



The speciation of dissolved copper, cadmium and zinc in Manila Bay, Philippines

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Abstract

At present, there is a very limited information on the levels and distribution of dissolved metals in Manila Bay. In this study, the horizontal and vertical distribution of operationally defined species (labile, bound and total) of dissolved copper (Cu), cadmium (Cd) and zinc (Zn) were determined using differential pulse anodic and cathodic stripping voltammetry in water samples obtained from 18 stations in November 1998. In addition, the 24-h variability in the concentrations of these species at different depths in the water column was determined. These measurements were complemented by the determination of temperature, salinity, dissolved oxygen, chlorophyll *a*, particulate organic carbon and nutrients. Results showed that more than 50% of total dissolved copper and cadmium were labile while 50% of total dissolved zinc was organically bound. Vertical profiles showed that Cu, Cd and Zn concentrations were generally high at the surface. Zinc and cadmium were characterised by the presence of a mid-depth minimum while copper did not show any clear vertical trend.

Dissolved Cu concentrations during the spatial and diurnal samplings ranged from 0.32 to 6.95 nM and 1.52 to 45.65 nM, respectively. For Cd, the concentrations in 18 stations ranged from 0.05 to 2.92 nM, and from 0.03 to 2.42 nM over a 24-h period. Zn concentrations ranged from 2.48 to 147.43 nM and 2.87 to 88.27 nM during the spatial and diurnal samplings, respectively. The large variation in the concentration of Cu, Cd and Zn in the bay was observed to be associated with the presence of a large vertical density gradient in the water column, which appeared to limit the exchange of materials between the surface and bottom waters. Elevated levels of these metals near point sources suggest anthropogenic inputs in the bay.

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1. Introduction

Elevated metal concentrations can be observed in estuarine systems due to input of contaminants from various sources. Physical transport of materials from rivers and discharges from urban and industrial areas together with the natural biogeochemical cycling of pollutants can contribute to the natural variability in concentration, distribution and fate of these metals in coastal estuaries (Dassenakis et al., 1997). Metal speciation studies can help in the measurement and understanding of the transformation of trace elements from its three major forms in the dissolved phase namely: (1) the free hydrated metal ion, (2) inorganic complexes and (3) organic complexes (Muller, 1996; Kozelka and Bruland,

1998). Among the three major forms, the free hydrated metal ion has been observed to be bioavailable and very toxic to phytoplankton while the inorganic and organic complexes are considered not bioavailable to organisms (Sunda and Guillard, 1976; Muller, 1996; Kozelka and Bruland, 1998). The free hydrated metals are present in trace amounts ranging between the concentration window of essential and toxic levels (Florence, 1982).

In this study, a combination of operationally defined physical and chemical separation techniques was utilised in the measurement of the different species of copper (Cu), cadmium (Cd) and zinc (Zn). The kinetically labile or bioavailable Cu, Cd and Zn (sum of free hydrated metal and inorganic complexes), bound Cu, Cd and Zn (organically bound complexes) and total Cu, Cd and Zn were measured in Manila Bay. Very little is known on the levels and distribution of metals in the country specifically in the marine environment. Hence this study

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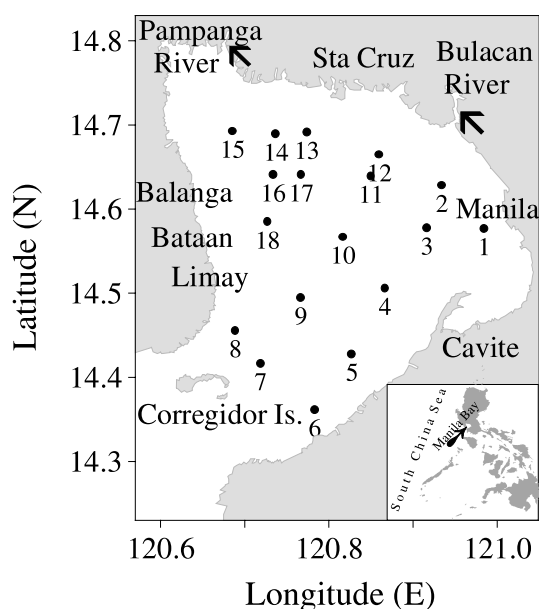


Fig. 1. Sampling stations in Manila Bay (November 1998).

was an initial attempt to characterise environmentally important metals in Manila Bay, which harbours the busiest national and international ports in the Philippines and remains one of the most important fishing grounds in the country.

