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Cadmium Mixing Behavior in Estuaries: Redox Controls on Removal and Mobilization

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ABSTRACT

This study investigates various hydrological and redox conditions controlling phase transformation, removal and remobilization of Cd in three different estuaries in Taiwan. It was found that Cd mixing patterns in estuarine waters are controlled mainly by redox conditions and salinity. In a highly urbanized estuary segment low oxygen conditions caused sulfide production and the formation of stable Cd sulfide minerals. In oxygen-replete waters [dissolved oxygen (DO) > 200 μM], high concentrations of Mn(II), likely from exchange with bottom sediments were oxidized into Mn oxides, on which Cd is adsorbed. However, in the lower estuary regions elevated chloride concentrations are likely able to compete for Cd, with large proportions of Cd becoming complexed with chloride. The stable Cd sulfide minerals, resistant to oxidation in estuaries having short flushing time, are likely settling out and depositing into bottom sediments. Reversible Cd adsorption onto Mn oxides can enhance Cd mobility in lower estuary and coastal regions where Cd chloro-complexes form, resulting in greater Cd transport fluxes into the ocean.

Key words: Cadmium, Manganese, Dissolved and particulate phases, Estuarine chemistry, Removal, Remobilization

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1. INTRODUCTION

Cadmium is a toxic element that can be bioaccumulated along food chains via trophic transfers, thus posing threats to aquatic organisms and human health (Rainbow 2007; Cassis et al. 2011; Liao et al. 2011; Taylor and Maher 2012). Cd uptake by both waterborne and diet borne routes have been reported (Alquezar et al. 2008; Cassis et al. 2011), with labile forms of Cd (ionic or weakly complexed) more mobile and more bioavailable (Degryse et al. 2006).

On a global scale, rivers are the predominant transport route for Cd whose concentrations are strongly influenced by anthropogenic activities from the continent to the ocean. Cd transport behavior in estuarine waters has been classified from mostly addition (Dai et al. 1995; Wen et al. 1999; Chiffoleau et al. 2001; Martino et al. 2002; Tang et al. 2002; Garnier and Guieu 2003; Waeles et al. 2005; Waeles et al. 2008;), to varying extents of removal (Paucot and Wollast 1997; Zwolsman et al. 1997; Jiann et al. 2005; Chaudry and Zwolsman 2008; Wen et al. 2011), resulting in modified Cd net fluxes out of estuaries into the ocean. The Cd removal features described above have been attributed to the formation of metal sulfides (Jiann et al. 2005) and adsorption onto Fe- and Mn oxides in suspended matter and sediments (Turner et al. 2008; Wen et al. 2008b). Cd also forms chloro-complexes when high concentrations of chloride are present, as is the case in lower estuary and coastal regions. Cd adsorbed onto particles can be partly desorbed and remobilized (Wen et al. 1999; Garnier and Guieu 2003; Waeles et al. 2004; Wen et al. 2008b), making Cd more mobile and potentially bioavailable to aquatic organisms.

There are many urbanized river/estuarine systems in the world where humans produce high domestic wastewater discharge, and consequently, low oxygen conditions that lead to suboxic to anoxic waters (Martino et al. 2002; Jiann et al. 2005; Chaudry and Zwolsman 2008). Cd behavior in suboxic waters becomes more complex by the presence of reduced forms of Mn that can be oxidized into Mn oxides when oxygen-rich waters from the coast are supplied to

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estuaries by tidal mixing. Under anoxic conditions the presence of sulfides will cause Cd removal from the water as sulfide minerals (Jiann et al. 2005).

Although Cd distribution in estuaries has been studied previously (see references above), its removal and adsorption mechanisms have not been directly related to the key controlling parameters beyond lab-scale studies. To this end, this study used water samples from three estuaries with different hydrochemical conditions, especially redox conditions, to investigate the mixing behavior of Cd.

