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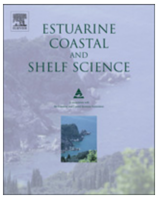

Processes controlling cobalt distribution in two temperate estuaries, Sagami Bay and Wakasa Bay, Japan

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ABSTRACT

Concentrations of cobalt (Co) in surface waters from the Sagami River to northern Sagami Bay and from the Yura River to southwestern Wakasa Bay in Japan were determined in order to investigate the factors governing the distribution of this metal during estuarine mixing. Dissolved (<0.2 μm) and particulate (>0.2 μm) Co showed non-conservative mixing behavior with low or mid-salinity maxima within those two estuarine regions, indicating benthic remobilization and/or sewage input apart from riverine input during the estuarine mixing. These results are supported by a suite of complementary measurements of other parameters, such as manganese, phosphate, and suspended particulate matter concentrations. In addition, the concentration ratio of dissolved Co to total Co (dissolved plus particulate) increased along the salinity gradient, implying the potential for desorption of this metal from suspended particulate matter on estuarine mixing.

To identify desorption of this metal from suspended particulate matter by salinity changes, laboratory desorption experiments were undertaken by mixing unfiltered river water and filtered estuarine water samples with a different volume of each water sample. The mixed water samples for the experiments had different salinity values of 4.0, 17, and 30. Although dissolved Co and particulate Co concentrations at salinity 4.0 were almost constant from 2 min after starting the experiment to 120 h, dissolved Co concentrations at salinities 17 and 30 increased with time in the experimental period. Declines in particulate Co concentrations were observed in those salinities. Also, a relatively high percentage of Co in the solid phase at salinity 30, as compared to the percentage at salinities 4.0 and 17, was desorbed from the particles. Furthermore, these experiments showed the potential for desorption of Co from riverine suspended particulate matter. It is suggested that changes in salinity contributed to the particle-solution exchange of Co. Thus, the combination of benthic remobilization, desorption from suspended particulate matter, and/or sewage input could be responsible for the non-conservative behavior of Co during the estuarine mixing in both estuarine areas.

1. Introduction

Cobalt (Co) is one of the biologically and geochemically important trace metals in the ocean (e.g., Martin et al., 1989; Bruland et al., 1991; Sunda and Huntsman, 1995; Saito et al., 2005; Krishnan et al., 2007; Panzeca et al., 2009). Although rivers are important pathways for the transport of Co to the ocean, in estuary boundary regions between rivers and the ocean, there are complicated processes affecting the behavior of this metal. For example, Co is introduced into estuaries from other sources (atmospheric input, remobilization from benthic and resuspended sediments, and industrial and municipal effluents) during the mixing of river water and seawater (Chiffoleau et al., 1994; Tovar-Sánchez et al., 2004; Radakovitch et al., 2008). In addition, transport of Co from rivers and estuarine areas could be dependent on the partitioning of this metal between dissolved and particulate phases (Martino et al., 2002; Tovar-Sánchez et al., 2004). This partitioning could be modified by several factors such as, the specific metal ion, metal concentration, pH, salinity, and dissolved oxygen (Stumm, 1992). Particle scavenging (Achterberg et al., 1999) and biological uptake would be important removal processes. Thus, the influence of these biogeochemical processes on the Co budget to the ocean is now being recognized.

In estuarine areas, particles can lead to additional metal release to the dissolved phase due to desorption of metals by salinity changes (e.g., Kraepiel et al., 1997). Desorption of metals can arise

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from riverine, resuspended or advected particulate matter. For Co, an increasing number of studies have shown that benthic flux (addition of metal-enriched pore water to the overlying water column, and resuspension of metal-enriched fine bed sediment) and sewage inputs could also affect Co distributions during estuarine mixing (Martino et al., 2002; Tovar-Sánchez et al., 2004; Audry et al., 2006; Santos-Echeandia et al., 2009). Furthermore, it has been reported that resuspension of metal-enriched, fine bed sediment may be a significant agency for Co remobilization during estuarine mixing (Chiffoleau et al., 1994; Martino et al., 2002). Thus, the potential for the desorption of Co which is attributable to riverine suspended particulate matter is not yet fully understood.

There are some studies available in the literature concerning the behavior of Co in estuaries (e.g., Chiffoleau et al., 1994; Martino et al., 2002; Tovar-Sánchez et al., 2004); however, published reliable data are scarce regarding Japanese estuarine waters (e.g., Akagi and Haraguchi, 1984). This study is an opportunity to establish the baseline status for this metal in Japanese estuarine areas in particular and estuarine areas in general. Here, we present Co concentration data for filtered (0.2 μm) and unfiltered water samples which were collected from two Japanese estuarine areas, northern Sagami Bay connected to the Sagami River and southwestern Wakasa Bay connected to the Yura River. Our aim is to investigate processes affecting the behavior of Co in these two estuarine areas. Data for water samples with manganese, which is a tracer for benthic sources (Chiffoleau et al., 1994; Roitz et al., 2002; Tovar-Sánchez et al., 2004), are also presented. The comparative distributions of Co and Mn are keys to a better understanding of the processes controlling Co behavior in these areas. In addition, laboratory desorption experiments were performed in order to elucidate desorption of Co from riverine suspended particulate matter by salinity changes. These experiments simulated estuarine mixing of river and saline waters, and can provide convincing evidence about the potential for desorption of this metal from riverine suspended particulate matter.

2. Experimental

2.1. Study area

The Sagami River (1680 km^2 catchment area; 109 km total length; 100 m^3/s mean annual freshwater discharge) is one of the rivers flowing into Sagami Bay (a surface area of approximately 2300 km^2), which lies south of Kanagawa Prefecture in Honshū, central Japan (Fig. 1). Monthly mean flow ranges from $<$100 m^3/s to $>$100 m^3/s during the spring (April–June) and summer–autumn (July–November) seasons, respectively. The freshwater wedge can extend 5–10 km into Sagami Bay. The land-uses of the lower catchment are agricultural and developed urban areas. The population of the lower catchment is approximately 2 million (Iwashita and Shimamura, 2003). Using Japanese environmental standards (Environment Agency of Japan, 1971) for many chemical species in ambient water established by the former government agency, now the Ministry of the Environment, it can be considered that heavy metal pollution in the river upstream is not a serious problem (Iwashita and Shimamura, 2003). Sewage farms are located between Stn 2 and Stn 3. We observed the northern Sagami Bay from three stations (i.e. Stns 1, 2, and 3) downstream in the river mouth to a final estuarine area station (Stn 16) at a 10 km distance from the river mouth.

Wakasa Bay is located on the Japan Sea side of Honshū and has a surface area of approximately 135 km^2 (Shiki, 1985). This southwestern Wakasa Bay area (Fig. 1) is predominantly affected by water discharge from the 146-km-long Yura River (37 m^3/s mean annual freshwater discharge (Shiki, 1985)). Monthly mean discharge varies within the range between 10 m^3/s and 60 m^3/s. The tidal excursion can reach between $<$2 and 5 km into the estuarine area under high- or low-flow river conditions. The land-use in the Yura River catchment is mostly as forest, with minor portions devoted to agriculture, stock farming, and urban development. Since there are no chemical and sewage plants downstream on the Yura River and in the estuarine area, contaminant discharges to the estuarine area from such plants are not serious problems.

2.2. Sampling

Sampling locations are shown in Fig. 1. One or two surface water samples at each station were collected from two estuarine areas, northern Sagami Bay connected to the Sagami River (sampling months: June, August, and November 2008) and southwestern Wakasa Bay connected to the Yura River (sampling months: July, September, and November 2007) using an acid-cleaned, Teflon-coated 5 L horizontal Niskin X water sampler (General Oceanics) from a boat. The samples for the dissolved trace metals ($<$0.2 μm fraction) were filtered by gravity filtration into precleaned 250 mL low-density polyethylene (LDPE) bottles by connecting a precleaned 0.2 μm pore size polytetrafluoroethylene (PTFE) filter (capsule cartridge type, Advantec) to each sampling bottle spigot. Unfiltered water samples for total metals were obtained in precleaned 250 mL LDPE bottles. The filtered and unfiltered water samples (250 mL) for Mn and Co analyses were acidified to pH $<$1.5 with a 15.3 M nitric acid solution (0.5 mL per 250 mL sample). The acidified samples were kept at room temperature in the laboratory until the analyses. The rest of the water in the sampler was used for the measurements of suspended particulate matter (SPM), nutrient, dissolved organic carbon (DOC), and dissolved oxygen (DO) concentrations. Salinity and pH were measured at the sampling stations at the time of collection.

