Flores-Vidal et al., 2005) and a 100-m-wide mouth formed by two breakwaters that are 500 m and 250 m long (Figure 1c). Water depths range from 1 to 9 m, with maximum depth occurring in the main navigation channel (Flores-Vidal et al., 2005). Inputs to this harbor are essentially from fishery companies dedicated to extraction, processing and production activities, as well as from blood and organic wastes discharged by docked fishing boats, and from the powder generated during the unloading of cement from large boats or vessels.

2.2. Field and laboratory methods

Sediment samples from Ensenada Harbor were obtained from one core (core 0E) collected at approximately 6 m water depth on November 2, 1998 (Carreón-Martínez et al., 2001). This core was collected within the dredged channel, close to Arroyo Ensenada and in front of the cruise terminal, which was still not constructed at that time. Six more cores (cores 1E to 6E) were collected on January 8, 2002 at water depths of approximately 9 m (Figure 1d) and beneath the docks, considered the areas least affected by sediment resuspension and dredging. Sediments had a hydrogen sulfide smell, were black along the length of the cores and did not show any oxidized portion close to the sediment-water interface. Cores from El Sauzal Harbor were collected on September 29, 2004 (cores 1S to 4S) at water depths ranging from 6 to 9 m (Figure 1c). A polycarbonate plastic core liner (7.2 cm internal diameter, 60 cm in length) was introduced into the sediment, retrieved and capped underwater by a diver who transferred it to a boat. Once on board, the core liner was capped with a plastic cap, sealed with electrical tape and transported to shore, where it was extruded and sliced every 1 cm with a plastic spatula. Each section was then transferred to a 50-mL centrifuge polypropylene tube and stored at –20ºC for further laboratory analysis. Only core 0E was sliced in a glove bag under nitrogen atmosphere to avoid precipitation of the reduced Fe and Mn dissolved in the anoxic portion of the interstitial water. The 10-13 cm sediment depths of core 2S consisted almost entirely of fish scales.

All laboratory materials were washed with phosphate-free soap, rinsed three times with distilled water and left for 24 hours in a 5% HCl solution. The material was then rinsed three times with deionized water (Milli-Q grade) and left semi-closed to dry at room temperature. Total metal concentrations were obtained after complete digestion of 0.5 g of sediment in Teflon beakers with concentrated HNO_3, $HClO_4$ and HF (Carignan and Tessier, 1988). Trace metal concentrations were measured by atomic absorption spectrometry (Thermo Jarrel Ash model Smith Hieftje 12 or Varian model SpectrAA 220 Fast Sequential). Certified Reference Material (CRM) Beaufort Chemistry Standard Sediment (BCSS-1; National Research Council of Canada) was used to ascertain the accuracy and precision of the total extraction procedure. Recovery percentages of the BCSS-1 CRM ranged from 90% for Cd to 104% for Cu (Table 1). Blanks were routinely run and analyzed in the same manner as the samples. Limits of detection for the different trace metals, calculated as three times the standard deviation of the procedural blanks, were (in µmol g^{-1}): 2.4 (Al), 0.0076 (Cd), 0.026 (Co), 0.024 (Cu), 0.014 (Fe), 0.0047 (Mn), 0.11 (Ni), 0.035 (Pb), 0.013 (Zn). In this paper, and for practical purposes, all metals associated with sediments will be designated as trace metals, regardless of their concentration level. Percentage of sediment grain size <62.5 µm (%GS) was measured using a Horiba laser scattering particle size distribution analyzer model LA-910, with size interval of 0.02-1000 µm. The analytical efficiency of the particle analyzer was determined with 0.9-µm sieved polystyrene spheres (CRM NIST 8010D and NIST 1690). Organic carbon (org-C) concentrations in the sediments were estimated using the loss on ignition (LOI) method (550°C for 5 h). These measurements were transformed to org-C concentrations through a calibration curve (org-C % = (0.206 ± 0.010)*LOI; $r^2 = 0.929$, $p<0.001$, $n = 33$) using org-C values from Todos Santos Bay sediments measured by a LECO model CHNS-932 elemental analyzer. Due to the lack of available samples, org-C and grain size were not measured in core 0E.

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

3. Results and discussion

3.1. Trace metal distributions

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

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

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

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

Figure 4 shows that total concentrations of Cd, Co, Fe, Mn, Ni and Pb are generally lower in El Sauzal Harbor than in Ensenada Harbor. These results probably cannot be ascribed to differences in org-C concentrations for Ensenada (1.50 ± 0.38 mmol g^{-1}; n = 139) and El Sauzal (1.78 ± 0.97 mmol g^{-1}; n = 74) harbors, since statistically both have similar average org-C levels (p = 0.142, Mann-Whitney rank sum test). The metal concentration results may suggest that Ensenada Harbor, which is approximately 30 years older than El Sauzal Harbor, tentatively has had more time to accumulate trace metal contaminants in its sediments. Alternatively, the sediments of both harbors may have, on average, different particulate sizes. A Mann-Whitney rank sum test of the %GS indicated that the average fraction <62.5 µm from Ensenada Harbor (80 ± 18%, n = 182) was significantly higher ($p \leq 0.001$) than the one measured for El Sauzal (73 ± 14%, n = 74). The differences in %GS distribution between the two harbors are also noticeable in Figure 5, in which plots of metal concentrations versus %GS are displayed. This figure shows that the sediments from El Sauzal (closed symbols) form distinctly different groups for Co, Fe, Ni, Mn, Pb and Cd, which tend to cluster in the lower portion of the concentration range and generally below the concentrations measured in Ensenada Harbor (open symbols). One of the most important factors controlling the natural distribution of trace metals in sediments is the variation in grain size (Cauwet, 1987; Grant, 1990; Ergin, 1995; Lin et al., 2002). It is widely accepted that metals are enriched in the fine (<62.5 µm) fraction of sediments (Gibbs, 1977; Helmke et al., 1977; de Groot et al., 1982; Förstner, 1982; Cauwet, 1987; Horowitz et al., 1989; Zhang et al., 2002) and that metals exhibit positive linear correlations with the fine-grained sizes (de Groot et al., 1982; Ackermann et al., 1983; Ergin, 1995; Meador et al., 1998; Charlesworth and Service, 2000; Zhang et al., 2002). Although grain size analysis is not suitable for differentiating natural baseline versus anthropogenic enrichments of trace elements, such an analysis may help to account for the natural diluting effect of sand.