2. MATERIALS AND METHODS

Water samples were collected from three estuaries (Fig. 1) with different hydrological and varying redox conditions. The Danshuei (DS) River Estuary is located in the highly urbanized metropolitan (6-million population) area of Taipei with some small-scale industry in its watershed. The DS Estuary is a macrotidal, partially to well- mixed estuary with high nutrient loading, leading to sub-oxic to anoxic conditions in the upper estuary (Wen et al. 2008a). The two sampling events reported in this study for the DS River Estuary represent wet (July 2001) and dry (May 2002) seasons (Wen et al. 2008a). The Tsengwen (TW) River flows through mostly agricultural plains and several townships in southwestern Taiwan. Its estuarine characteristic is between a salt wedge estuary and a partially mixed estuary. Flowing through plains results in segments of the estuary having stagnant water under low-flow conditions. The Gaoping (GP) River is a typical mountainous river (slope 1/150) with its watershed including parts of the 3-million population metropolitan area of Kaohsiung in its lower reaches. The GP River is one of the most extensively used watersheds in Taiwan, and its lower reaches form a salt wedge estuary. The TW and

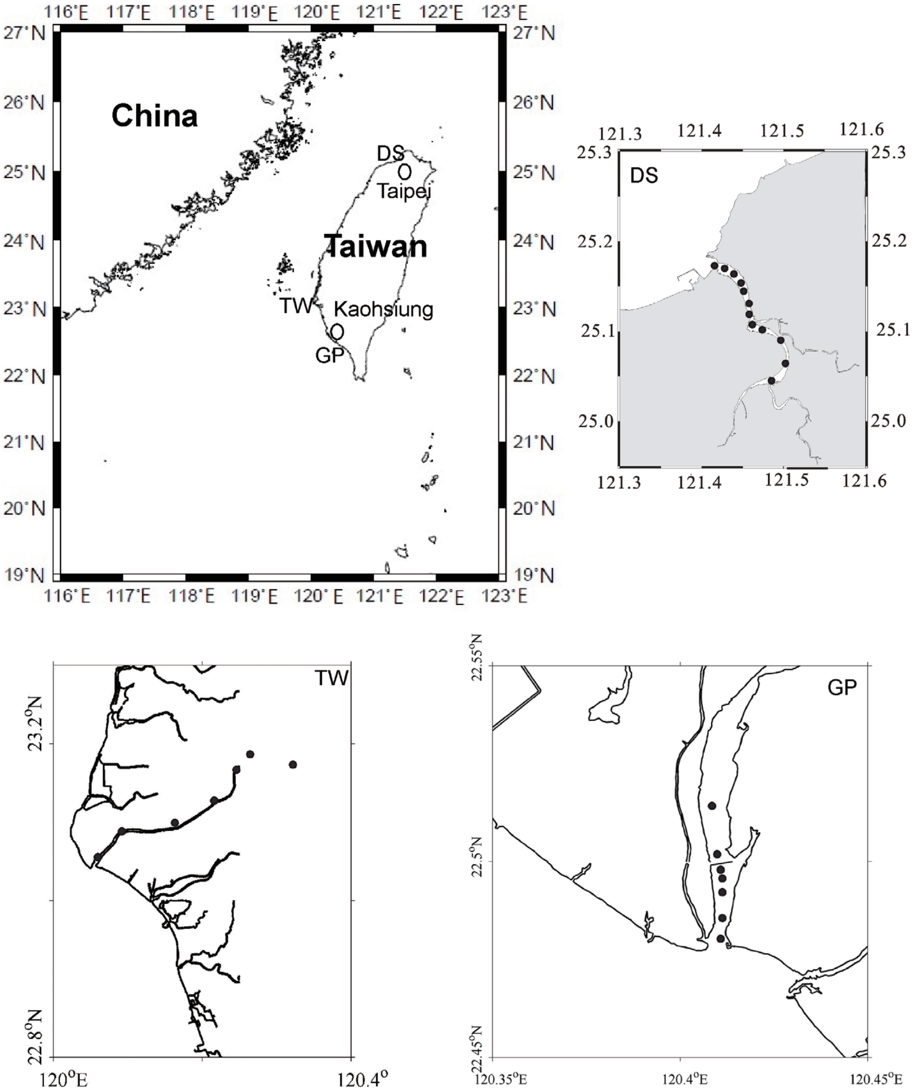

Fig. 1 Regional maps of the Danshuei (DS) River, Tsengwen (TW) River, and Gaoping (GP) River Estuaries, and locations of these estuaries in Taiwan.