2.3. Laboratory experiments for simulation of estuarine mixing of river water and seawater

In September 2007, we obtained unfiltered and filtered river water samples (salinity: 0.75) from the Yura River (Stn 1) and filtered estuarine water samples (salinity: 33.4) at Stn 13 in southwestern Wakasa Bay for the desorption experiments. These water samples were stored in the dark without acidification until brought to the laboratory, where the unfiltered river water and the filtered estuarine water samples were mixed in 1 L reaction bottles in varying proportions in order to simulate the estuarine salinity gradient. Each sample solution was prepared by adding 100 mL, 500 mL, and 900 mL of filtered estuarine water to each 900 mL, 500 mL, and 100 mL of unfiltered river water in the bottle. Salinities for each bottle were 4.0, 17, and 30. These values were calculated based on data on the salinities and sample volumes of the unfiltered river and the filtered estuarine water samples. In addition, controls were prepared in other 1 L reaction bottles in which the filtered river and estuarine water samples were mixed to verify there was no removal of dissolved Co through adsorption onto the bottle walls. All the preparations and experiments were performed in a laminar flow cabinet to avoid inadvertent trace metal contamination.

Desorption experiments were started by introducing the unfiltered river water and the filtered estuarine water into the 1 L reaction bottles. The reaction bottles were shaken mechanically under a dark condition at 25 °C and the pH values were nearly constant within the range 7.8–8.2 during the experimental periods. At selected time intervals (2 min, 30 min, 2 h, 6 h, 24 h, 72 h, and 120 h) under these conditions, 60 mL aliquots were withdrawn from the reaction bottles and filtered using 0.2 μm pore size PTFE

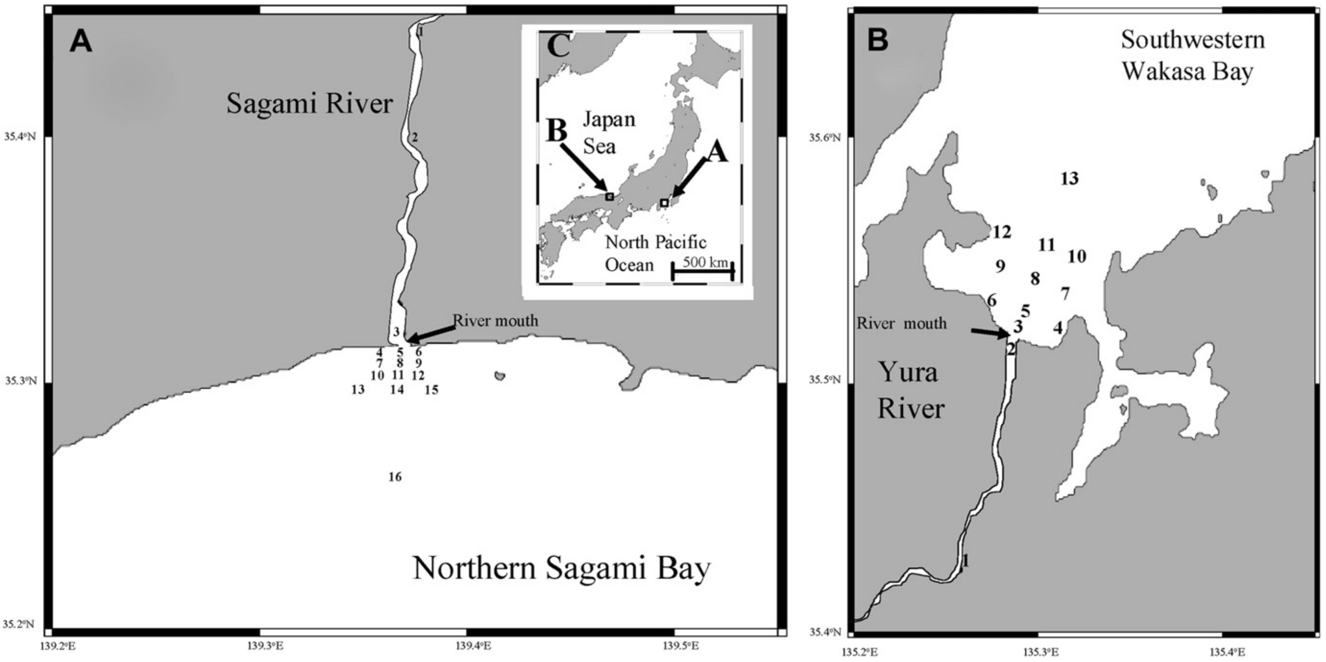

Fig. 1. Map of the locations of (A) northern Sagami Bay area, (B) southwestern Wakasa Bay area, and (C) the main Japanese islands. Station numbers are shown in both estuarine areas.

filters (H020A047A, Advantec). At the same sampling time, another 60 mL portion collected from each reaction bottle was also used as an unfiltered water sample. The filtered and unfiltered water samples were acidified to pH <1.5 with nitric acid and stored in the dark for Co analysis, which was carried out in triplicate for each sample. At the same time throughout the 120 h reaction period, samples were also withdrawn from the control bottles and were filtered using 0.2 μm filters to check the bottle wall adsorption. No evidence for wall adsorption or flocculation of colloids was observed during the experimental period.

2.4. Analysis in the water samples

Analyses for Co and Mn were performed on water samples by using solid-phase extraction with NOBIAS-CHELATE PA1 chelating resins (polyamines and polycarboxyl functional groups immobilized on hydrophilic methacrylates; Hitachi High-Tech.) and inductively coupled plasma mass spectrometer (ICP-MS), as described in Sakamoto et al. (2006) and Takata et al. (2009). In this study, we defined total and dissolved metals (<0.2 μm fraction) as those metals retainable on the NOBIAS-CHELATE resin in the unfiltered water samples and 0.2 μm filtrates, respectively, at pH 5.7 for Mn and Co. The concentrations of these two metals were determined by ICP-MS equipped with an octapole collision reaction cell (Agilent 7500c, Yokogawa Analytical Systems). A mixed rhodium (Rh) and bismuth (Bi) internal standard solution for ICP-MS was prepared by dilution of 1000 mg/L single standard solutions (CertiPUR, Merck). The accuracy of the analytical procedure was checked using a reference seawater material, CASS-4 (National Research Council of Canada), with the recoveries higher than 95%. This percentage was within the range of the respective certified values. The precision was estimated to be better than 10% at the trace metal concentrations in the reference seawater. Analytical blanks by measurement of deionized water from a Milli-Q water purification system (Millipore) ($n = 3$) were 0.0022 nM for Co and 0.01 nM for Mn, yielding detection limits (3σ) of 0.0046 nM for Co and 0.026 nM for Mn.

SPM concentrations in the water samples were determined by separate filtration under vacuum on 0.45 μm filters (GB-140, ADVANTEC). After filtration of the water samples, air-dried filters were weighed. The concentrations of silicate and phosphate were determined using an autoanalyzer (AACS–III, BLTEC). DOC samples were collected in a pre-combusted amber glass bottle and measurements were made using a catalytic high temperature DOC analyzer (Shimadzu, TOC 5000). We measured water pH with an Orion 1215000 compact pH meter (Thermo). DO was determined by the Winkler titration method with visual observation of the decoloration of the blue starch–iodine complex or potentiometric end-point using a Titrino analyzer (Metrohm, 798 MPT). Hydrographic data (sampling depth and salinity) were obtained using a CTD (Conductance-Temperature-Depth) recorder (Alec Electronics Co., ASTD 687).

3. Results and discussion

3.1. Hydrographic conditions

There were no remarkable differences in the pH values (range: 7.4–8.4) within the water samples in each estuarine area. DO and DOC were within narrow concentration ranges of 6.8–11.6 mg/L and 51–122 μM, respectively, in each estuarine area. For SPM, a slight increase in concentration was observed at stations near the mouth of the rivers in both estuarine areas (Fig. 2A and B). For northern Sagami Bay, the maximum for each sampling period was observed at Stn 3 (June and November) and Stn 5 (August) located near the mouth of the Sagami River. In addition, the relatively high SPM concentration observed at northern Sagami Bay in August (Fig. 2A), compared to other sampling periods, was attributed to well developed turbidity resulting from release of impounded water from the Miyagase dam upstream on the Sagami River. When SPM concentrations are plotted as a function of distance from the mouth of the river, a slight increase was observed near the mouth of the river at each sampling period (Fig. 3A). In southwestern Wakasa Bay, high SPM concentrations in July and November were observed