Study site. Manila Bay is located on the western part of Luzon between 14.23° and 14.87°N and 120.53° and 121.03°E (Fig. 1). It is a semi-enclosed body of water with an area of $\approx 1700 \text{ km}^2$, an average depth of 17 m and with an estimated volume of $2.89 \times 10^{10} \text{ m}^3$ (Jacinto et al., 1998). The tide is predominantly diurnal with an average tidal range of 1.2 m during spring tide and 0.4 m during neap tide. The estimated residence time of the water in the bay is ≈ 31 days. It supports significant fisheries and aquaculture activities and serves as a sink and transit area for the discharge of domestic and industrial wastes from Metro Manila and the surrounding provinces (Velasquez and Jacinto, 1995).

2. Materials and methods

2.1. Field sampling

Eighteen (18) stations within the bay were occupied for the spatial sampling (Fig. 1) in November 1998. Water samples were collected every 5 m from the surface to the bottom using a 5l Niskin sampler. Samples for trace metals, nutrients and dissolved oxygen analyses were collected in duplicate. Aliquot samples from the same sampler were collected for particulate organic carbon (POC), pH and chlorophyll *a* determinations. All samples for trace metal analyses were filtered using $0.45 \mu\text{m}$ acid-washed Nucleopore filters, stored in

Nalgene high-density polyethylene (HDPE) bottles and stored at 0–4 °C. Sub-samples for total metal (TM) analysis were acidified to pH 2 using Supra pur hydrochloric acid and stored. Samples for nutrient analysis were filtered using GF/C Whatman filters. Samples for chlorophyll *a* and POC analyses were collected using $0.45 \mu\text{m}$ membrane and GF/C filters respectively. Dissolved oxygen and pH were measured on site. Salinity and temperature of the water were measured in situ using a conductivity-temperature-depth (CTD) profiler from the surface to the deepest sampling depth. The density of the water was computed from the measured salinity and temperature.

The 24-h sampling was conducted in the northwestern part of the bay (Station 18, Fig. 1). Water samples were collected every three hours following the same procedures that were used for the spatial sampling. Salinity and temperature measurements were done every hour.

2.2. Laboratory analyses

Nitrate, phosphate and silicate in water were analysed based on the modified technique for autoanalysers using a Skalar nutrient analyser (Grasshoff et al., 1983). POC was determined using the dichromate-acid oxidation method (Parsons et al., 1984). Pigments for chlorophyll *a* determination were extracted overnight using 90% acetone and analysed using a spectrophotometer (Parsons et al., 1984).

Trace metal concentrations were measured using cathodic and anodic stripping voltammetry. Copper was analysed by differential pulse cathodic stripping voltammetry (DPCSV) using a Metrohm compact polarographic/voltam(pero)metric apparatus with Model 646 VA Processor. The method is based on the formation of a catechol-copper complex (Van den Berg, 1984, 1989) and their adsorption on a hanging mercury drop electrode (HMDE) at a controlled potential of -0.5 V versus the combined reference electrode (Ag/AgCl, 3 M KCl). The pre-concentration was done for two minutes and the pH (7.8 ± 0.4) was maintained by the addition of $100 \mu\text{l}$ HEPES (*N*-2-hydroxyethylpiperazine-*N'*-2-ethanesulfonic acid) buffer to every 10 ml sample. The sample was stirred at a controlled rate throughout the analysis and the metal-cathecol complex was reduced from the electrode using a linear potential ramp with pulses superimposed.

Zinc and cadmium were analysed by differential pulse anodic stripping voltammetry using a segmented voltage scan. The sensitivity for each segment was adjusted to match the expected concentration of the metal. The method is based on the pre-concentration of metals by electrodeposition on a HMDE at a controlled potential of -1.1 V vs a combined reference electrode, Ag/AgCl with 3 M reference electrolyte (Van den Berg, 1989). The

pre-concentration was done for three minutes and the sample was stirred at a controlled rate throughout the analysis. The metal was stripped (oxidised) from the mercury using a linear potential ramp with pulses superimposed and the stripping current was measured.

Prior to all analyses, the DPCSV and DPASV methods were validated using a certified reference standard for trace metals in seawater (CASS-2 from NRCC). The UV-irradiation period for samples obtained in Manila Bay was validated using 2, 4 and 8 h irradiation periods.