GP estuaries were sampled in February and March, 2009, respectively (for illustration purposes, because flow rates in the two rivers peak only after sudden intensive precipitation events such as typhoons).

Water samples for dissolved constituent determination were collected from each estuary under strict "clean sampling" guidelines (Wen et al. 1999; Jiann and Presley 2002) by pumping estuarine waters (~30 - 50 cm depth) directly through Teflon tubing and a 0.45 μm capsule filter (Osmonics, Westborough, MA, USA) into acid-cleaned low-density polyethylene bottles (LDPE, Nalgene). For the collection of suspended particulate matter (SPM) a subsample was collected through the same sampling assemblage by bypassing the filtration system. Particles were collected by vacuum filtration onto polycarbonate membrane filters (0.4 μm, Nuclepore) that had been acid-cleaned and weighed. Only surface waters were collected in order to ensure that the samples were in the tidal ranges. The results obtained allowed for the assessment of estuarine processes.

Filtered water samples were acidified (2 mL of NHO_3, Seastar Baseline grade) to pH < 2 immediately after sample collection and stored in coolers. Once returned to the lab, the samples were transferred to Teflon bottles in a class-100 laminar flow bench, UV-irradiated (8 lamps of 15 W each for 24 hours) to liberate Cd and Mn (Ostapczuk 1993; Wen et al. 1999; Jiann and Presley 2002), and preconcentrated on Chelex-100 resins (NH_4^+-form after acid cleaning, Bio-Rad, 100 - 200 mesh), as described in earlier studies (Jiann and Presley 2002; Jiann et al. 2009). After a washing step to eliminate major cations (Na, K, Mg, Ca), 7 mL of 2N HNO_3 (Seastar, Baseline grade) was used to elute Cd and Mn from the column (~8 mL collected due to shrinking of the Chelex-100 resins), resulting in a preconcentration factor of ~125 from ~1-L samples. Blanks (milli-Q water) and standard reference material (SLEW-3 estuarine water, from National Research Council of Canada) were processed along with samples for quality control and quality assurance purposes.

The filters on which SPM was retained were freeze-dried and weighed to yield SPM concentration. The particles on the filters were then totally digested by heating in Teflon vessels, with the addition of nitric acid, hydrofluoric acid and boric acid (Lauenstein and Cantillo 1998). Blanks (blank filters with reagents) and standard reference material MESS-3 (marine sediment, from National Research Council of Canada) were processed together with the samples in order to assess contamination control and digestion efficiency.

Additional sets of SPM samples were collected during our visits to the TW (February and July, 2009) and GP (March and July, 2009) Estuaries in order to conduct leaching experiments following the method developed by Landing and Lewis (1991) to elucidate the Cd and Mn distribution in SPM. Membrane filters were sequentially leached using 25% acetic acid and then aqua regia to obtain the metal fractions associated with surface adsorption (exchangeable fractions), and Fe- and Mn-oxides and organic matter, respectively.

Cd concentration determination was performed on a graphite furnace atomic absorption spectrometer (Perkin Elmer AAnalyst 600), and Mn using a flame atomic absorption spectrometer (Perkin Elmer AAnalyst 200). The detection limits for dissolved and particulate Cd concentrations were 2 pM and 0.005 $\mu g\ g^{-1}$, respectively, and 0.5 nM and 0.5 $\mu g\ g^{-1}$ for Mn. Blanks were all below the detection limits and recoveries for SLEW-3 and MESS-3 were 106% (Cd) and 98% (Mn), and 102% (Cd and Mn), respectively (Table 1).

Salinity was measured in the field using a portable conductivity meter (WTW). Dissolved oxygen (DO) concentrations were determined according to a colorimetric method (Pai et al. 1993) following fixation of DO in the field by adding Winkler reagents immediately after sampling.

3. RESULTS AND DISCUSSION

3.1 Redox Conditions

Estuarine processes in the DS Estuary are strongly influenced by freshwater input, tides and anthropogenic perturbations (Wen et al. 2008a). The upper DS Estuary is under suboxic to anoxic conditions except after very high precipitation events that lead to elevated river discharges and consequently higher DO concentrations (Jiann et al.