3.2. Trace metals and grain size

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

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

follow the same trends as the ones observed for Ensenada and El Sauzal harbors (Figures 5c,f,h). Only Cd and Pb (Figures 5a, g) exhibited a differential behavior, with average SCB concentrations well below the ones observed for Ensenada and El Sauzal sediments (Co, Fe and Mn were not measured by Schiff, 2000). Similar results (Figure 5) were obtained for the average values of Santa Monica Bay (SMB, 457.4 km^2), outfalls of publicly owned treatment works (POTWs, 292.8 km^2) and stormwater areas (STW, 81.1 km^2), the latter located within 3 km of the 11 largest river and creek mouths draining directly into the SCB (Schiff, 2000). Pristine sediments from Strangford and Carlingford loughs (Charlesworth and Service, 2000), as well as from anthropogenically impacted regions of Mexico (Mazatlan Harbor: contaminated with oil, sewage and industrial discharges; Osuna-López et al., 1986) and Europe (Belfast Lough: domestic and industrial inputs from the city of Belfast; Charlesworth and Service, 2000) follow trends similar to the ones observed for Ensenada and El Sauzal sediments (Figure 5). Only Ni and, to a certain extent, Zn in the Belfast samples show higher concentrations than those measured for sediments with similar %GS. Hence, apparently the grain size:metal relationship is not a useful indicator of trace metal enrichment: sediments with similar %GS, but far more contaminated by sewage effluents and industrial inputs (*e.g.*, San Diego-PLOO, Los Angeles-SMB, Belfast) than our study area have metal concentrations that are generally below or at the same level as the ones measured in Ensenada and El Sauzal harbors (Figure 5).

3.3. Organic carbon

The concentrations of org-C in Ensenada Harbor showed considerable variation with depth (except core 2E, Figure 2k), but without any noticeable trend. In contrast, El Sauzal Harbor showed no substantial changes with depth, except core 2S. This core had the highest concentrations of the four cores, probably because it was collected where docked fishing boats wash their decks, discharging in the process blood and organic wastes into the water and underlying sediment. The concentrations of org-C in core 2S were especially high between 8 and 13 cm (Figure 3k), probably reflecting past high inputs of organic wastes, whose degraded remains are represented by the 10-13 cm sediment depth, consisting almost entirely of fish scales. Additionally, this core showed anomalously high org-C concentrations with respect to the %GS μm (Figure 5i), suggesting that anthropogenic contributions are considerable in the west corner of the harbor (core 2S, Figure 1). There was a significant correlation between %GS and org-C for both El Sauzal ($r = 0.54$, $p \leq 0.001$, $n = 74$) and Ensenada ($r = 0.71$, $p \leq 0.001$, $n = 139$) harbors (Table 3); however, the correlation for El Sauzal increased substantially when core 2S was eliminated ($r = 0.84$, $p \leq 0.001$, $n = 61$; data not shown), further supporting the contention of the anthropogenic origin of the sedimentary org-C.

3.4. Correlations between the different sediment components

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

3.5. Enrichment factors

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

Metal/aluminum (Me/Al) ratios for both Ensenada and El Sauzal harbors increase in the following order: $Cd/Al < Pb/Al < Ni/Al \approx Co/Al \approx Cu/Al < Zn/Al < Mn/Al << Fe/Al$ (Figure 6). The Me/Al ratios of Pb, Co, Ni and Fe were significantly higher for Ensenada Harbor relative to El Sauzal Harbor, whereas the ratios for Cd, Mn, Zn and Cu were statistically equivalent for both harbors. Hence, geochemical normalization suggests that metal concentrations in sediments from El Sauzal show some similarities with those from Ensenada Harbor, but that the latter sediments are more enriched in some elements. Proximity to a larger urban settlement (City of Ensenada) may explain the higher Pb/Al ratio for Ensenada; however, explaining the higher values for the other three metal ratios is more difficult. It can be hypothesized that the presence of more intense reducing conditions and greater flushing times (due to its smaller size) in El Sauzal Harbor may explain the deficiency in Fe, Pb, Co, Ni and, to a certain extent, Mn. Fishing boats are routinely cleaned inside this harbor and blood and organic waste end up accumulating in the sediments. For example, the last 6 cm (7–13 cm interval) of core 2S were almost entirely made up of fish scales, an indirect indication of the magnitude of organic matter contribution to the sediments. All this waste could conceivably drive the sediment redox conditions toward a reducing condition, which is probably not so intense in Ensenada Harbor due to the absence of this type of wastes. Fe and Mn are dynamic participants in the redox cycle and their more active reductive dissolution in the El Sauzal sediments with subsequent diffusion to the water column, coupled with a rapid flushing out of this harbor may explain the differences between Fe/Al and Mn/Al in El Sauzal and Ensenada sediments. However, since the reaction of Mn with oxygen is several orders of magnitude slower than that for reduced Fe (Jørgensen and Boudreau, 2001), Mn will be preferentially lost to the water column due to its slower oxidation kinetics of precipitation. Cobalt enrichment could be associated with primary productivity since this element is associated with vitamin B12 (cobalamin), an essential component for the growth of many phytoplankton species (Okbamichael and Sañudo-Wilhelmy, 2004). Furthermore, high concentrations of dissolved B12 are generally found in shallow harbors and bays with limited flushing (Okbamichael and Sañudo-Wilhelmy, 2004), characteristics that should favor the accumulation of Co in Ensenada Harbor.

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

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

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

The high EF_{Me} values of Cd may be a consequence of the Cd-enriched plankton (10 to 20 ppm; Martin and Broenkow, 1975) found in Baja California waters, which probably transfer this element to the sediments after their death and subsequent sedimentation. Additional Cd enrichment in the sediments can be produced by upwelling processes (Segovia-Zavala et al., 1998; Muñoz-Barbosa et al., 2004), which are common off the northwest coast of Baja California during spring and summer (Alvarez-Borrego and Alvarez-Borrego, 1982). The metals showing slight enrichment were those generally associated with anthropogenic contamination (Pb, Zn), or probably related to primary productivity and its relationship with vitamin B12, as was previously discussed for Co. However, it is surprising that Cu was among the metals neither enriched nor impoverished, since granular copper mine tailings were routinely employed to sandblast ships in a dry dock facility located adjacent to Ensenada Harbor. It is highly probable that the high enrichment value ($EF_{Cu} = 13$) obtained for core 1E (Figure 7) was due to the use of this sandblasting tailing. Impoverishment of Mn and Ni can be the result of the slow kinetics of precipitation of the former (Jørgensen and Boudreau, 2001), and the known association of the latter with Mn oxides (Murray, 1975; Sclater et al., 1976; Balistrieri and Murray, 1986; Tessier et al., 1996; Kay et al., 2001; Trivedi and Axe, 2001), at least for the case of Ensenada Harbor, where a significant correlation was found between these two elements (Tables 3 and 4). Hence, Ni is probably released into the interstitial water upon reductive dissolution of the Mn oxides and, most likely, diffuses towards the sediment-water interface and is lost to the water column together with the dissolved Mn.

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

3.6. Pollution Load Index

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

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

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

3.7. Geoaccumulation index

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

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

where $[Me]_{baseline}$ represents the metal concentration in average shales taken from Turekian and Wedepohl (1961) and Li and Schoonmaker (2005), with a "1.5" factor included because of possible variations in the background data due to lithogenic effects (Salomons and Förstner, 1984). Results from this exercise indicated that 79.3% (Ensenada Harbor) and 86.1% (El Sauzal Harbor) of the elements belonged to I_{geo} classes 0 and 1 (unpolluted to moderately polluted), with only 6.3% (Ensenada Harbor only) positioned in I_{geo} class 4 (0% for El Sauzal Harbor; Table 6). The only element that consistently ranked high in the I_{geo} classes (3 or 4), for both harbors and all cores (except 0E), was Cd (Table 6). It is clear that Ensenada has more metals in the "polluted" I_{geo} classes (2 to 6; Table 6) than El Sauzal (20.6% vs. 13.9%, respectively). None of the analyzed elements were positioned in the last two, more polluted classes (5 and 6).