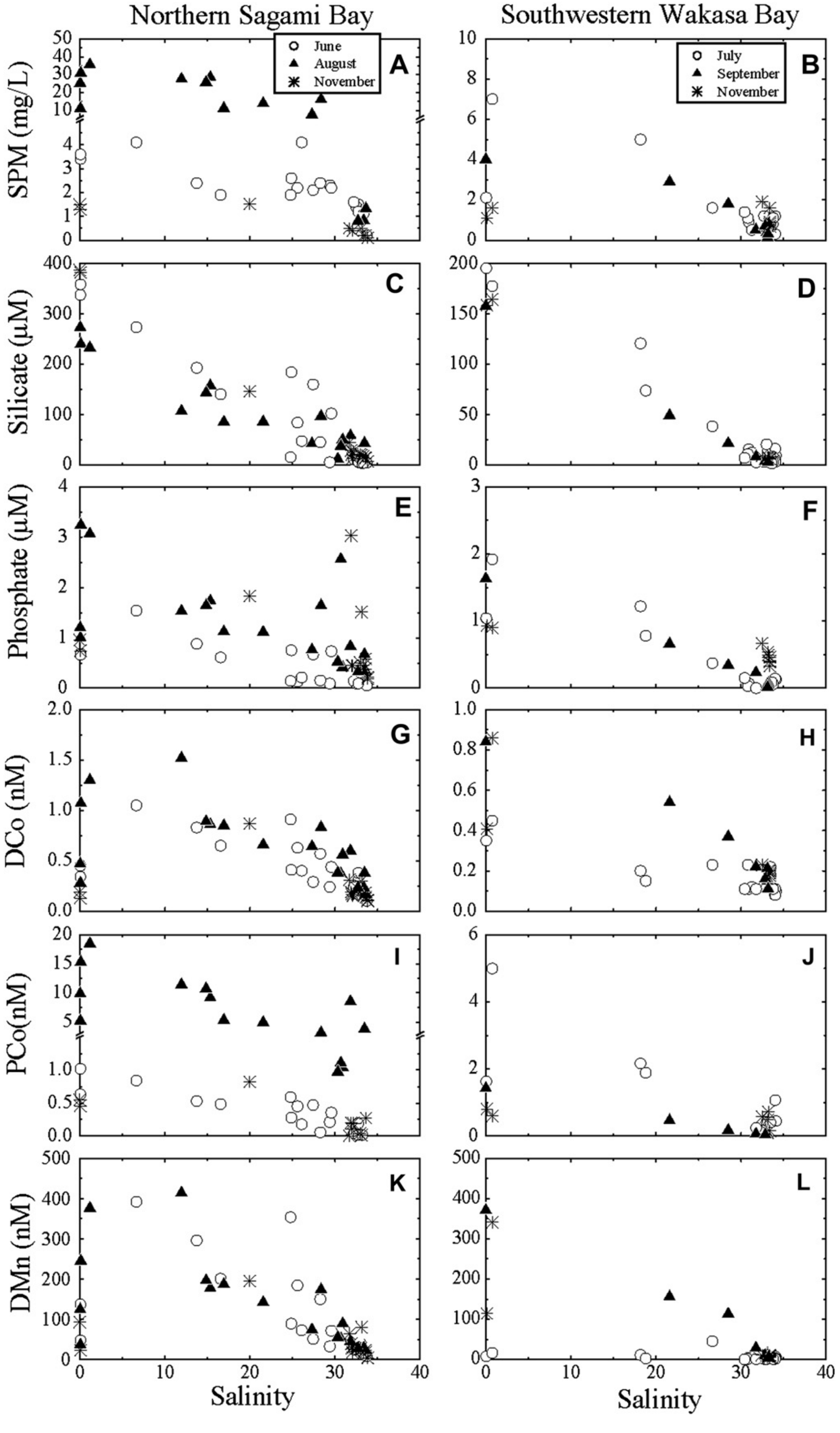

Fig. 2. (A, B) Suspended particulate matter (SPM), (C, D) silicate, (E, F) phosphate, (G, H) dissolved Co (DCo), (I, J) particulate Co (PCo), and (K, L) dissolved Mn (DMn) concentrations versus salinity in waters of northern Sagami Bay (left side figures) and southwestern Wakasa Bay (right side figures).

at Stn 2 located near the mouth of the river, compared to those at Stn 1 in the Yura River (Fig. 4A).

Distribution of silicate showed a decrease in concentration with increasing salinity in both estuarine areas (Fig. 2C and D). Silicate concentrations in the low salinity zone (<10) ranged between 240 μM and 388 μM and then decreased to less than 70 μM in the high salinity zone (>30) in northern Sagami Bay. Similar distributions were also observed in southwestern Wakasa Bay. No significant increase in the concentrations was observed during each sampling period near the mouths of the rivers in both estuarine areas (Figs. 3B and 4B). At each estuarine area, silicate appeared to display conservative behavior, indicating that riverine input is its main source. This behavior in estuaries has been reported previously (Maeda, 1952, 1953; Chiffoleau et al., 1994).

Concentrations of phosphate showed a non-conservative distribution in northern Sagami Bay during each sampling period (Fig. 2E). Phosphate concentrations in Stns 3, 5, and 6 near the mouth of the Sagami River were differentiated from Stns 1 and 2 in the Sagami River by the increasing concentrations of phosphate (Fig. 3C). In southwestern Wakasa Bay, a slight increase in phosphate concentration was observed at Stn 2 located near the mouth of the Yura River in July (Fig. 4C), in association with an increase in SPM concentration (Fig. 4A).

3.2. Cobalt and manganese

3.2.1. Northern Sagami Bay

Dissolved Co in northern Sagami Bay plotted as a function of salinity had non-conservative distributions, characterized by maxima at salinities between 0.1 and 20 and by subsequent decrease with increasing salinity during three sampling periods (Fig. 2G). The highest concentration of dissolved Co at each sampling period was found at Stn 3 (June: 1.05 nM; and November: 0.87 nM) and at Stn 6 (August: 1.52 nM) (Fig. 3D). Both stations were located near the mouth of the Sagami River (Fig. 1). The concentration of particulate Co with low or mid-salinity showed maxima and then a decrease (Fig. 2I); this behavior was similar to that of dissolved Co, indicating that high levels of Co were affected by the presence of an additional source or sources (e.g., remobilization from benthic and resuspended sediments, industrial and municipal effluents, and desorption from riverine suspended particulate matter) near the mouth of the river.

In this study, slight increases in SPM concentrations (Fig. 3A) were observed between Stns 2 and 5 near the mouth with shallow water depth (<5 m) where the flow of the river and tide (tidal range: ~ 2 m) form a high turbidity zone, resulting in the addition of sedimentary particles from the seabed. Dissolved Mn (as a tracer of benthic flux) concentrations at each sampling period were also higher than those of other stations (Fig. 3E) in association with the increase in Co concentrations at the stations. Similar behavior has been found for estuarine and coastal waters where high concentrations of those two metals were observed in a high turbidity zone, and increases in metal concentrations were thought to be related to the additional sources (Chiffoleau et al., 1994; Martino et al., 2002; Tovar-Sánchez et al., 2004). In this study, additional metal release to the dissolved phase would be partially related to the occurrence of benthic remobilization. Dissolved Co and Mn exhibited addition on estuarine mixing, and it was more intense than for SPM. Dissolved Co and Mn concentrations at Stn 3 were more than twice those at Stn 2 during three sampling periods, while a 2–22% increase in SPM concentrations was observed between Stn 2 and Stn 3. In addition, dissolved Co and Mn distributions were not always similar to SPM distributions in northern Sagami Bay. For example, in August, the SPM maximum was at Stn 5 though Mn and Co maxima were seen at Stn 6.

Sewage discharge might also influence high Co concentrations in estuarine areas (Tovar-Sánchez et al., 2004). Yamada and Matsushita (2006) argued that sewage discharge mostly contributed to the elevated phosphate concentrations near the mouth of the Sagami River. In this study, phosphate did not correlate with either dissolved Co or Mn in northern Sagami Bay ($r < 0.7$, $p < 0.1$). For Mn, data from existing studies suggest that anthropogenic inputs have little influence on estuarine dissolved Mn distributions, even in heavily urbanized estuaries (Yang and Sanudo-Wilhelmy, 1998; Roitz et al., 2002). However, dissolved Co concentrations and even dissolved Mn concentrations in all the sampling periods increased between Stn 2 and Stn 3 (sewage farms are located between those two stations), and the values at Stn 3 were more than twice those at Stns 1 and 2 (Fig. 3D and E). Similarly, the difference in phosphate concentration between Stn 2 and Stn 3 in each sampling period was a factor of more than 2 (Fig. 3C). The similarity of phosphate, dissolved Co, and dissolved Mn behaviors near the mouth of the Sagami River infers that sewage input would also be responsible for the elevated Co and Mn concentrations near the mouth of the river.

3.2.2. Southwestern Wakasa Bay

Dissolved and particulate Co concentrations as a function of salinity showed some variations at low salinity (Fig. 2H and J). Compared to concentrations of Co at Stn 1, relatively high concentrations of dissolved Co at Stn 2 were observed in July and November. This phenomenon was consistent with higher concentrations of dissolved Mn (Fig. 2L) and SPM (Fig. 2B), indicating additional sources of Co during the mixing of river water and seawater. Since there are no chemical plants or sewage farms near the mouth of the Yura River, benthic remobilization and desorption from suspended particulate matter could be important for explaining the excess of dissolved metals observed in these sampling periods.