Table 1. Analytical results of estuarine water reference material (SLEW-3) and marine sediment reference material (MESS-3).

	SLEW-3 ($\mu g\ L^{-1}$, n = 6)		MESS-3 ($mg\ kg^{-1}$, n = 6)	
	Cd	**Mn**	**Cd**	**Mn**
Certified	0.048	1.61	0.24	324
Std. dev.	0.004	0.22	0.01	12
Observed mean	0.051	1.57	0.24	329
Std. dev.	0.004	0.12	0.01	12
Recovery (%)	106	98	102	102

2005; Wen et al. 2008a). However, surface waters at the river mouth are mostly oxygen saturated because of exchanges with oxygen-replete coastal waters. Therefore, redox interfaces present in the DS Estuary are influenced by the varying magnitude and duration of tidal inflows from coastal seawater. In May 2002, DO concentrations in the upper DS Estuary were near complete depletion and as low as 40 μM in July 2001 (Fig. 2). For waters in the TW Estuary, DO concentrations were high and remained in a narrow range (200 - 250 μM). DO concentrations in waters of the GP Estuary (135 - 220 μM) showed a much different distribution pattern than the other two estuaries, with higher DO concentrations in the upper reaches and significantly lower ones in the lower estuary. Oxygen saturation rates ranged from ~0 - 100% in the DS Estuary, 80 - 100% in the TW, and 60 - 80% in the GP systems. Various redox conditions in the waters of these three estuaries were observed, in which, due to the urbanized watershed of the DS Estuary and having at least part of the estuaries with stagnant water in the TW and GP systems, parts of all three estuaries were observed to be substantially oxygen depleted.

Also shown in Fig. 2 are SPM distributions in the three estuaries. Except for waters in the upper DS Estuary collected in July 2001 (wet season) when SPM concentrations were as high as ~140 mg L^{-1}, SPM concentrations were in general near or < 20 mg L^{-1}.

3.2 Cd Distribution

Cd distribution patterns in the three estuaries showed distinctively different spatial and temporal variability (Fig. 3). In the DS Estuary, both addition and removal mixing behaviors were observed for dissolved Cd. Evidence for drastic removal of dissolved Cd in the upper DS Estuary can be gleaned from the concave mixing curve, with dissolved Cd concentrations in mid-estuary being even lower than the coastal end-member concentrations. Furthermore, in the lower DS Estuary, dissolved Cd concentrations were much higher than in the particulate phase, while conservative mixing and slight addition behavior (i.e., convex curvature) were observed because removal of dissolved Cd was so extensive that dissolved Cd concentrations in the DS estuarine waters were often lower than those in coastal waters.

In the TW Estuary significant addition of dissolved Cd was found in the mid-estuarine region and the dissolved Cd pool was much greater than that in the particulate Cd phase (Fig. 3). In the GP Estuary dissolved Cd concentrations in the upper estuary were much lower than in the coastal region (Fig. 3) and an unusual inverse conservative mixing behavior of dissolved Cd was observed. In the upper GP Estuary, particulate Cd concentrations were higher than dissolved Cd concentrations and they showed a reverse distribution pattern along the salinity gradient.

3.3 Mn Distribution

Mn, when it is present at elevated levels in the dissolved phase as Mn(II), is an indicator of suboxic conditions either in the water (Klinkhammer and McManus 2001) or in the bottom sediments (Chiffoleau et al. 1994; Roitz et al. 2002; Tovar-Sánchez et al. 2004). Mn(II) has a long residence time in waters owing to its slow oxidation kinetics (Davison 1993). In a laboratory-scale study freshly synthesized Mn oxide was shown to have a stronger affinity for Cd adsorption than Fe oxide and estuarine sediments (Turner et al. 2008). Therefore, Mn oxides formed in waters can provide a carrier phase for Cd in estuarine waters (Wen et al. 2008b), provided its abundance is high enough. Thus, it becomes necessary to understand the distribution and partitioning of Mn in order to further relate it to Cd behavior in estuarine waters.