3.8. Sediment quality guidelines

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

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

4. Conclusions

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

Acknowledgments

We thank Rafael Blanco-Betancourt, who collected all cores for this study, and two anonymous reviewers, whose insightful comments greatly improved the content of the manuscript. This research was partially supported by grants from Fondo Sectorial SEMARNAT-CONACYT (SEMARNAT-2002-C01-0016) and Fondo CONACYT-BC (SINVE 001-EC) to M.A. Huerta-Diaz.

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Figure legends

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

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

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

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

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

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

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

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

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

Figure 1

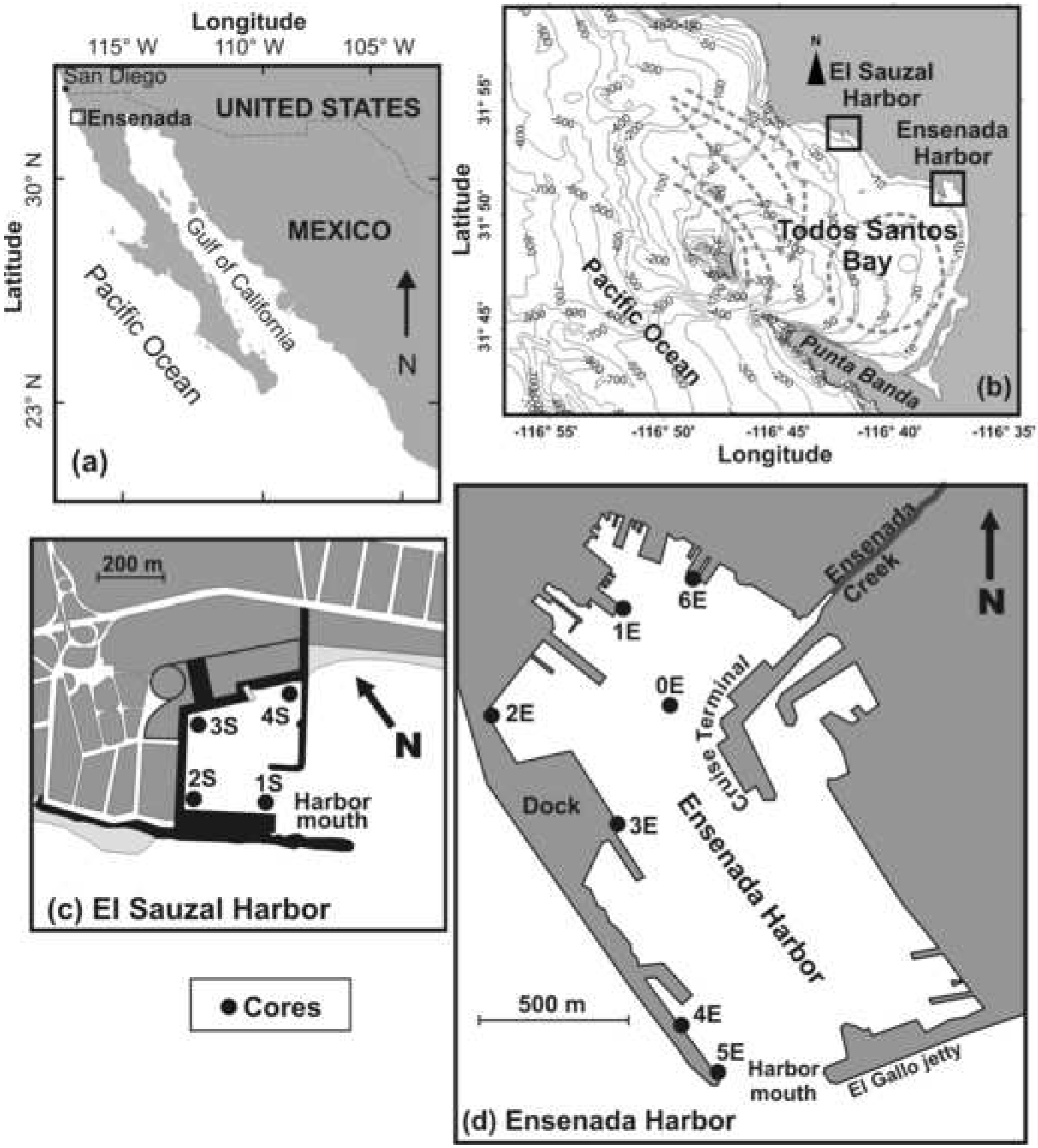

Longitude
115° W
110° W
105° W
San Diego
Ensenada
UNITED STATES
MEXICO
Gulf of California
Pacific Ocean
Latitude
30° N
23° N
N
(a)
El Sauzal Harbor
Ensenada Harbor
Todos Santos Bay
Pacific Ocean
Punta Banda
Latitude
31° 55'
31° 50'
31° 45'
-116° 55'
-116° 50'
-116° 45'
-116° 40'
-116° 35'
Longitude
(b)
200 m
3S
4S
2S
1S
Harbor mouth
N
(c) El Sauzal Harbor
Cores
Ensenada Creek
N
6E
1E
0E
2E
Cruise Terminal
Dock
3E
Ensenada Harbor
500 m
4E
5E
Harbor mouth
El Gallo jetty
(d) Ensenada Harbor