When dissolved Co and Mn concentrations were plotted as a function of distance, behaviors of those two metals were remarkably different in each sampling period (Fig. 4D and E). Dissolved Co and dissolved Mn concentrations in July slightly increased between Stns 1 and 2 (dissolved Co: 0.35 nM–0.45 nM; dissolved Mn: 8.7 nM–16.2 nM), respectively, where SPM concentrations rapidly increased from 2.1 mg/L to 7.0 mg/L between them. In contrast, in November, rapid increases in dissolved Co and dissolved Mn concentrations were observed between these stations, while SPM concentrations increased slightly. Furthermore, dissolved Mn concentrations at Stns 1 and 2 were more than 10 times higher in September and November than in July, while dissolved Co concentrations were approximately three times higher. These results would be related to seasonal differences in the redox conditions and the extent of benthic flux in the estuarine sediments. It has been reported that benthic metal fluxes influence levels of heavy metals in shallow overlying estuarine water and pore water (Johnson et al., 1988, 1992; Audry et al., 2006; Santos-Echeandia et al., 2009). For Mn, high dissolved concentrations are thermodynamically permissible under sub-oxic and anoxic conditions where reduction of oxidized solid phases is favored (Yeats and Strain, 1990; Rue et al., 1997). Seasonal differences in dissolved Mn concentrations are also related to primary production and the extent of benthic flux (Roitz et al., 2002). In this study, high dissolved Mn concentrations in the Yura River in September and November would be due to the mixing of manganese-rich pore water with the overlying water. In July, dissolved Mn exhibited addition on estuarine mixing; this would be less intense than that in the other sampling months.

The release of Co into the pore water also occurs in the sediment (sub-oxic or anoxic condition) and concomitantly to the reductive

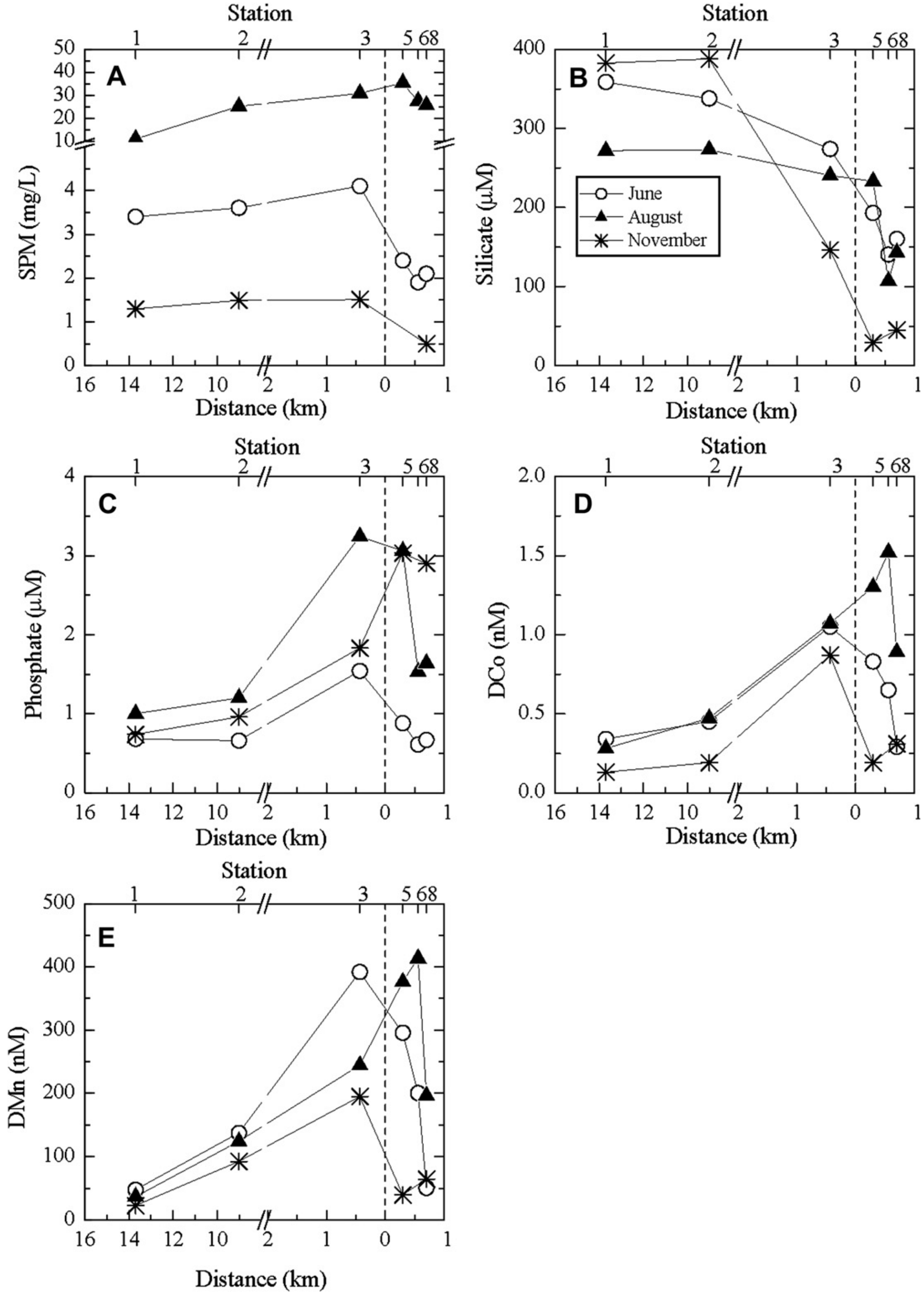

Fig. 3. Master variables in northern Sagami Bay as a function of distance from the mouth of the Sagami River (0 km); (A) suspended particulate matter (SPM), (B) silicate, (C) phosphate, (D) dissolved cobalt (DCo), and (E) dissolved manganese (DMn) concentrations. Dashed lines indicate the mouth of the Sagami River. To the left of the dashed line is the fluvial area, including Stns 1–3. To the right of the dashed line is the estuarine area, including Stns 5, 6, and 8.

dissolution of Mn oxides. Co is released from sediments associated with Mn oxides into the pore water when Mn oxides are reduced. This mechanism was described previously by, for example, Santos-Echeandia et al. (2009). In addition, they estimated benthic flux of dissolved Co and the main riverine dissolved Co input in the Vigo Ria estuarine area (Spain), and concluded that riverine input is more important than the benthic flux (this flux represented approximately 15% of the main riverine input). In this study, benthic remobilization leading to variation of the dissolved Co concentration appeared to be responsible for the elevated dissolved Co concentrations, although this might be less intense than that for dissolved Mn. Therefore, seasonal differences in dissolved Co concentrations would be less pronounced in southwestern Wakasa Bay.