2.3. Speciation

The labile fractions are referred to as those metals that were measured by DPASV and DPCSV under the natural pH (7.5–8.5) of the waters of the bay. These consist of free hydrated metal ions, the inorganically bound, and the weak organically bound complexes. The measurement of labile metals (M), involves titrating the untreated water sample (filtered) with standard metal solution and measuring the DPASV (Zn, Cd) or DPCSV (Cu) peak height of the metal in the sample after each standard addition. A known equilibrium period (60 s) was allowed to pass after each addition before the measurement was carried out.

The TM fraction was obtained from the measured concentration of acidified (pH 2) and irradiated samples. Analyses were done by the standard addition technique using the HMDE. For Zn determination, 10 μ l of 1000 mg/l Ga was added to each of the samples before analysis. The addition of Ga reduces the intermetallic interaction between Cu and Zn (Copeland et al., 1974; Scollary et al., 1993).

Concentrations of bound metal (bound metal = total metal – labile metal) fractions, comprised of strongly bound organic complexes, were determined by subtracting the amount of the labile fraction of the metals from the TM concentration.

3. Results

Fig. 2 shows representative plots which were generated using a surface mapping system software (Surfer, Win32, version 6.04 from Golden Software Inc.). These plots illustrate the spatial distribution of dissolved metal fractions in Manila Bay. The horizontal distribution of dissolved Zn at 1 m showed high concentrations along the northern part of the bay (Pampanga–Bulacan areas). From 5 to 15 m, Zn concentrations were higher near the mouth of the bay (along the Cavite area) compared to the concentrations that were measured in the Pampanga and Bulacan sites. The measured Zn_{total} concentration along the Cavite area from 5 to 15 m ranged from >20 to 147 nM while in the northern area the values ranged

from 2.48 to 26 nM. Values greater than 100 nM were recorded in Stations 4 and 6. However for Station 5, no measurement was done below 5 m. The ranges of concentration of the bound Zn fractions for both areas were very similar to Zn_{total} . The labile fraction was more regularly distributed ($Zn_{labile} = 1–7$ nM). Zinc was uniformly distributed at 20 m in the middle portion of the bay.

Surface concentrations of labile Cd were high in stations facing Pampanga River and nearshore stations along Bulacan and Pasig rivers ($Cd_{labile} = 0.70–0.99$ nM). However, labile Cd concentrations from 5 to 20 m, which were generally below 0.30 nM, were comparable among stations. Elevated levels of total and bound Cd ($Cd_{total} = 0.40–2.9$ nM and $Cd_{bound} = 0.40–2.8$ nM) were observed near the head of the bay (Pampanga–Bulacan areas) from 1 to 10 m of the water column. A decline in concentration was observed from 15 to 20 m but the distribution was uniform.

Labile Cu was evenly distributed at 1 m in the entire bay. Below 1 m, higher concentrations of labile Cu were detected at the northern part of the bay extending down to the middle part of the bay. Distinct high values were also observed near Pasig–Cavite areas ($Cu_{labile} = 2.6–3.5$ nM) and Pampanga ($Cu_{labile} = 1.6–9.0$ nM). Similar trends were observed for total and bound Cu for the entire bay. The highest Cu_{total} was 26.95 and 23.85 nM for Cu_{labile} .

Vertical profiles of the average nutrients (NO_3 , PO_4 and SiO_4) concentrations of 18 stations in Manila Bay showed increasing trends from the surface to the bottom (Fig. 3). The mean concentrations of chlorophyll *a*, POC, dissolved oxygen and pH decreased from the surface to the bottom (Fig. 3).

Figs. 3 and 5 show the vertical profiles of water density, which is expressed in sigma-tee units (σ_t), and is referred to as the in situ value. Since lower density values occur in coastal waters, only the last four digits in the measured density is expressed, which is given in a form of quantity called sigma-tee ($\sigma_t = \text{density} - 1000$, where density is in units of kg/m^3). Fig. 3 shows increasing salinity and density with depth while temperature readings slightly dropped by <0.1 °C at 5 m, increased by 0.5 at 5–15 m and decreased by ≈ 0.15 °C at 20 m. The measured pH of the water was constant at the upper 5 m but dropped by 0.05 pH unit at 10 m. The same pH was observed at 15 m but a drop of 0.05 pH unit was again observed at 20 m. A similar trend was observed for the water column profile of total and bound Zn (Fig. 4). Total and labile Cd trends were similar to POC, chlorophyll *a* and DO, except at 20 m where a slight increase in Cd concentration was observed. Tables 1 and 2 summarise the correlation of selected metal species with other water quality parameters using a multivariate regression model. Total and labile Zn and Cd correlated positively with chlorophyll *a*, while labile Cu was in-