Figure 2a

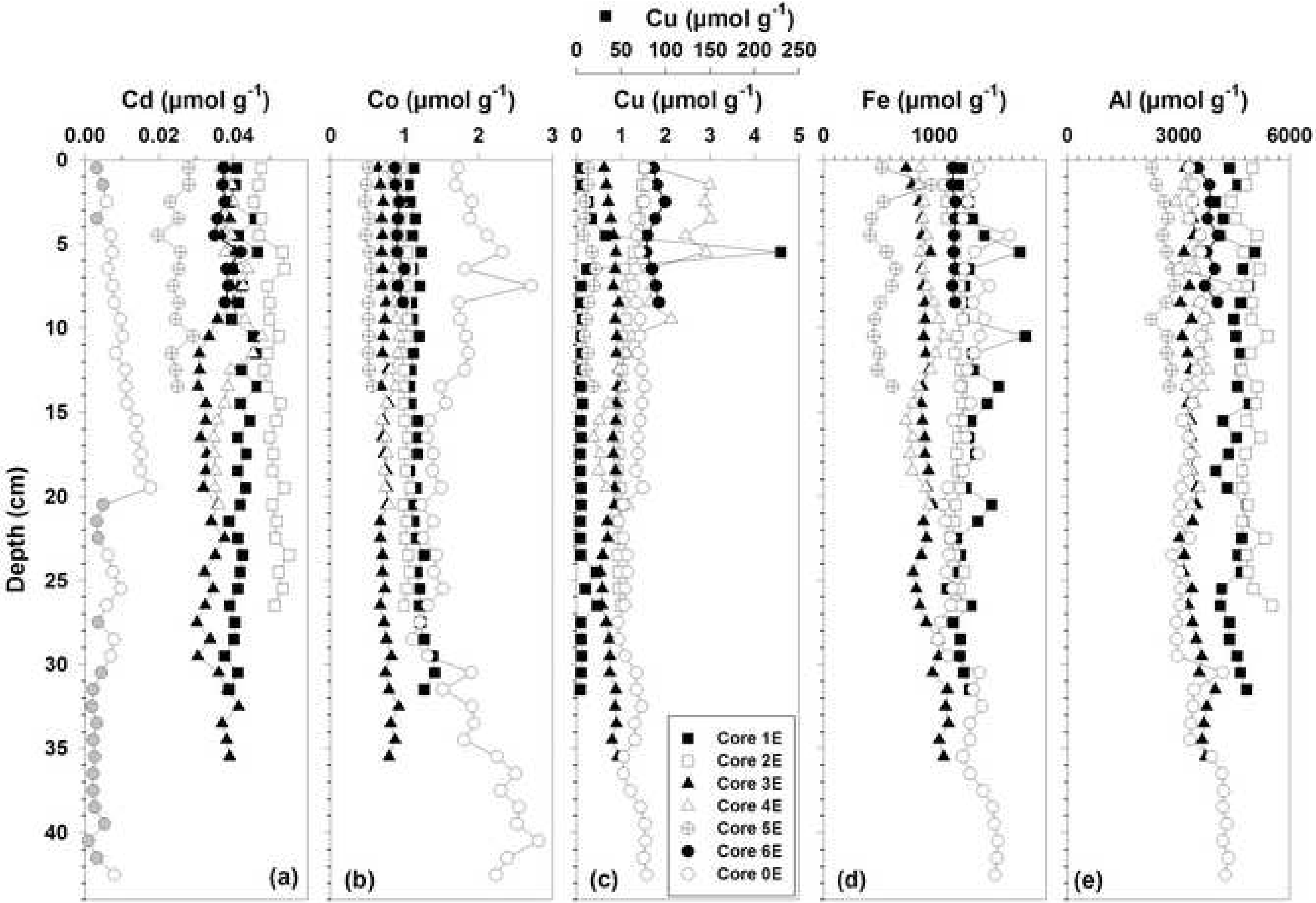
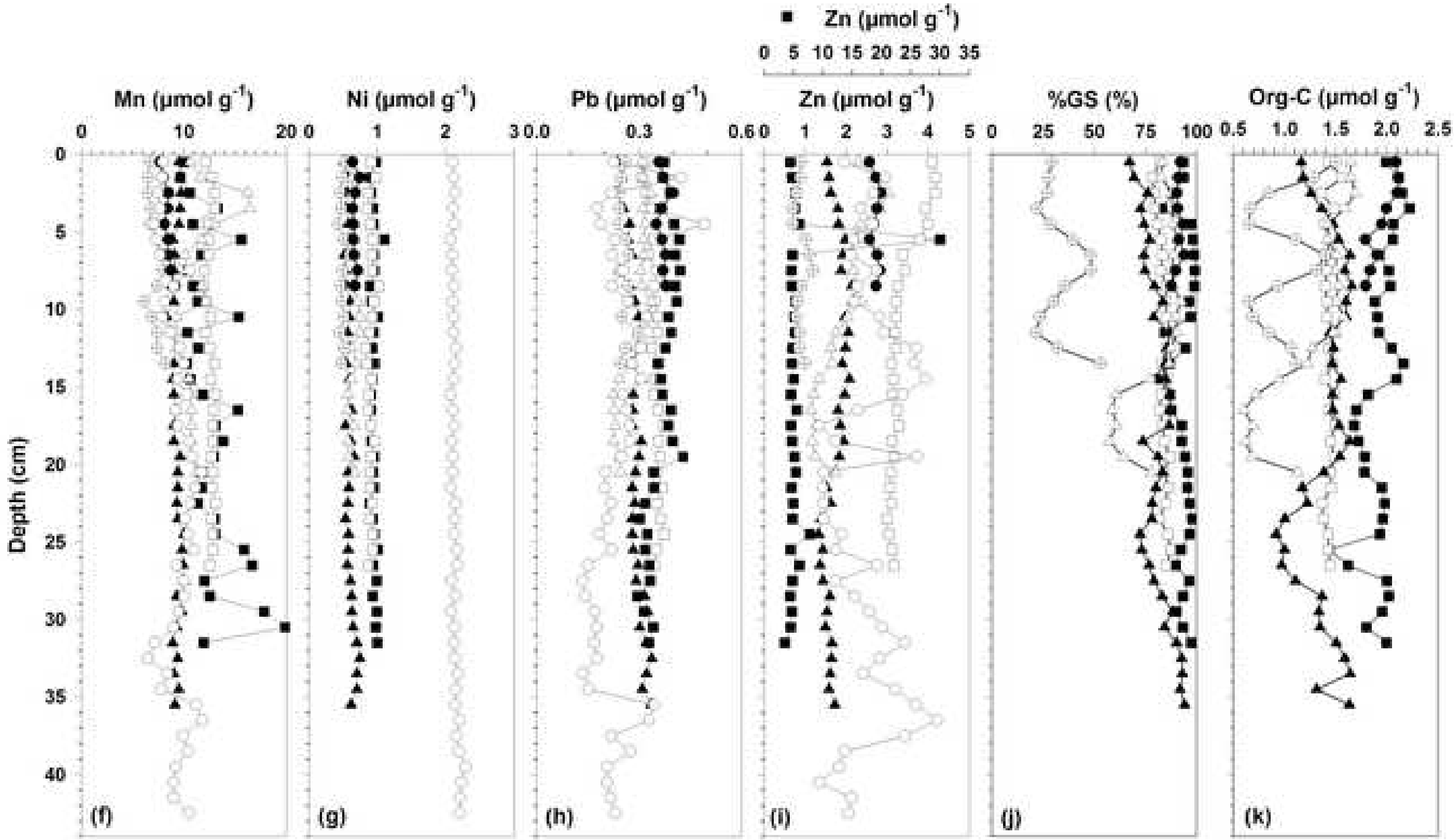

Cu (µmol g-1)
0 50 100 150 200 250
Cd (µmol g-1)
0.00 0.02 0.04
Co (µmol g-1)
0 1 2 3
Cu (µmol g-1)
0 1 2 3 4 5
Fe (µmol g-1)
0 1000
Al (µmol g-1)
0 3000 6000
Depth (cm)
0 5 10 15 20 25 30 35 40
(a)
(b)
(c)
(d)
(e)
Core 1E
Core 2E
Core 3E
Core 4E
Core 5E
Core 6E
Core 0E