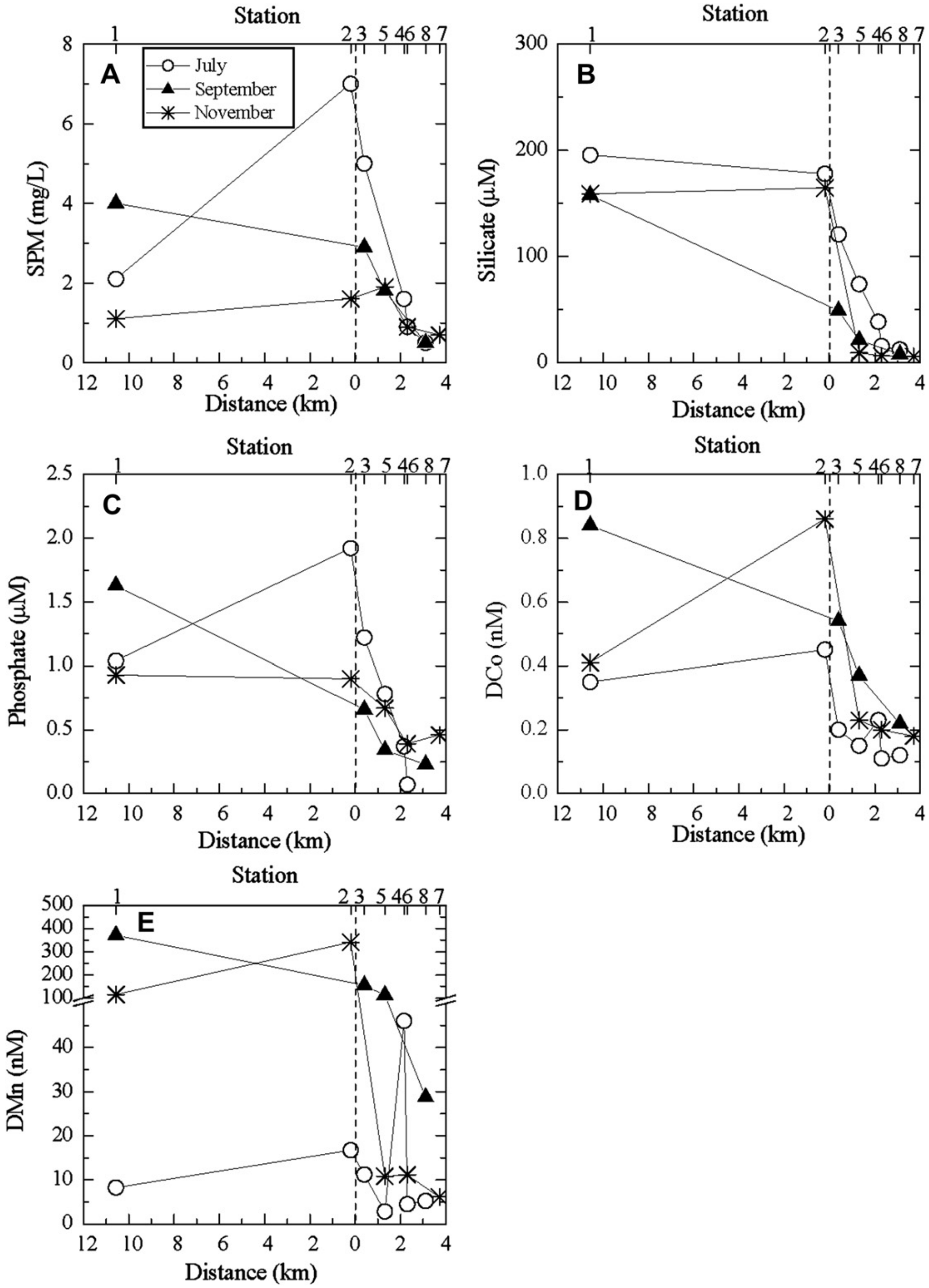

Fig. 4. Master variables in southwestern Wakasa Bay as a function of distance from the mouth of the Sagami River (0 km) during the three surveys: (A) suspended particulate matter (SPM), (B) silicate, (C) phosphate, (D) dissolved cobalt (DCo), and (E) dissolved manganese (DMn) concentrations. Dashed line indicates the mouth of the Yura River. To the left of the dashed line is the fluvial area, including Stns 1 and 2. To the right of the dashed line is the estuarine area, including Stns 3, 4, 5, 6, 7, and 8.

3.3. Comparison of Co and Mn behaviors in estuarine mixing

It has been reported that behavior of dissolved Co is similar to that of dissolved Mn in estuarine and coastal waters (Chiffoleau et al., 1994). In this study, dissolved Mn had non-conservative mixing behavior in northern Sagami Bay and southwestern Wakasa Bay (Fig. 2K and L). Similar non-conservative patterns were observed for dissolved Co in those two areas (Fig. 2G and H). When dissolved Co/dissolved Mn concentration ratios, however, were plotted as a function of salinity, the ratios in both estuarine areas differed along the salinity gradient (Fig. 5A and B). The concentration ratios were in the narrow value range of 2.0×10^{-3}–7.7×10^{-3} within a low salinity

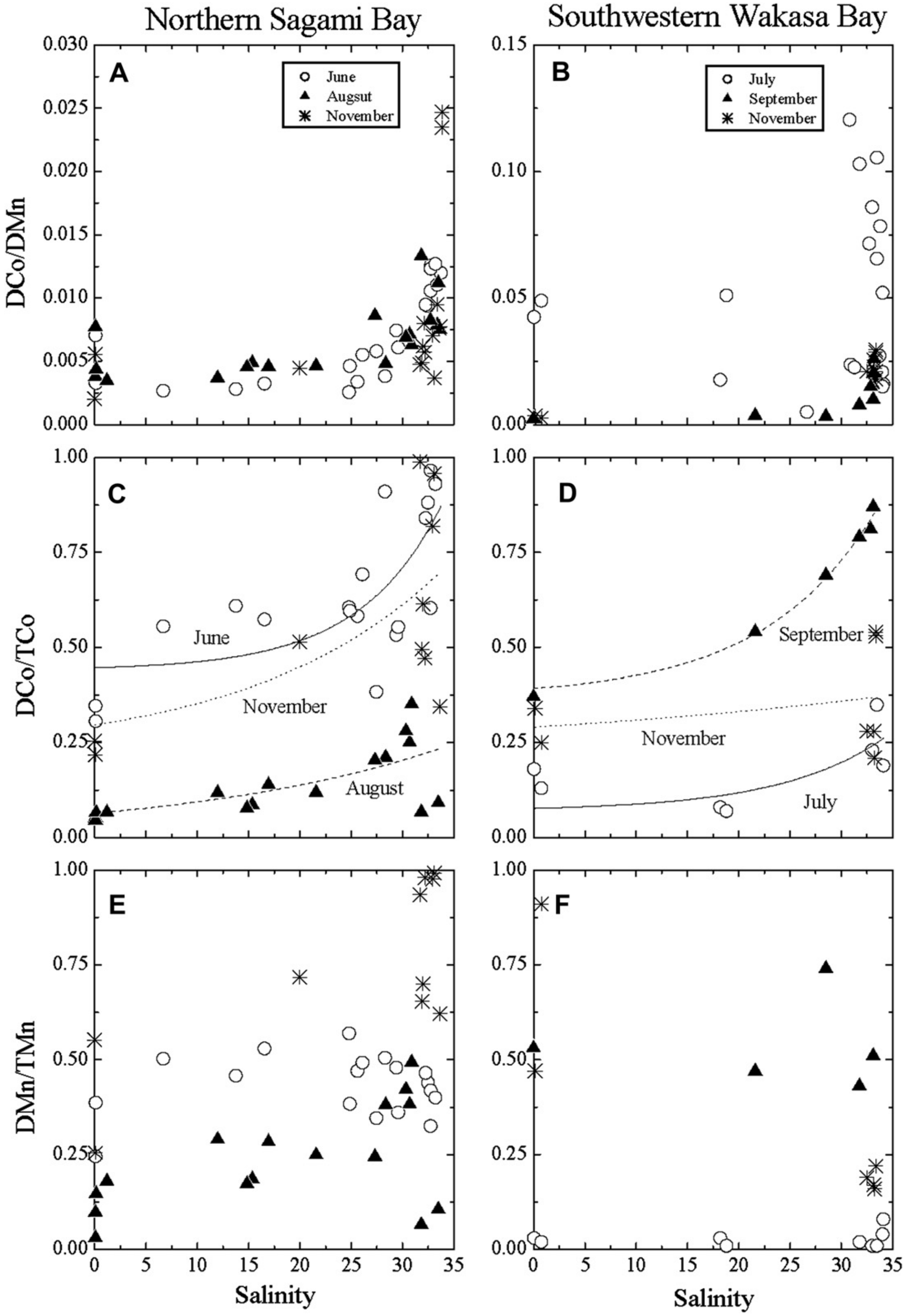

Fig. 5. (A, B) dissolved Co/dissolved Mn concentration ratio (DCo/DMn), (C, D) dissolved Co/total Co concentration ratio (DCo/TCo), and (E, F) dissolved Mn/total Mn concentration ratio (DMn/TMn) versus salinity in northern Sagami Bay (left side figures) and southwestern Wakasa Bay (right side figures) waters. Fitted lines are best-fit, exponential regression between the 2 parameters.

range between 0 and 10 in northern Sagami Bay during each sampling period, and then the ratios increased with salinity. In southwestern Wakasa Bay, dissolved Co/dissolved Mn concentration ratios (mean: 4.2×10^{-2}) in the high salinity zone (>30) were higher than those (mean: 1.6×10^{-2}) in the low salinity zone (<10). The increase in the ratios suggested that there was decoupling between dissolved Co and dissolved Mn during the estuarine mixing. Different processes could control those two metal behaviors during the estuarine mixing. For example, it has been assumed that there is a competition between complexation of metals to organic