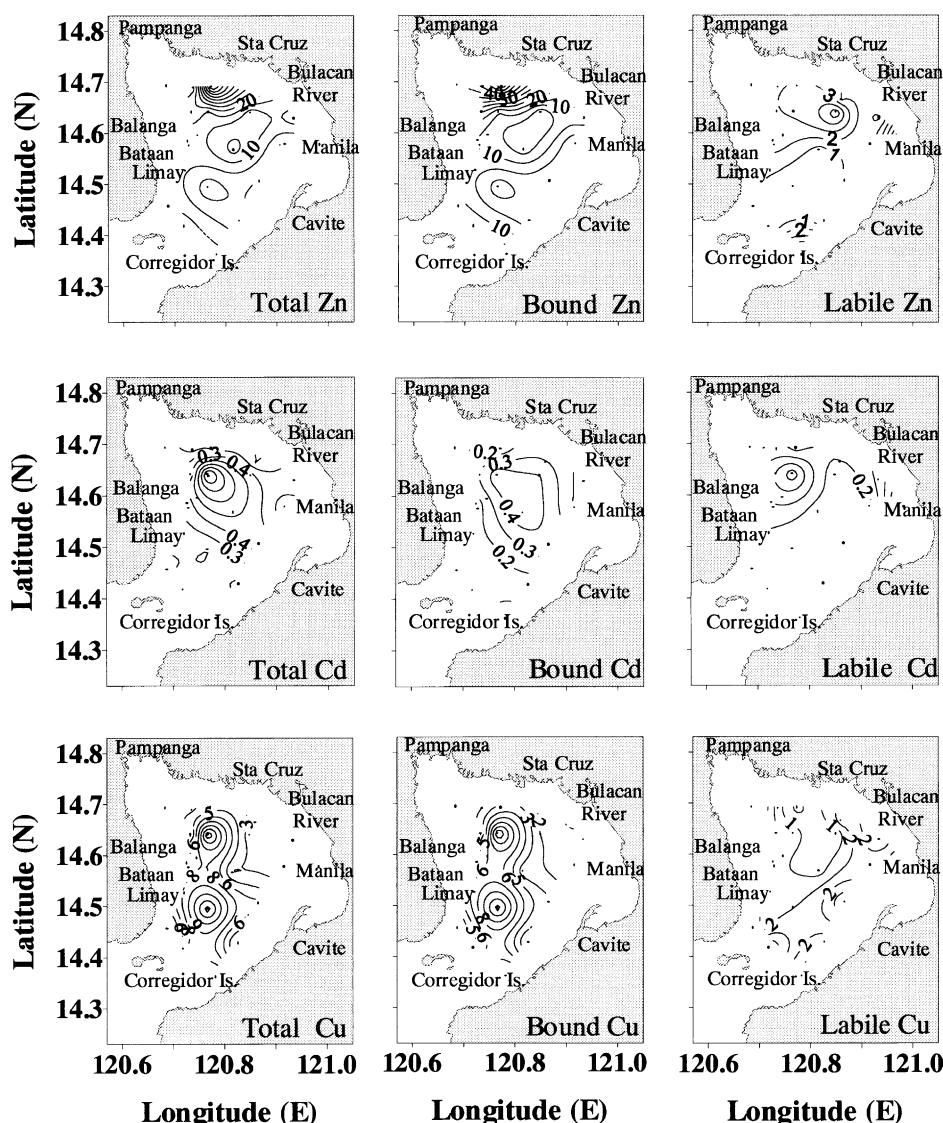


Fig. 2. Horizontal distribution of dissolved metals (nM) at 1 m depth in Manila Bay.

versely correlated to chlorophyll *a* (Table 1). Total and labile Zn and Cd were positively correlated with POC. Dissolved Cu did not show any down column trend; however, all metals exhibited a marked concentration gradient between 5 and 10 m (Fig. 4).

The diurnal (24-h) down column profiles of mean nutrient concentrations are shown in Fig. 5. Nutrient concentrations increased from the surface to the bottom, while chlorophyll *a*, POC, DO and temperature decreased downcolumn. However, temperature slightly increased at 15 m. The pH of the water did not change vertically over the 24-h period except for a very small drop (~ 0.05 pH unit) at 15 m. The density and salinity profiles at Station 18 were similar to that observed at different stations in the bay.