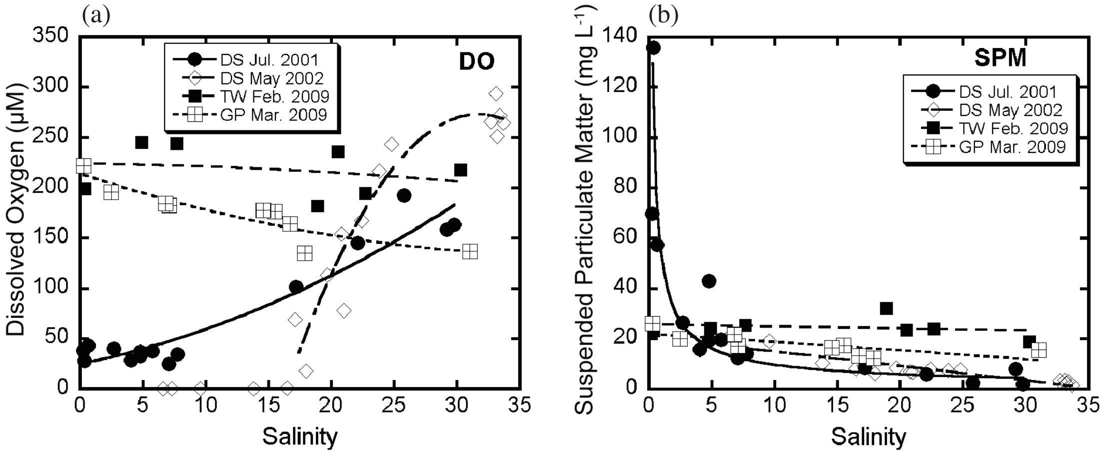

Fig. 2 Distribution of (a) dissolved oxygen (DO) and (b) suspended particulate matter (SPM) along salinity gradients in the three estuaries (total 4 cruises shown). Because dissolved and particulate phases do not behave the same, distribution patterns at times do not show typical estuarine behavior. Therefore, the fitted curves displayed in the figures are for visual purposes.