Figure 2b



Zn (μmol g-1)
0 5 10 15 20 25 30 35
Mn (μmol g-1)
Ni (μmol g-1)
Pb (μmol g-1)
Zn (μmol g-1)
%GS (%)
Org-C (μmol g-1)
0 10 20
0 1 2 3
0.0 0.3 0.6
0 1 2 3 4 5
0 25 50 75 100
0.5 1.0 1.5 2.0 2.5
Depth (cm)
0 5 10 15 20 25 30 35 40
(f)
(g)
(h)
(i)
(j)
(k)

Figure 3a

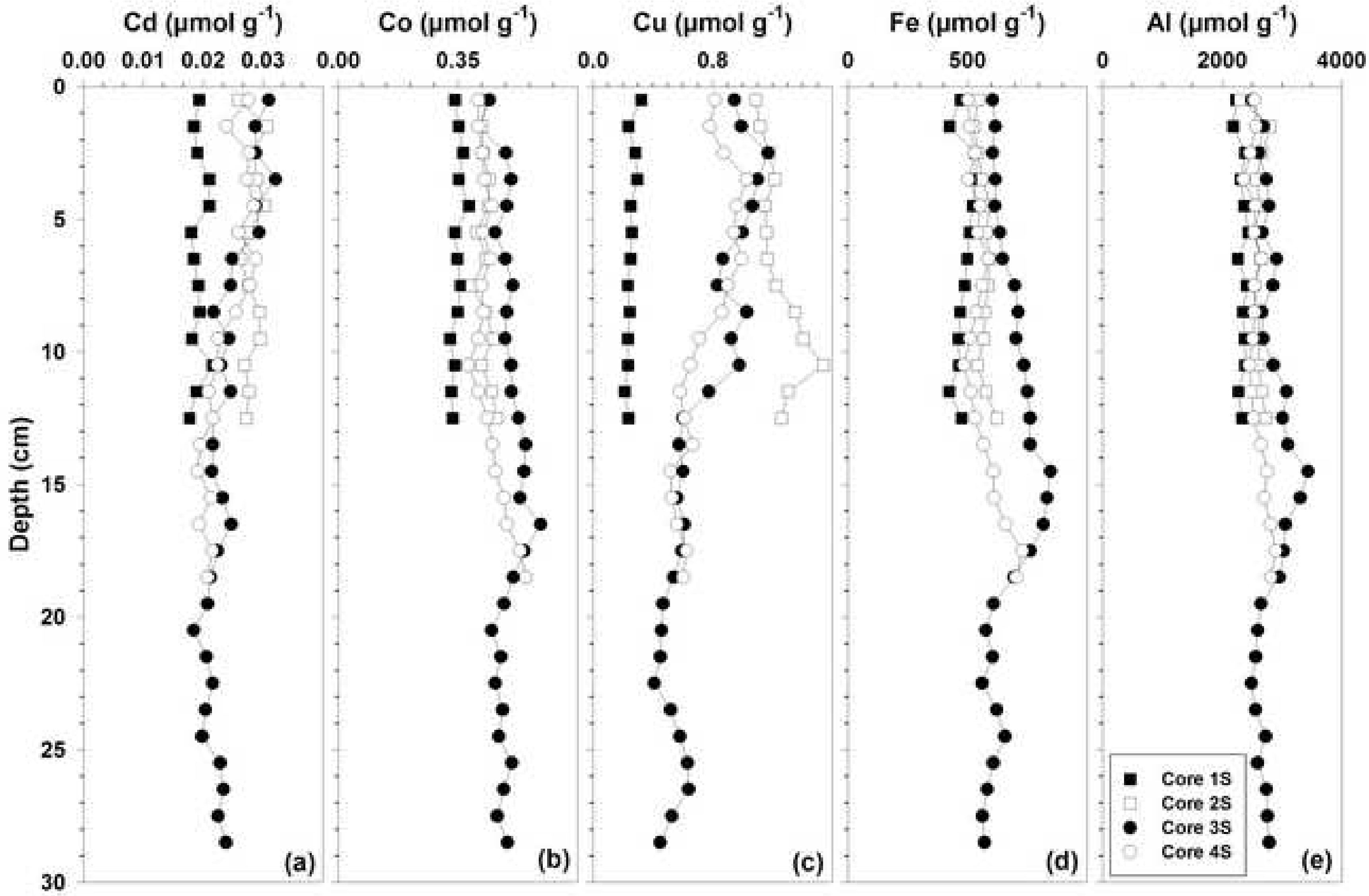

Cd (µmol g-1)
0.00 0.01 0.02 0.03
Co (µmol g-1)
0.00 0.35
Cu (µmol g-1)
0.0 0.8
Fe (µmol g-1)
0 500
Al (µmol g-1)
0 2000 4000
Depth (cm)
0 5 10 15 20 25 30
(a)
(b)
(c)
(d)
(e)
Core 1S
Core 2S
Core 3S
Core 4S