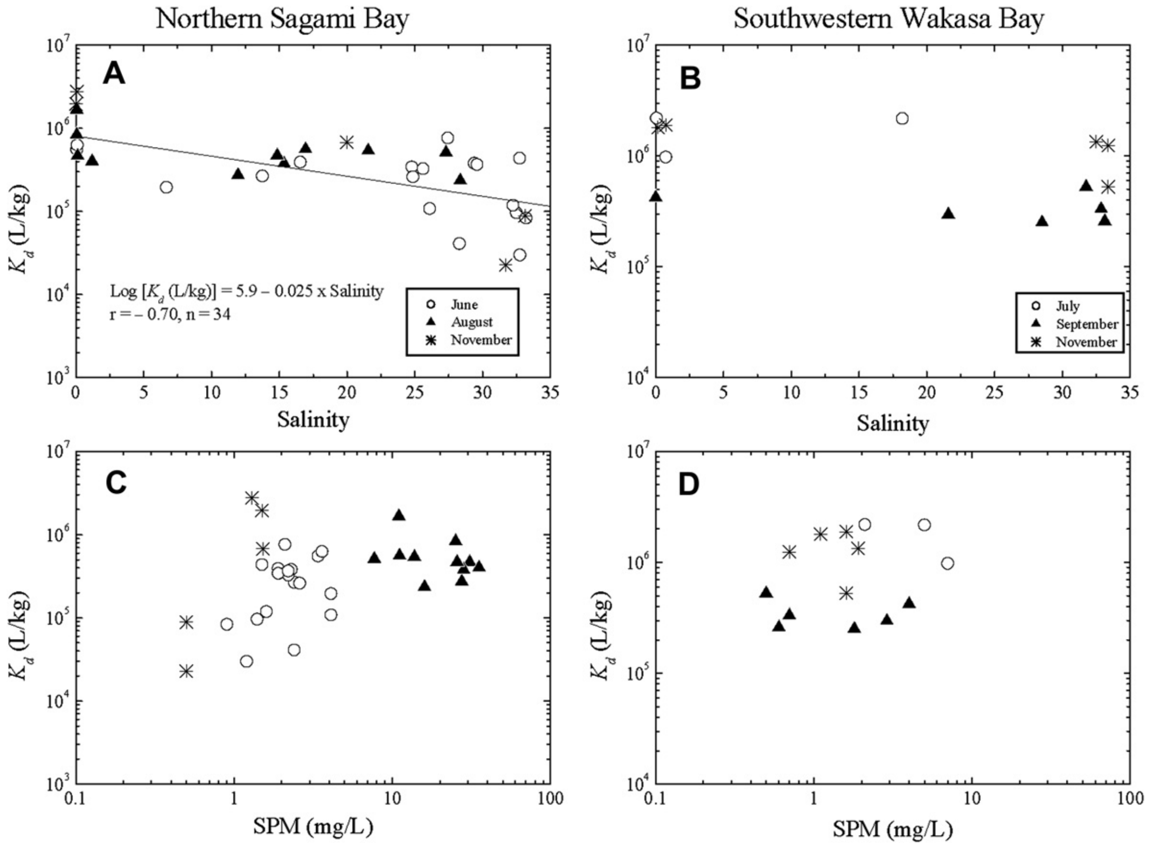

Fig. 6. (A, B) Partition coefficient, K_d, of Co versus salinity and (C, D) K_d of Co versus SPM in northern Sagami Bay (left side figures) and southwestern Wakasa Bay (right side figures) waters.

ligands, which would hinder metal removal by particle scavenging (e.g., Santschi et al., 1997). Although dissolved Mn concentrations in oxygenated waters should be extremely low (Balzer, 1982), benthic flux can raise the concentration of dissolved Mn released through a reduction in bed sediment where the magnitude of release of Mn may be assisted by changes in pH and redox conditions, or by bacterial or chemical degradation of particulate organic matter (Johnson et al., 1992; Rue et al., 1997; Roitz et al., 2002). In addition, since the complexation of Mn with organic ligands is considered to be relatively inconsequential in natural waters (e.g., Roitz and Bruland, 1997) and Mn is a particle reactive metal (Evans et al., 1977), dissolved Mn can be immediately removed from the water column by sorption onto particles (Hunt, 1983). For Co, several studies have indicated the presence of Co binding ligands (e.g., Ellwood and van den Berg, 2001; Saito and Moffett, 2001). Some organic matter, especially in heavily urbanized estuaries like the San Francisco Bay estuary, could contain high levels of anthropogenic ligands (Ndung'u et al., 2003). Although the composition of DOC was not examined, DOC concentrations in northern Sagami Bay and southwestern Wakasa Bay (DOC value range: 51–122 μM) were lower than those in other developed estuarine and coastal areas (Martino et al., 2002; Ndung'u et al., 2003). Therefore, complexation of Co with organic ligands could be less important in both our studied estuarine areas.

Particle-solution exchange during estuarine mixing (Yang and Sanudo-Wilhelmy, 1998; Martino et al., 2002; Tovar-Sánchez et al., 2004) is another possible reason for the decoupling in both estuarine areas. Although both dissolved Co and particulate Co showed non-conservative behaviors along the salinity gradient in northern Sagami Bay (Fig. 2G and I), the ratio of dissolved Co concentration to total Co concentration in each sampling month showed that dissolved Co was progressively enriched along the salinity gradient (Fig. 5C), implying desorption of Co from particles. In southwestern Wakasa Bay, the ratios in the high salinity zone (salinity of >30) were higher than those in the low salinity zone (salinity of <10) during each sampling period (Fig. 5D). Conversely, since dissolved Mn/total Mn ratios were nearly independent of salinity in northern Sagami Bay (June and August) and southwestern Wakasa Bay (Fig. 5E and F), it was less evident that Mn was desorbed from suspended particulate matter at the freshwater/seawater interface. Moreover, comparing the ratios of concentration of dissolved metal to that of total concentration for those two metals in northern Sagami Bay in June and in southwestern Wakasa Bay in September, we saw the ratios for Co tended to increase along the salinity gradient; however, those for Mn were scattered. It was likely that a particle-solution exchange during the estuarine mixing would also be attributable to the decoupling between Mn and Co, and that Co was released from suspended particulate matter in response to salinity changes during the estuarine mixing.

3.4. Desorption process for cobalt

Desorption of Co from suspended particulate matter is another possible source of dissolved Co in northern Sagami Bay and southwestern Wakasa Bay. To evaluate the desorption process partition coefficient K_d (L/kg) of Co was obtained. The partitioning of a metal between the particulate and dissolved phases is commonly quantified in terms of K_d (Balls, 1988; Benoit et al., 1994). High particle reactivity for a metal tends to increase with the K_d value. Since K_d is a measure of the tendency of a metal to be associated and transported with the particulate phase, it is an important factor in biogeochemical processes between particulate and dissolved phases in estuarine water. The K_d of a particular metal between the dissolved and particulate fractions is defined as the ratio of the trace metal concentration in suspended particulate matter (X, in mol/kg) to that in the filter-passing fraction (D, in mol/L), as given in Eq. (1).

$$K_d = X/D \tag{1}$$

The K_d values of Co in northern Sagami Bay were in the range of 2.3×10^4–2.8×10^6 and tended to decrease with increasing salinity (Fig. 6A). A similar decline in K_d values of Co along the salinity gradient has been reported in the Hudson River estuary and San Francisco Bay by Tovar-Sánchez et al. (2004). They argued that the decline was due to the release of Co from suspended particulate matter in response to salinity changes during estuarine mixing. The K_d values of Co as a function of salinity tended to decrease in both estuaries as seen in the correlations between K_d and salinity ($\log K_\mathrm{d} = 5.81 - 0.03 \cdot$Salinity: Hudson River estuary; $\log K_\mathrm{d} = 5.92 - 0.02 \cdot$Salinity: San Francisco Bay) (Tovar-Sánchez et al., 2004). The correlation in each estuary was similar to that in northern Sagami Bay (Fig. 6A). In southwestern Wakasa Bay, the K_d values in the high salinity zone (mean $\log K_\mathrm{d}$: 5.9) were slightly lower than those in the low salinity zone (mean $\log K_\mathrm{d}$: 6.2). The K_d values seemed to be slightly dependent on salinity (Fig. 6B).

Some previous studies have demonstrated inverse linear relationships between metal $\log K_\mathrm{d}$ value and SPM concentration when SPM concentration is plotted on a log scale (Tang et al., 2002 and references therein). These relationships are explained by the particle concentration effect which is attributed to an increased colloid concentration in the filtered fraction in proportion to the quantity of suspended particles retained by the filter (Tang et al., 2002). Inverse linear $\log K_\mathrm{d}$ versus SPM relationships for metals suggest operation of the particle concentration effect in estuaries. In contrast, a positive correlation for metals is likely due to desorption reactions occurring during estuarine mixing (Tang et al., 2002). In this study, little dependency of $\log K_\mathrm{d}$ value on SPM concentration was observed in both estuarine areas (Fig. 6C and D). It appeared that the particle concentration effect was less pronounced in them. As described in Section 3.2, the distribution and biogeochemical behavior of dissolved Co in both estuarine areas were functions of the complex dynamics of those environments. Other additional mechanisms (i.e. benthic flux and/or sewage input) could also account for the non-conservative excess of dissolved Co observed along the salinity gradient of both estuarine areas. Therefore, we thought that relationships between $\log K_\mathrm{d}$ and SPM concentration did not show clear evidence for the particle concentration effect.