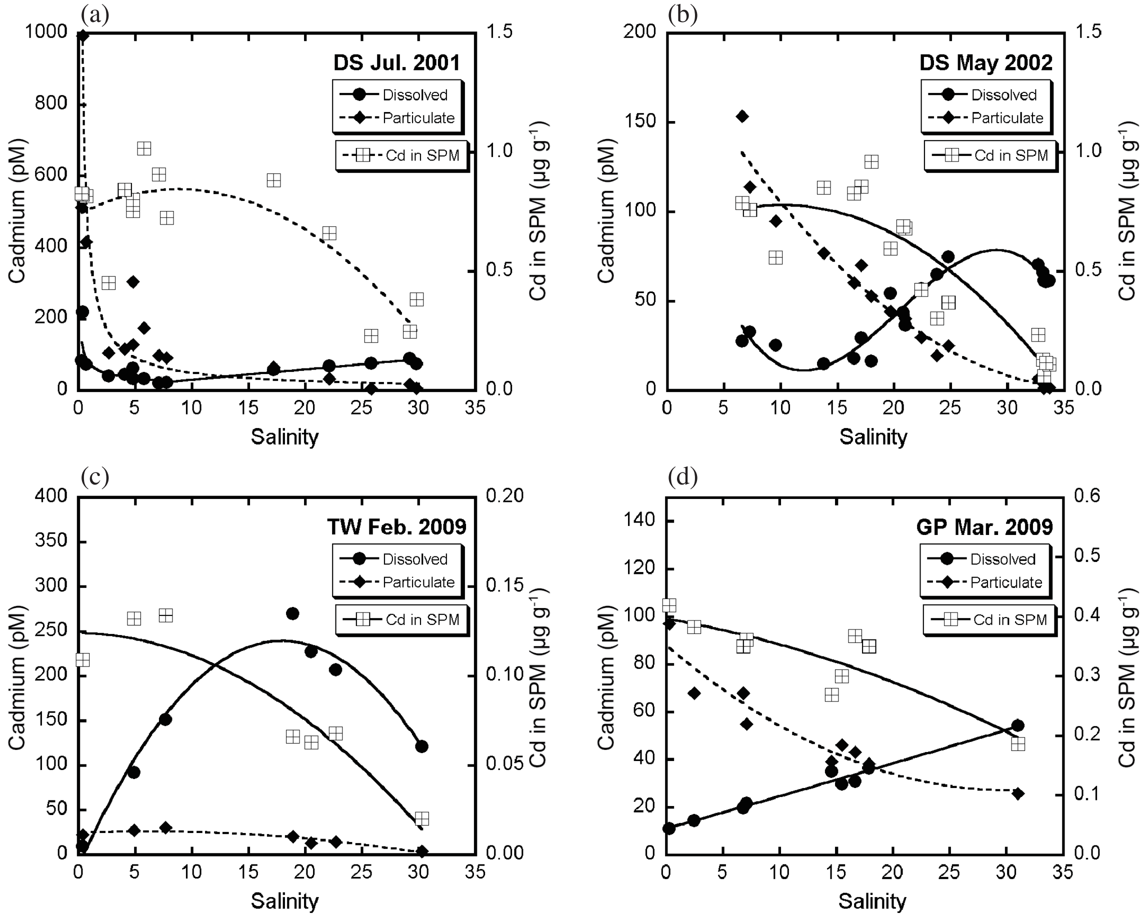

Fig. 3 Distribution of dissolved and particulate Cd along salinity gradients in the Danshuei River Estuary [(a) Jul 2001, (b) May 2002], the Tsengwen River Estuary (c), and the Gaoping River Estuary (d). Because dissolved and particulate phases do not behave the same, distribution patterns at times do not show typical estuarine behavior. Therefore, the fitted curves displayed in the figures are for visual purposes.

Elevated dissolved Mn concentrations and different estuarine mixing behaviors were observed in the three estuaries (Fig. 4). Dissolved Mn concentrations ranged from 27 - 2800 nM (July 2001) and from 266 - 4650 nM (May 2002) in the DS Estuary, from 246 - 2537 nM in the TW Estuary (February 2009), and from 214 - 8547 nM in the GP Estuary (March 2009). Mn concentrations in SPM (mass/mass) also showed large variations, ranging from 368 - 3106 μg g^{-1} (July 2001) and from 110 - 5153 μg g^{-1} (May 2002) in the DS Estuary, from 1097 - 2329 μg g^{-1} in the TW Estuary, and from 1881 - 10317 μg g^{-1} in the GP Estuary.

These variations in dissolved Mn concentrations were primarily due to dilution effects from estuarine mixing, but also caused by in situ Mn oxide formation, especially in the oxygen-replete lower estuarine regions. This phenomenon is further indicated by the progressive increases in Mn concentrations in SPM (Fig. 4) with increasing salinity in the lower DS Estuary. The Mn oxide formation is a function of DO concentration, as particulate Mn concentrations were significantly elevated when DO concentration was higher than 200 μM regardless of the salinity (Fig. 5a), at levels above average crustal abundance (~1000 μg g^{-1}), reflecting the strong hypoxic (more oxygen-deplete) conditions in the DS system relative to the other two estuaries. The TW and GP estuarine waters also had relatively high DO concentrations and consequently higher particulate Mn concentrations (1000 - 10000 μg g^{-1}), especially in the upper estuaries. However, largely due to the decreases in dissolved Mn and corresponding increases in particulate Mn concentrations, the distribution coefficients (K_d) of Mn in general increased along the salinity gradients, as shown in Fig. 5b.

3.4 Cd Phase Partitioning Controls

Depending on the hydrochemical variability (i.e., redox condition and salinity), Cd can be present in estuarine waters as Cd sulfides (Jiann et al. 2005), associated with colloidal material (Muller 1998; Wells et al. 1998), adsorbed on particulate matter, especially on Mn oxides (Turner et al. 2008; Wen et al. 2008b), and as complexes with chloride (Stumm and Morgan 1995). Owing to the low DO (Fig. 2) and low particulate Mn (Fig. 4) concentrations in the upper