Figure 3b

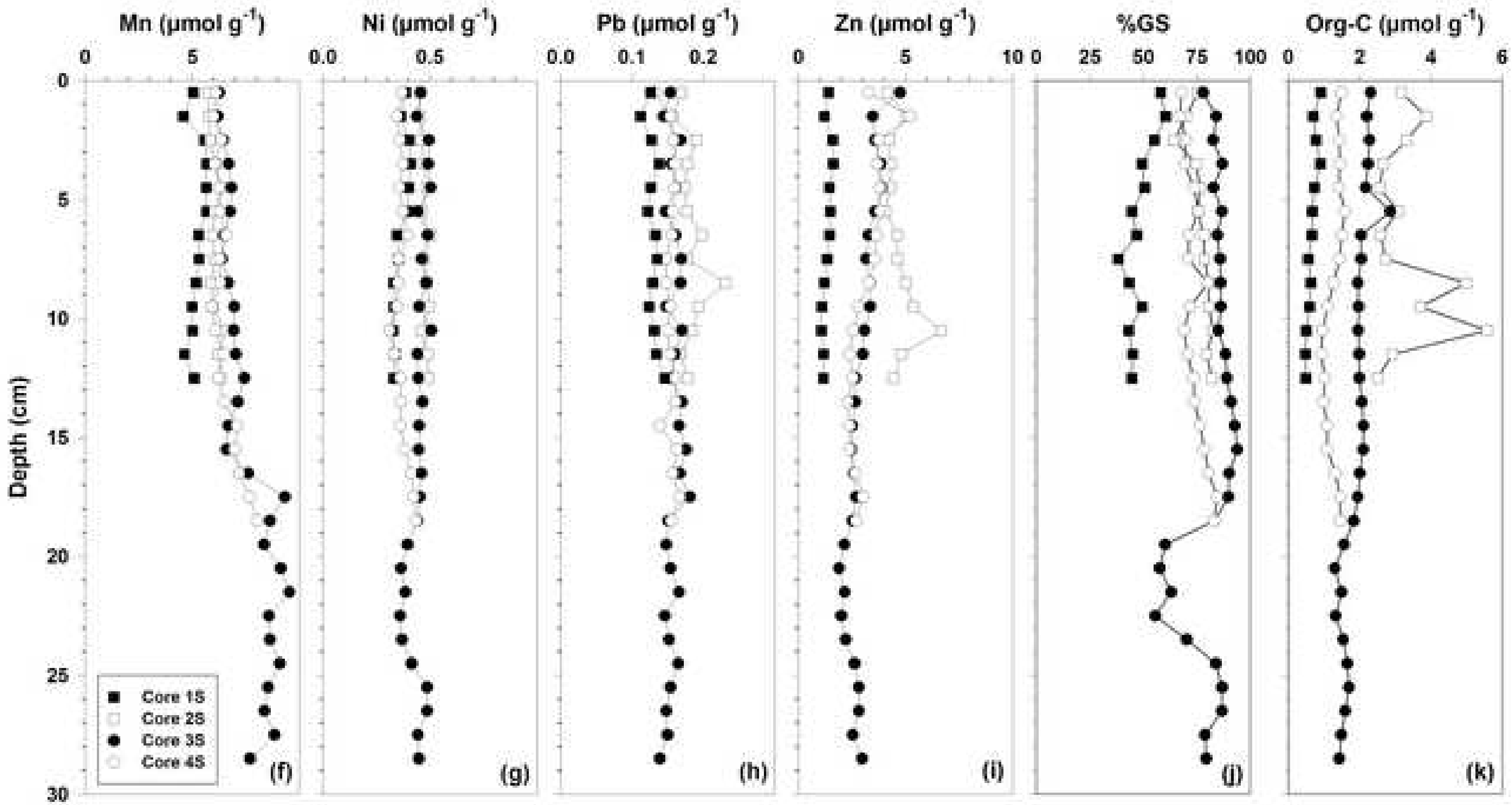

Mn (μmol g-1)
Ni (μmol g-1)
Pb (μmol g-1)
Zn (μmol g-1)
%GS
Org-C (μmol g-1)
Depth (cm)
Core 1S
Core 2S
Core 3S
Core 4S
(f)
(g)
(h)
(i)
(j)
(k)

Figure 4

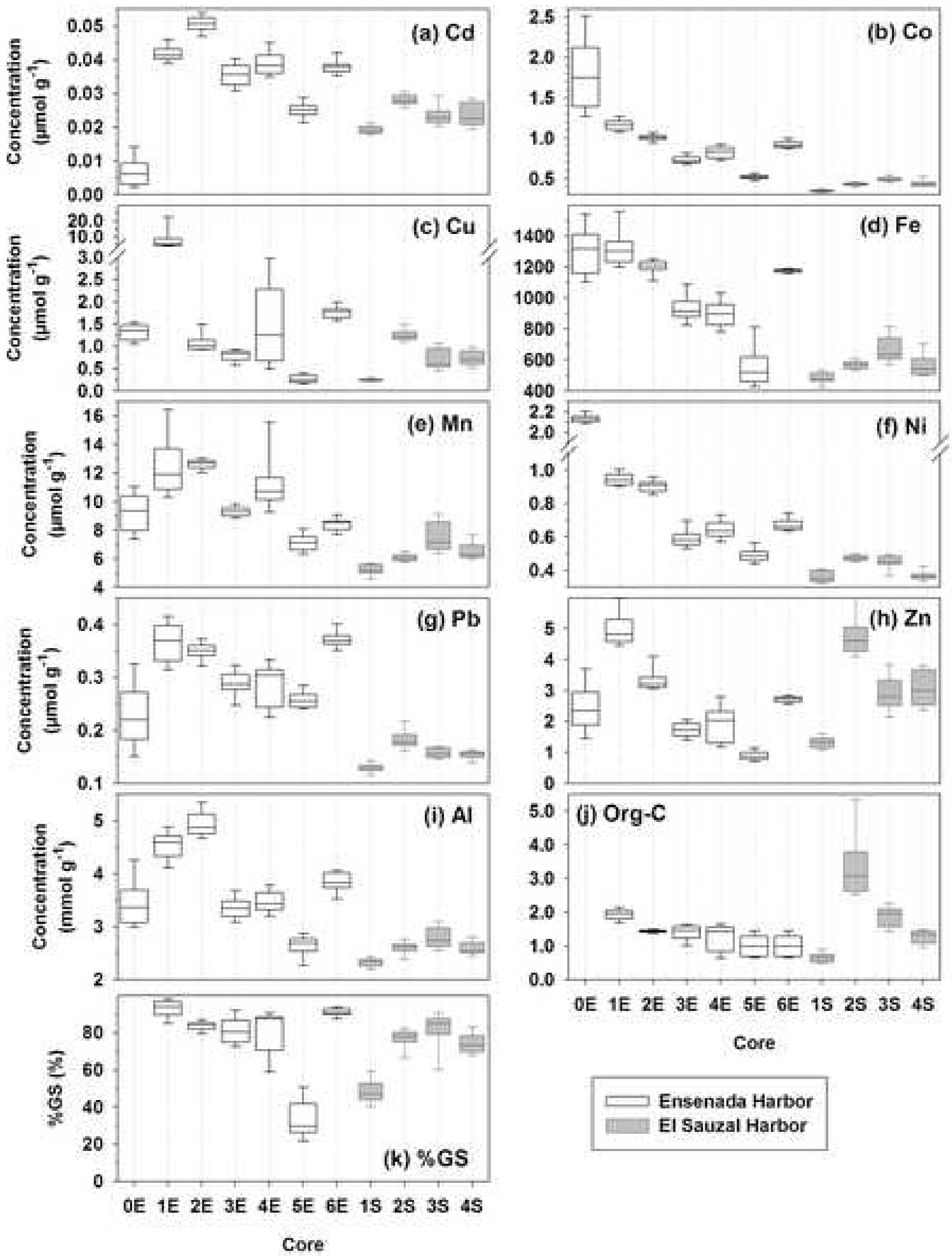

(a) Cd
(b) Co
(c) Cu
(d) Fe
(e) Mn
(f) Ni
(g) Pb
(h) Zn
(i) Al
(j) Org-C
(k) %GS
Concentration (µmol g⁻¹)
Concentration (mmol g⁻¹)
%GS (%)
0E 1E 2E 3E 4E 5E 6E 1S 2S 3S 4S
Core
Ensenada Harbor
El Sauzal Harbor