3.5. Laboratory experiments: implication of desorption of Co from riverine suspended particulate matter

Although riverine suspended particulate matter may supply a substantial source of SPM in estuarine waters, desorption of Co can arise from resuspended or advected particulate matter as well as riverine particulate matter. Moreover, resuspension of metal-enriched bed sediment could be an agency for Co remobilization in estuarine mixing. Thus, the importance of desorption from riverine suspended particulate matter as an additional source of this metal is not well known. We performed a series of experiments to investigate desorption of Co from riverine suspended particulate matter in the river water at different salinity values. The experiments were undertaken using unfiltered river water and filtered estuarine water samples collected in this study, which were mixed at different amounts to simulate the estuarine salinity gradient. The mixed water samples for the experiments had different salinity values of 4.0, 17, and 30.

Fig. 7 shows the time-dependent behavior of dissolved Co and particulate Co concentrations. At salinity 4.0, dissolved Co was approximately constant throughout the experimental period. Dissolved Co concentrations at salinity 17 slightly increased from 0.15 nM at 2 min to 0.19 nM at 6 h. The increase in dissolved Co concentrations after 120 h in the reaction bottle was approximately 15%. At salinity 30, the increase in dissolved Co concentrations was approximately 86% during the 120 h experimental period. Enrichment of Co in the dissolved phase could be accounted for by the loss of Co in the particulate phase, as total Co concentrations in all the reaction bottles were nearly almost constant.

For salinity 4.0, high particulate Co concentrations were measured (mean value: 0.47 nM) in the water samples, while significant desorption of Co from riverine suspended particulate matter was not observed during the experimental period (120 h) (Fig. 7A). At salinity 30, although the water samples contain low particulate Co and high salinity, an increase in dissolved Co concentrations and a decrease in particulate Co concentrations were clearly observed during the

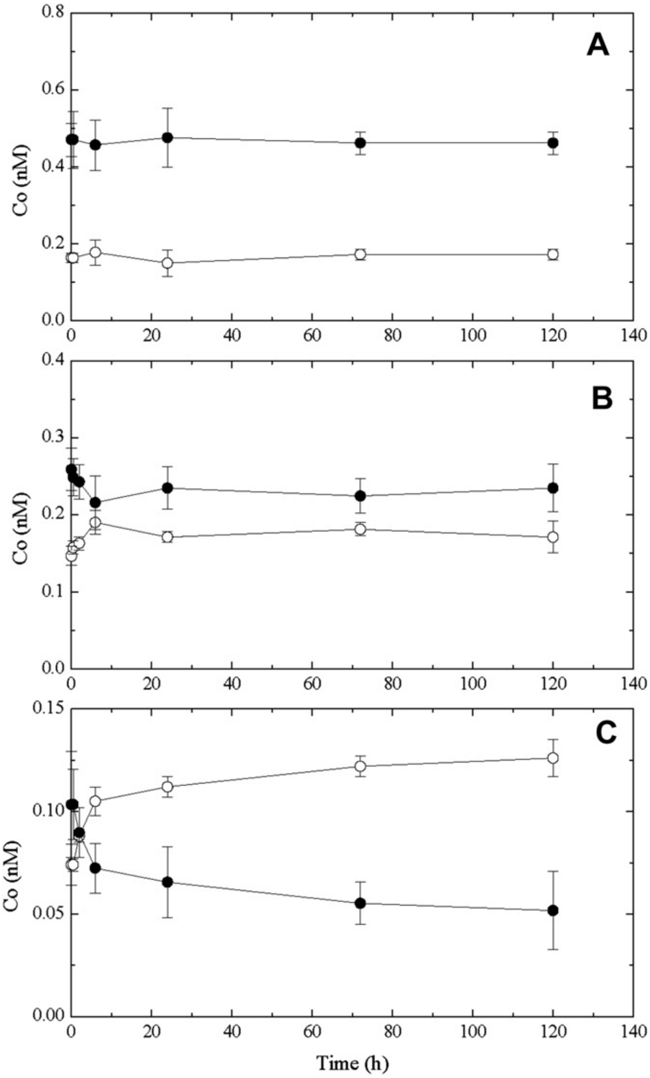

Fig. 7. Dissolved Co and particulate Co concentrations versus time for salinities (A) 4.0, (B) 17, and (C) 30. Open and solid circles indicate dissolved and particulate Co, respectively. The error bars are the result of three analyses. Initial conditions: dissolved Co concentrations were about 0.16 nM, 0.15 nM, and 0.07 nM for salinities, 4.0, 17, and 30. Dissolved Co comprised about 26%, 36%, and 42% of total Co for salinities, 4.0, 17, and 30.

experimental period (Fig. 7C). Desorption of Co from particles seemed to be an important source of the increase in dissolved Co concentration. The apparent desorption of Co could be explained by the presence of seawater ions and/or dissolved organic ligands in seawater. There is competitive adsorption by seawater cations and the formation of stable and soluble chloro-, sulphato-, and carbonato-complexes, and/or complexation with dissolved organic ligands in seawater. The effects of competitive adsorption and complexation reflect the changes in salinity. In this study, approximately 10% and 50% of Co in the particulate phase at salinities 17 and 30 were desorbed through the process during the experimental period. The higher percentage of desorption of Co at higher salinity indicated that changes in salinity contributed mainly to the particle-solution exchange of Co.

Additionally, at salinity 30, although most of the Co was desorbed from riverine suspended particulate matter within 6 h, after that, dissolved Co increased slightly with increasing reaction time (Fig. 7C). The desorption behavior of metals is dependent on the chemical composition of riverine suspended particulate matter and the speciation of the sorbed metal. For example, in laboratory experiments, Comans and Van Dijk (1988) equilibrated ^{109}Cd labeled particles in media of varying salinity and over a few days observed a reversible desorption of Cd which increased with salinity. It has been usually believed that Cd, which is loosely held on a particle surface, readily undergoes rapid exchange and chloro-complexation (Turner et al., 1993; Schlekat et al., 1998). The relatively slight increase in dissolved Co concentrations in this study indicated that some Co would bind tightly to Fe or Mn (hydro) oxides and particulate organic matter, and be more resistant to desorption.

4. Conclusions

Rapid increases in dissolved Co and particulate Co concentrations were observed near the mouth of the Sagami River in northern Sagami Bay. In southwestern Wakasa Bay, riverine inputs were insufficient to account for the relative excesses of Co near the mouth of the Yura River in July and November sampling months. The ratio of concentration of dissolved Co to that of total Co showed that dissolved Co was progressively enriched along the salinity gradient. Furthermore, the partition coefficient, K_d, values of Co in northern Sagami Bay appeared to decrease with increasing salinity.

Benthic remobilization and/or sewage inputs appeared to be responsible for the elevated Co concentrations in shallow overlying estuarine waters near the mouths of these two rivers. In addition, laboratory desorption experiments showed that most of the Co was desorbed from riverine suspended particulate matter at high salinities, suggesting that the desorption process (competitive adsorption by seawater cations and the occurrence of complexation with seawater materials) involved in salinity changes also contributed to the non-conservative behavior of Co during the estuarine mixing in both estuarine areas.

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References

Achterberg, E.P., Colombo, C., van den Berg, C.M.G., 1999. The distribution of dissolved Cu, Zn, Ni, Co and Cr in English coastal surface waters. Continental Shelf Research 19, 537–558.

Akagi, T., Haraguchi, H., 1984. Distribution and behaviors of trace heavy metals in the Tama River estuary and Tokyo Bay. Chikyu Kagaku 18, 81–88 (in Japanese, with English abstract).

Audry, S., Blanc, G., Schäfer, J., Chaillou, G., Robert, S., 2006. Early diagenesis of trace metals (Cd, Cu, Co, Ni, U, Mo, and V) in the freshwater reaches of a macrotidal estuary. Geochimica et Cosmochimica Acta 70, 2264–2282.

Balls, P.W., 1988. The control of trace metal concentrations in coastal seawater through partition onto suspended particulate matter. Netherlands Journal of Sea Research 22, 213–218.

Balzer, W., 1982. On the distribution of iron and manganese at the sediment/water interface: thermodynamic versus kinetic control. Geochimica et Cosmochimica Acta 46, 1153–1161.

Benoit, G., Oktay-Marshall, S.D., Cantu II, A., Hood, E.M., Coleman, C.H., Corapcioglu, M.O., Santschi, P.H., 1994. Partitioning of Cu, Pb, Ag, Zn, Fe, Al, and Mn between filter-retained particles, colloids and solution in six Texas estuaries. Marine Chemistry 45, 307–336.