For the dissolved metal fractions, Cu, Cd and labile Zn were generally high from the surface to 5 m with a marked decrease in the concentration at 10 m. From 10

to 20 m, a slight increasing downcolumn trend was observed during the 24-h sampling. However, the other Zn species did not show any clear vertical trend over a diurnal period. Large concentration gradients were also observed between 5 and 10 m for all metals at Station 18 during the 24-h sampling (Fig. 6). Furthermore, correlation estimates showed that total and labile Cu correlated positively with nutrients while labile zinc and cadmium had negative correlation with nutrients. Cadmium, bound and labile Zn and bound and total Cu behaviour were positively correlated to the measured pH of the water during the 24-h sampling (Table 2).

Table 3 shows the range of concentrations of water quality parameters determined in November 1998 in Manila Bay. Nutrient concentrations were within the range previously observed in Manila Bay. The concentrations of dissolved oxygen from the surface to 10 m throughout the bay were generally above 4 mg/l. However,

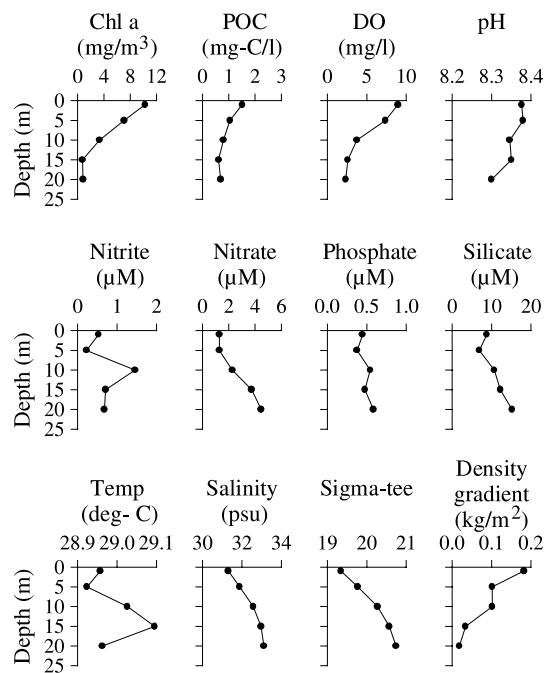


Fig. 3. Vertical profiles of average concentrations of water quality parameters at 18 stations in Manila, November 1998. Number of samples (n) per depth: surface = 16; 5 m = 16; 10 m = 13; 15 m = 10 and 20 m = 9.

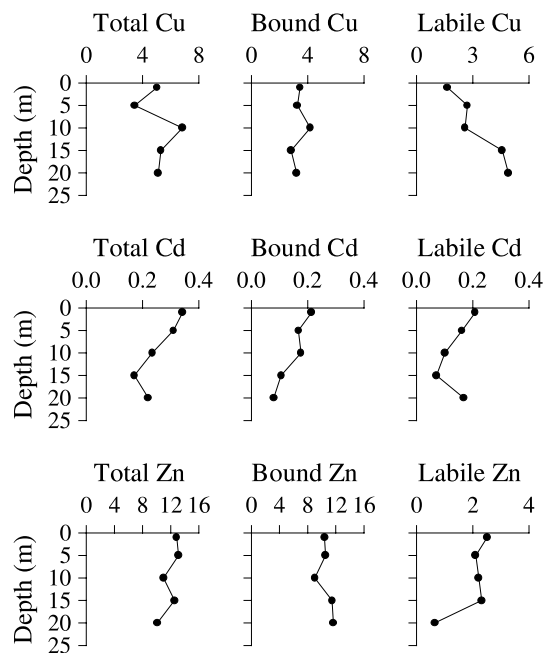


Fig. 4. Vertical profiles of average concentrations of dissolved metals (nM) at 18 stations in Manila Bay, November 1998. Number of samples (n) per depth: surface = 16; 5 m = 16; 10 m = 13; 15 m = 10 and 20 m = 9.

below 10 m a drastic decrease was observed. Minimum dissolved oxygen concentrations observed especially during the 24-h sampling were very low (DO = 0 mg/l)