Figure 5

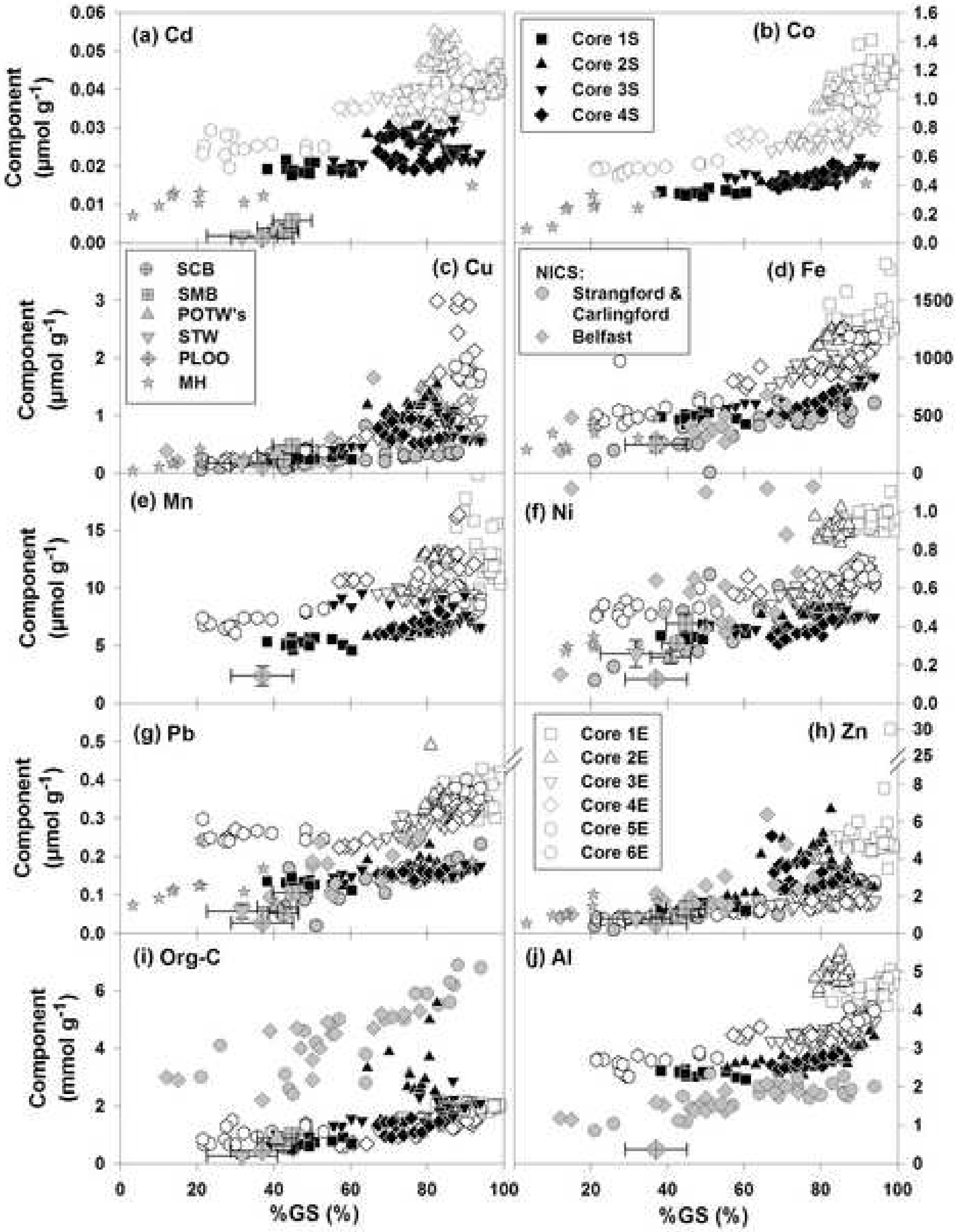
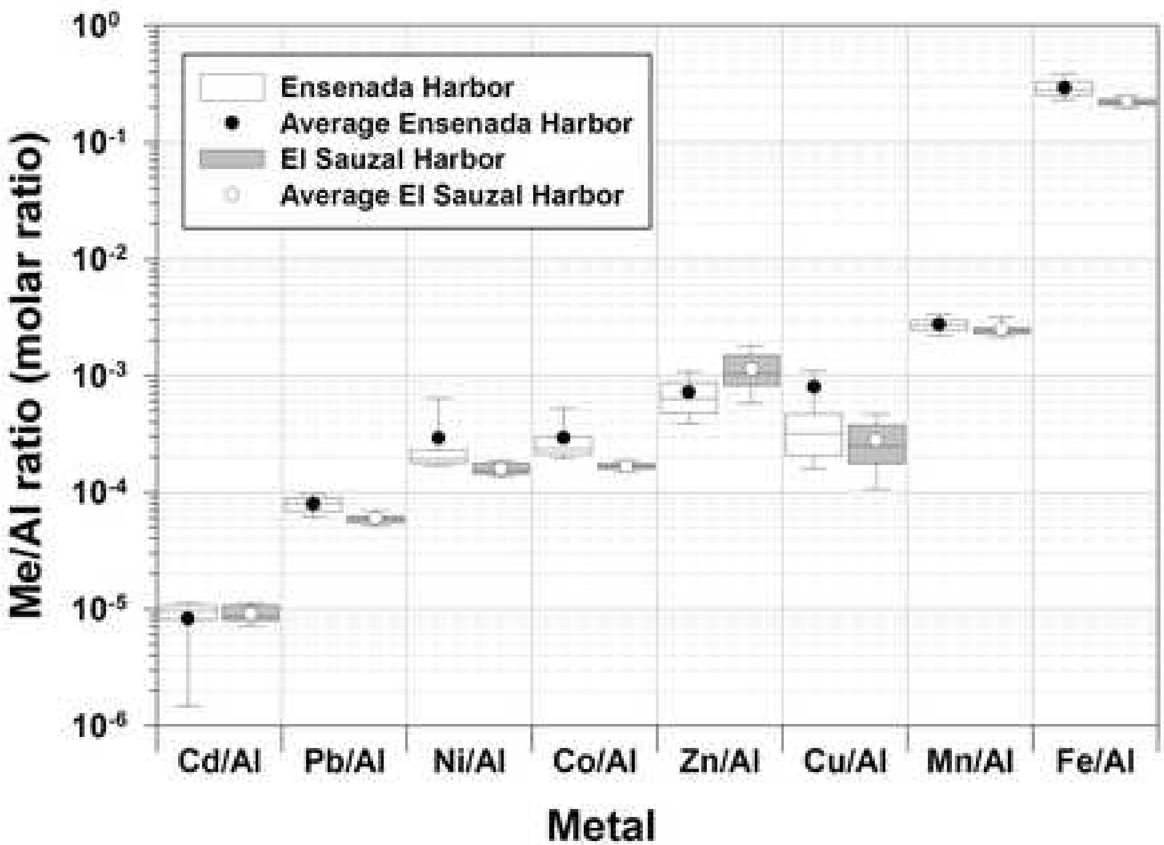

(a) Cd
(b) Co
(c) Cu
(d) Fe
(e) Mn
(f) Ni
(g) Pb
(h) Zn
(i) Org-C
(j) Al
Core 1S
Core 2S
Core 3S
Core 4S
SCB
SMB
POTW's
STW
PLOO
MH
NICS:
Strangford & Carlingford
Belfast
Core 1E
Core 2E
Core 3E
Core 4E
Core 5E
Core 6E
Component (µmol g-1)
Component (mmol g-1)
%GS (%)

Figure 6



Ensenada Harbor
Average Ensenada Harbor
El Sauzal Harbor
Average El Sauzal Harbor
Me/Al ratio (molar ratio)
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
Cd/Al
Pb/Al
Ni/Al
Co/Al
Zn/Al
Cu/Al
Mn/Al
Fe/Al
Metal