Bruland, K.W., Donat, J.R., Huchins, D.A., 1991. Interactive influences of bioactive trace metals on biological production in oceanic waters. Limnology and Oceanography 36, 1555–1577.

Chiffoleau, J.-F., Cossa, D., Auger, D., Truquet, I., 1994. Trace metal distribution, partition and fluxes in the Seine estuary (France) in low discharge regime. Marine Chemistry 47, 145–158.

Comans, R.N.J., Van Dijk, C.P.J., 1988. Role of complexation processes in cadmium mobilization during estuarine mixing. Nature 336, 151–154.

Ellwood, M.J., van den Berg, C.M.G., 2001. Determination of organic complexation of cobalt in seawater by cathodic stripping voltammetry. Marine Chemistry 75, 33–47.

Environment Agency of Japan, 1971. Notification No.59 (in Japanese).

Evans, D.W., Cutshall, N.H., Cross, F.A., Wolfe, D.A., 1977. Manganese cycling in the Newport River estuary, North Carolina. Estuarine and Coastal Marine Science 5, 71–80.

Hunt, C.D., 1983. Incorporation and deposition of Mn and other trace metals by flocculent organic matter in a controlled marine ecosystem. Limnology and Oceanography 28, 302–308.

Iwashita, M., Shimamura, T., 2003. Long-term variations in dissolved trace elements in the Sagami River and its tributaries (upstream area), Japan. Science of the Total Environment 312, 167–179.

Johnson, K.S., Stout, P.M., Berelson, W.M., Sakamoto-Arnold, C.M., 1988. Cobalt and copper distributions in the waters of Santa Monica Basin, California. Nature 332, 527–530.

Johnson, K.S., Berelson, W.M., Coale, K.H., Coley, T.L., Elrod, V.A., Fairly, W.R., Iams, H.D., Kilgore, T.E., Nowicki, J.L., 1992. Manganese flux from continental margin sediments in a transect through the oxygen minimum. Science 257, 1242–1245.

Kraepiel, A.M.L., Chiffoleau, J.-F., Martin, J.-M., Morel, F.M.M., 1997. Geochemistry of trace metals in the Gironde estuary. Geochimica et Cosmochimica Acta 61, 1421–1436.

Krishnan, A.A., Krishnakumar, P.K., Rajagopalan, M., 2007. *Trichodesmium erythraeum* (Ehrenberg) bloom along the southwest coast of India (Arabian Sea) and its impact on trace metal concentrations in seawater. Estuarine, Coastal and Shelf Science 71, 641–646.

Maeda, H., 1952. The relation between chlorinity and silicate concentration of the water observed in some estuaries. Publications of the Seto Marine Biological Laboratory 2, 249–255.

Maeda, H., 1953. The relation between chlorinity and silicate concentration of the water observed in some estuaries II. Journal of the Shimonoseki College of Fisheries 3, 167–180.

Martin, J.H., Gordon, R.M., Fitzwater, S., Broenkow, W.W., 1989. Vertex: phytoplankton/iron studies in the Gulf of Alaska. Deep Sea Research Part A 36, 649–680.

Martino, M., Turner, A., Nimmo, M., Millward, G.E., 2002. Resuspension, reactivity and recycling of trace metals in the Mersey Estuary, UK. Marine Chemistry 77, 171–186.

Ndung'u, K., Franks, R.P., Bruland, K.W., Flegal, A.R., 2003. Organic complexation and total dissolved trace metal analysis in estuarine waters: comparison of solvent-extraction graphite furnace atomic absorption spectrometric and chelating resin flow injection inductively coupled plasma-mass spectrometric analysis. Analytica Chimica Acta 481, 127–138.

Panzeca, C., Beck, A.J., Tovar-Sánchez, A., Segovia-Zavala, J., Taylor, G.T., Gobler, C.J., Sañudo-Wilhelmy, S.A., 2009. Distributions of dissolved vitamin B_{12} and Co in coastal and open-ocean environments. Estuarine, Coastal and Shelf Science 85, 223–230.

Radakovitch, O., Roussiez, V., Ollivier, P., Ludwig, W., Grenz, C., Probst, J.-L., 2008. Input of particulate heavy metals from rivers and associated sedimentary deposits on the Gulf of Lion continental shelf. Estuarine, Coastal and Shelf Science 77, 285–295.

Roitz, J.S., Bruland, K.W., 1997. Determination of dissolved manganese(II) in coastal and estuarine waters by differential pulse cathodic stripping voltammetry. Analytica Chimica Acta 344, 175–180.

Roitz, J.S., Flegal, A.R., Bruland, K.W., 2002. The biogeochemical cycling of manganese in San Francisco Bay: temporal and spatial variations in surface water concentrations. Estuarine, Coastal and Shelf Science 54, 227–239.

Rue, E.L., Smith, G.J., Cutter, G.A., Bruland, K.W., 1997. The response of trace element redox couples to suboxic conditions in the water column. Deep Sea Research Part I 44, 113–134.

Saito, M.A., Moffett, J.W., 2001. Complexation of cobalt by natural organic ligands in the Sargasso Sea as determined by a new high-sensitivity electrochemical cobalt speciation method suitable for open ocean work. Marine Chemistry 75, 49–68.

Saito, M.A., Rocap, G., Moffett, J.W., 2005. Production of cobalt binding ligands in a *Synechococcus* feature at the Costa Rica upwelling dome. Limnology and Oceanography 50, 279–290.

Sakamoto, H., Yamamoto, K., Shirasaki, T., Inoue, Y., 2006. Pretreatment method for determination of trace metals in seawater using solid phase extraction column packed with polyamino-polycarboxylic acid type chelating resin. Bunseki Kagaku 55, 133–139 (in Japanese, with English Abstract).

Santos-Echeandia, J., Prego, R., Cobelo-García, A., Millward, G.E., 2009. Porewater geochemistry in a Galician Ria (NW Iberian Peninsula): implications for benthic fluxes of dissolved trace elements (Co, Cu, Ni, Pb, V, Zn). Marine Chemistry 117, 77–87.

Santschi, P.H., Lenhart, J.J., Honeyman, B.D., 1997. Heterogeneous processes affecting trace contaminant distribution in estuaries: the role of natural organic matter. Marine Chemistry 58, 99–125.

Schlekat, C.E., Decho, A.W., Chandler, G.T., 1998. Sorption of cadmium to bacterial extracellular polymeric sediment coatings under estuarine conditions. Environmental Toxicology and Chemistry 17, 1867–1874.

Shiki, T., 1985. Wakasa-wan. In: Coastal Oceanography Research Committee of the Oceanographic Society of Japan (Ed.), Coastal Oceanography of Japanese Islands. Tokai Univ. Press, Shizuoka, pp. 947–957 (in Japanese).

Stumm, W., 1992. Chemistry of the Solid–Water Interface. Wiley, New York, 428 pp.

Sunda, W.G., Huntsman, S.A., 1995. Cobalt and zinc interreplacement in marine phytoplankton: biological and geochemical implications. Limnology and Oceanography 40, 1404–1417.

Takata, H., Tagami, K., Aono, T., Uchida, S., 2009. Determination of trace levels of yttrium and rare earth elements in estuarine and coastal waters by inductively coupled plasma mass spectrometry following preconcentration with NOBIAS-CHELATE resin. Atomic Spectroscopy 30, 10–19.

Tang, D., Warnken, K.W., Santschi, P.H., 2002. Distribution and partitioning of trace metals (Cd, Cu, Ni, Pb, Zn) in Galveston Bay waters. Marine Chemistry 78, 29–45.

Tovar-Sánchez, A., Sañudo-Wilhelmy, S.A., Flegal, R.A., 2004. Temporal and spatial variations in the biogeochemical cycling of cobalt in two urban estuaries: Hudson River Estuary and San Francisco Bay. Estuarine, Coastal and Shelf Science 60, 717–728.

Turner, A., Millward, G.E., Bale, A.J., Morris, A.W., 1993. Application of the K_D concept to the study of trace metal removal and desorption during estuarine mixing. Estuarine and Coastal Shelf Science 36, 1–13.

Yamada, Y., Matsushita, S., 2006. Estimation of pollution loads of nitrogen, phosphorus and COD to Sagami Bay by using water quality data of the influent rivers. Bulletin of Kanagawa Prefectural Fisheries Technology Center 1, 43–49 (in Japanese).

Yang, M., Sanudo-Wilhelmy, S.A., 1998. Cadmium and manganese distributions in the Hudson River estuary: interannual and seasonal variability. Earth and Planetary Science Letters 160, 403–418.

Yeats, P.A., Strain, P.M., 1990. The oxidation of manganese in seawater: rate constants based on field data. Estuarine, Coastal and Shelf Science 31, 11–24.