Table 1
Correlation of average (Me) with POC and chlorophyll a

	R_{POC}	R_{Chl}
Copper _{total}	0.37	-0.37
Cadmium _{total}	0.12	0.96
Zinc _{total}	0.53	0.64
Copper _{labile}	-0.27	-0.75
Cadmium _{labile}	-0.23	0.71
Zinc _{labile}	0.89	0.54

Table 2
Correlation of average (Me) with pH and nutrients

	R_{pH}	$R_{nitrate}$	$R_{phosphate}$	$R_{silicate}$
Copper _{total}	0.60	0.60	0.75	0.71
Cadmium _{total}	0.94	0.12	0.23	0.28
Zinc _{total}	0.39	0.44	-0.01	-0.20
Copper _{labile}	0.28	-0.84	0.89	0.74
Cadmium _{labile}	0.65	0.80	-0.57	-0.51
Zinc _{labile}	0.61	-0.87	-0.72	-0.58

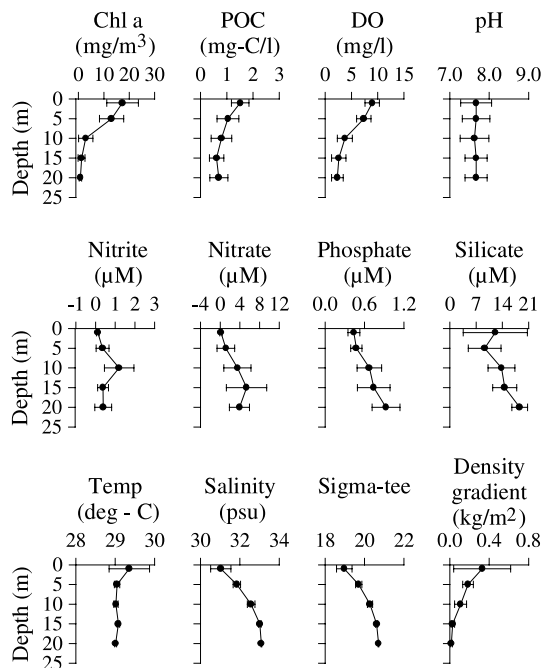


Fig. 5. Tidally integrated profiles of water quality parameters during a 24-h sampling in Manila Bay, November 1998. The number of samples (n) for each sampling depth varied between 6 and 8.

compared to the concentrations observed in previous studies (DO \sim 2 mg/l) conducted in the bay.

The percentages of the different metal species measured in the bay are shown in Table 4. In general, more than 50% of dissolved Cu and Cd were labile and more than 50% of dissolved Zn was organically bound. The findings on the percentage labile Cu was similar to the results obtained by Donat et al. (1994) in San Francisco Bay. The reported labile Cu was 4.2 nM in San Francisco Bay, which according to Kozelka and Bruland

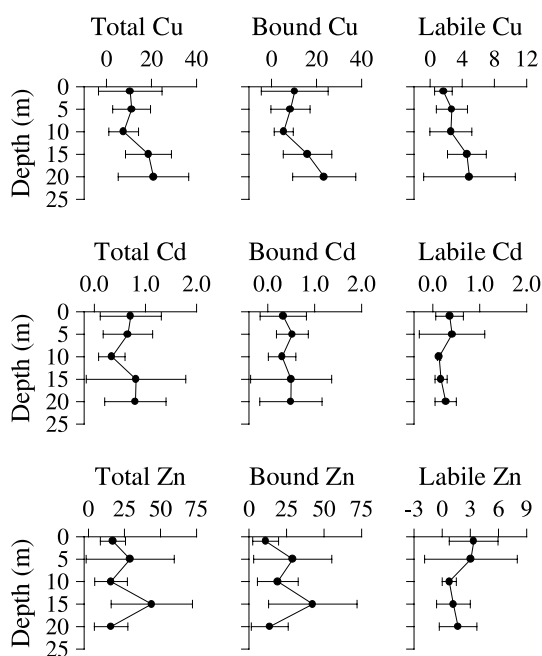


Fig. 6. Tidally integrated metal profiles (nM) during a 24-h sampling in Manila Bay, November 1998. The number of samples (n) for each sampling depth varied from 6 to 8.

(1998) is the highest ambient estuarine Cu concentration that was reported in the area. The highest labile Cu concentration that was observed in Manila Bay (24–45 nM) was 5–10 \times higher than what was observed in San Francisco Bay.