Figure 7

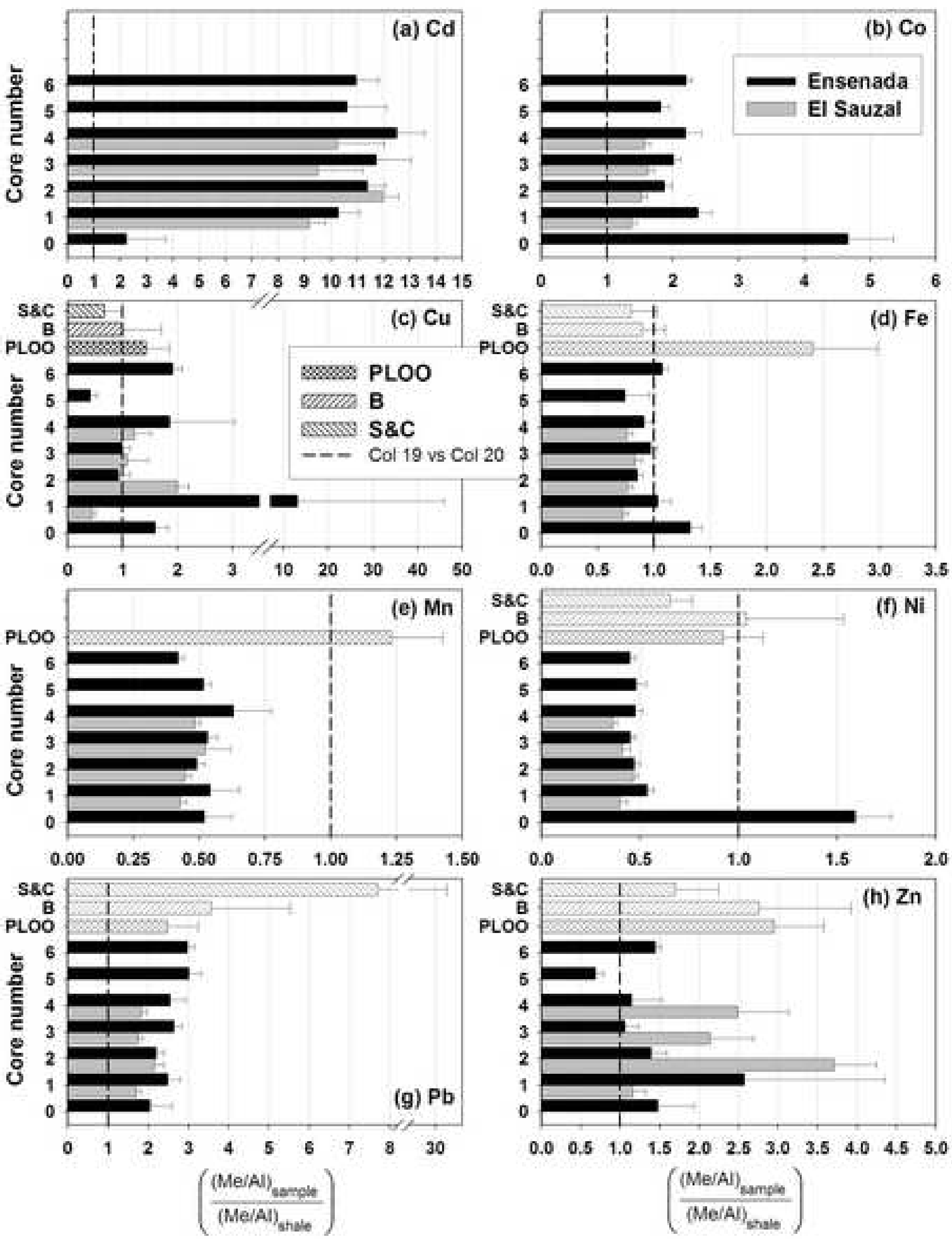
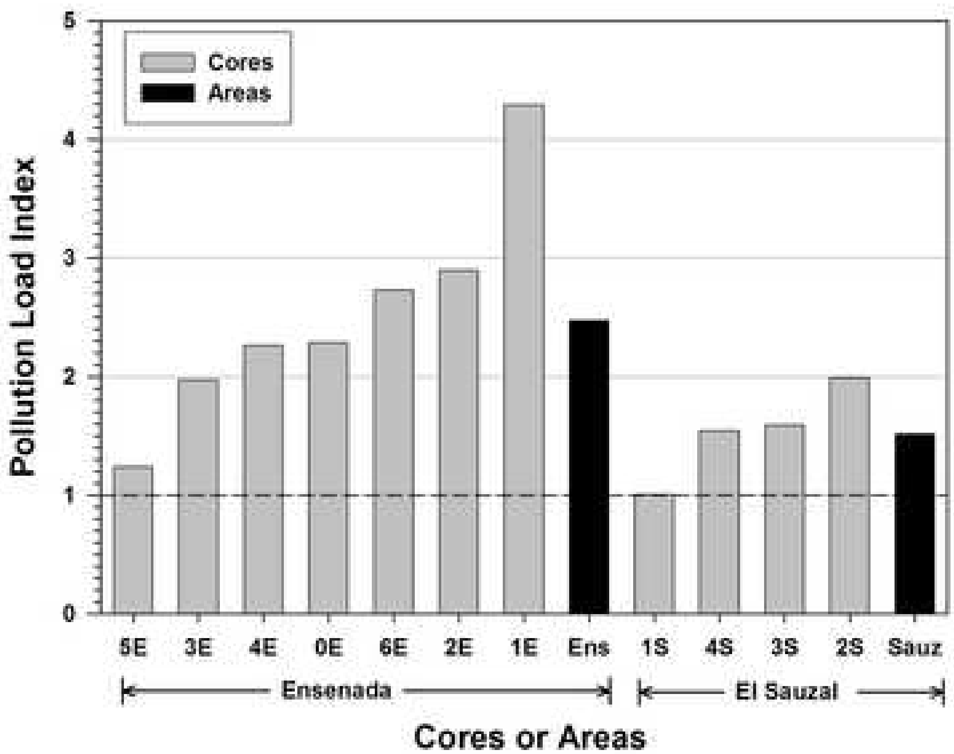

(a) Cd
(b) Co
Ensenada
El Sauzal
(c) Cu
(d) Fe
PLOO
B
S&C
Col 19 vs Col 20
(e) Mn
(f) Ni
(g) Pb
(h) Zn
Core number
(Me/Al)sample / (Me/Al)shale

Figure 8



Pollution Load Index
Cores
Areas
5
4
3
2
1
0
5E
3E
4E
0E
6E
2E
1E
Ens
1S
4S
3S
2S
Sauz
Ensenada
El Sauzal
Cores or Areas

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

Element	Measured concentration (μg g^{-1})	Certified concentration (μg 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* **≤ 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 (µmol/g)	ERM (µmol/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)

[a]Taken from Long et al. (1995); [b]Percentage and number of data entries within each concentration range divided by the total number of entries for all ranges.