The observed percent labile Zn in the bay is similar to what was observed in an industrialised bay like Naraganset Bay (Kozelka and Bruland, 1998). The percent

labile Cd was also higher than what Kozelka and Bruland (1998) observed. However, reports on the percent labile Cd varies for different areas. The range of Cu, Cd and Zn concentrations that were obtained in Manila Bay are comparable to the concentrations that were obtained in other estuarine environments (Table 5). However, the spread of the values in Manila Bay is larger compared to Funka Bay of Japan (Cd), San Francisco Bay (Cu) and Scheldt Estuary (Eaton, 1979; Abe and Matsunaga, 1988; Baeyens et al., 1998).

4. Discussion

The spatial distribution of dissolved Cu, Cd and Zn at the surface suggests a strong surface source, with possible contributions from the two major river systems that drain into the bay, Pampanga and Bulacan Rivers. Elevated levels of metals may increase outside the river mouth due to the process of desorption (Featherstone and O'Grady, 1997). Below the surface, Cd concentration was low and uniformly distributed throughout the bay, which suggests that the Cd source in the bay is largely anthropogenic. In contrast, Zn concentrations peaked near the mouth of the bay within the Cavite area. This may be due to intensive shipping activities in the area. It serves as a transit site for incoming and outgoing ships in the bay. In addition, the navy shipyard is situated in Cavite, which may be utilising materials that are high in zinc. Unlike cadmium and zinc, which peaked at specific sites, high concentrations of copper were observed in almost all parts of the bay. Copper in the bay may be coming from industrial effluents and

Table 3
Concentrations of various water quality parameters obtained in Manila Bay in November 1998

	NO ₂ (μ M)	NO ₃ (μ M)	PO ₄ (μ M)	SiO ₄ (μ M)	Chl <i>a</i> (μ g/l)	DO (mg/l)
Diurnal ($n = 45$)	<0.06–2.22	<0.06–14.33	0.31–1.25	<0.1–22.67	0.0–25.67	0.0–11.71
Spatial ($n = 62$)	<0.06–2.98	<0.06–9.41	<0.03–1.03	1.14–22.67	0.0–25.67	1.14–13.85

Table 4
Concentration ranges of dissolved metals in Manila Bay, November 1998

	Zn _{total} (nM)	Zn _{bound} (nM)	Zn _{labile} (nM)	Zn _{labile} (%)	Zn _{bound} (%)
Zinc					
Diurnal ($n = 35$)	2.87–88.27	1.56–78.26	0.05–14.68	0.1–51.3	48.7–99.9
Spatial ($n = 56$)	2.48–147.43	0.00–123.31	0.02–9.66	0.1–100.0	0.0–99.9
Copper					
Diurnal ($n = 35$)	1.52–45.65	0.97–45.65	0.00–15.24	0.0–71.7	28.3–100.0
Spatial ($n = 62$)	0.32–26.95	0.00–23.85	0.00–9.45	4.0–100.0	0.0–96.0
Cadmium					
Diurnal ($n = 35$)	0.03–2.42	0.00–2.23	0.02–2.23	7.8–100.0	0.0–92.2
Spatial ($n = 62$)	0.05–2.92	0.00–2.87	0.01–0.99	0.0–100.0	0.0–100.0

Table 5

Comparison of trace metal concentrations obtained from different sites

Site	Source	
<i>Zinc</i>		
	Zinc (nM)	
Estuarine, Athens	44.97	Dassenakis et al. (1997)
Mombasa, Kenya	367–1055	Williams et al. (1997)
Narragansett Bay	71.5	Kozelka and Bruland (1998)
Scheldt Estuary	25–226	Baeyens et al. (1998)
Manila Bay	2.48–147.43	This study
<i>Copper</i>		
	Copper (nM)	
San Francisco Bay-surface	3.15–83.4	Eaton (1979)
Pacific ocean	0.54–3.02	Bruland (1980)
	0.63–1.48	Mart et al. (1982)
Narragansett Bay	0.80	Kozelka and Bruland (1998)
Scheldt Estuary	12.3–32.4	Baeyens et al. (1998)
Manila Bay	0.32–45.65	This study
<i>Cadmium</i>		
	Cadmium (nM)	
Pacific ocean	0.09–1.12	Boyle et al. (1976)
	0.009–0.49	Nurnberg and Mart (1985)
Surface	0.006–0.06	Mart et al. (1982)
Narragansett Bay	0.80	Kozelka and Bruland (1998)
Funka Bay, Japan	0.05–0.60	Abe and Matsunaga (1988)
Scheldt Estuary	0.38–1.8	Baeyens et al. (1998)
Manila Bay	0.03–2.92	This study

from agricultural activities in the provinces surrounding the bay.

Nutrient concentrations may not clearly exhibit the extent of influx of contaminants in the bay since the values that are being measured are already residuals. However, the variation in concentration spatially and over a 24-h period, which was very high, may indicate the extent of variability in the distribution of nutrients in Manila Bay. The variation could be due to biological and physical processes occurring in the area and the continuous and irregular inputs from point sources. There are four major river systems that drain in the bay (Pampanga, Bulacan, Pasig and Cavite) that can affect the distribution of nutrients and other materials in the water. The observed gradient in the dissolved oxygen concentration between 10 and 15 m can be due to the presence of a strong density gradient, which limits the exchange of the bottom water and the surface waters. The vertical stratification coupled with high load of organic materials due to the presence of the *Noctiluca scintillans* bloom can cause the depletion of oxygen near the bottom.

Tidally integrated profiles (average concentration at each depth) were used to show the vertical characteristics of all parameters to eliminate bias brought about by tidal oscillation in the area. For a tide-dominated embayment like Manila Bay, variations within a day may be high. Therefore, it is very difficult to assess important features that are being masked by these variations. A

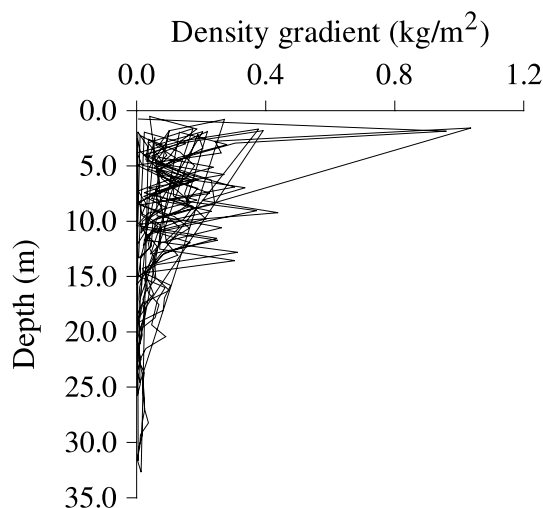


Fig. 7. Density gradient profiles for all stations occupied in Manila Bay indicating the presence of a stable water layer from 1 to 15 m.

large density gradient (Fig. 7) was observed between 5 and 10 m sometimes extending to 15 m, which suggests the presence of a very stable water layer. This gradient appeared to be a barrier between the surface and bottom waters.

The large variation in the distribution and speciation of Cu, Cd and Zn aside from anthropogenic inputs, may be influenced by the unstable water quality condition of the bay due to physical and biological processes, as discussed above. A drastic drop in the oxygen levels due to high inputs of organic compounds and the presence of a plankton bloom within the water column favours redox processes and could affect the dissolved metal concentration in the system (Baeyens et al., 1998).

The speciation of the different fractions of metals especially Cu, which is generally observed to have high affinity for organic ligands, can be affected by several factors. In cases where the total copper concentration exceeds the natural ligand concentration, the weaker ligand that is available in the system can act to bind the metal. However, the conditional stability constants of these weak ligands are also low resulting to a higher free metal ion, as in the case of San Francisco Bay (Donat et al., 1994; Kozelka and Bruland, 1998). Moreover, the standard separation technique that is used to distinguish between dissolved and particulate fractions using 0.45 μm filter can also affect metal speciation. The dissolved metal fraction that passed through a 0.45 μm filter may include colloidal fractions; hence, it becomes available as a thermodynamically unstable dispersion rather than in solution. (Muller, 1996). The colloidal components are often not accounted for in the calculation of TM concentration because of its transient nature and its role as a shuttle transferring metals (Muller, 1996). Benoit et al. (1994) showed that truly dissolved Cu (<0.2 μm) fractions accounts for more than 50% of Cu present in

0.45 μm and the truly dissolved and colloidal fractions show a large inter-estuarine and seasonal variations.

5. Conclusion

The speciation of dissolved Cu, Cd and Zn in Manila Bay is dominated by labile Cu and Cd and organically bound Zn fractions. The physical (i.e., tidal oscillations) and biological processes in the bay can significantly influence the distribution, transport and changes of the different metals species. Elevated levels of the total dissolved metal concentration near point sources suggest anthropogenic inputs in the bay.

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