DS Estuary, the correspondingly high Cd concentrations in SPM (Fig. 3) were possibly due to the formation of Cd sulfides (Al-Farawati and van den Berg 1999; Jiann et al. 2005; Chaudry and Zwolsman 2008). During the dry season the DS Estuary often had anoxic conditions in the upper estuarine waters (Jiann et al. 2005; Wen et al. 2008a), in which particulate Cd concentrations were higher than dissolved Cd concentrations, as shown in the case for May 2002. In the

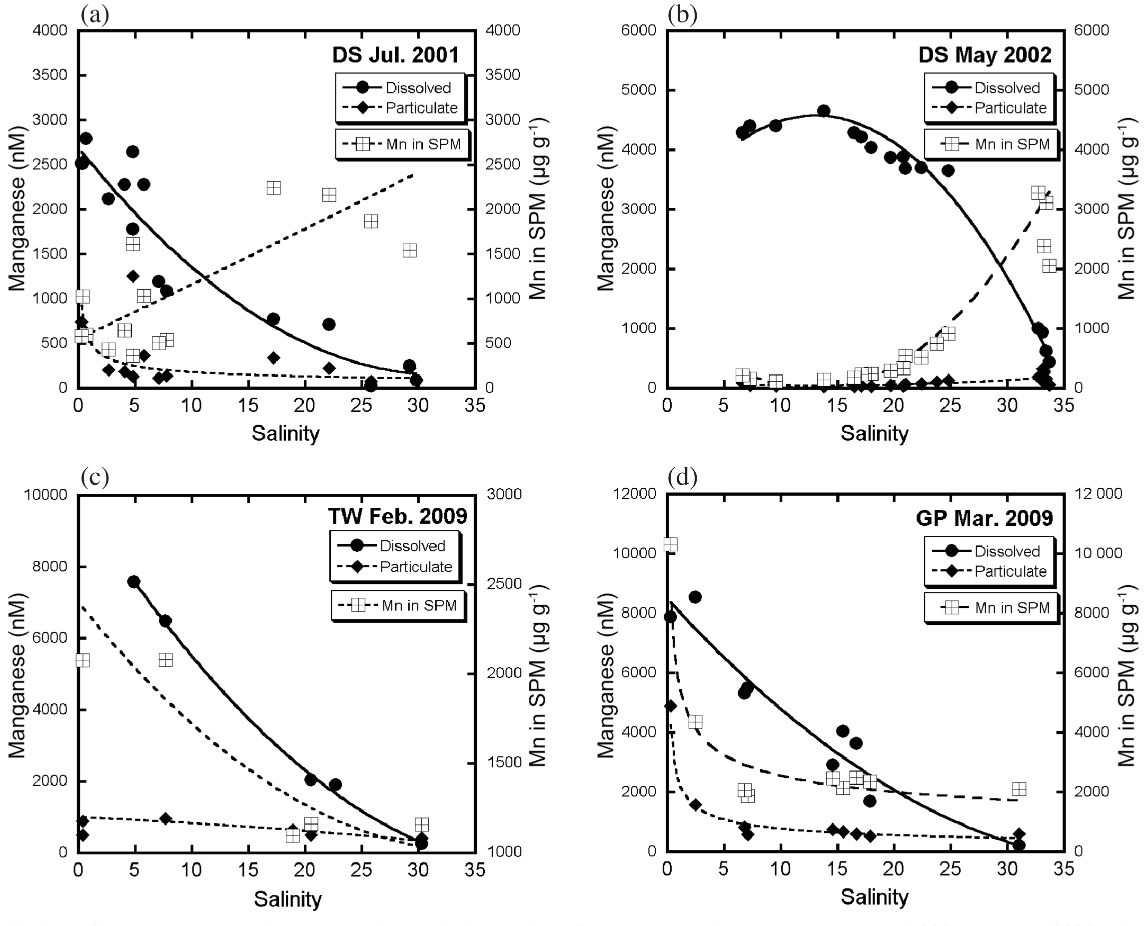

Fig. 4 Distribution of dissolved and particulate Mn along salinity gradients in the Danshuei River Estuary [(a) Jul 2001, (b) May 2002], the Tsengwen River Estuary (c), and the Gaoping River Estuary (d). Because dissolved and particulate phases do not behave the same, distribution patterns at times do not show typical estuarine behavior. Therefore, the fitted curves displayed in the figures are for visual purposes.

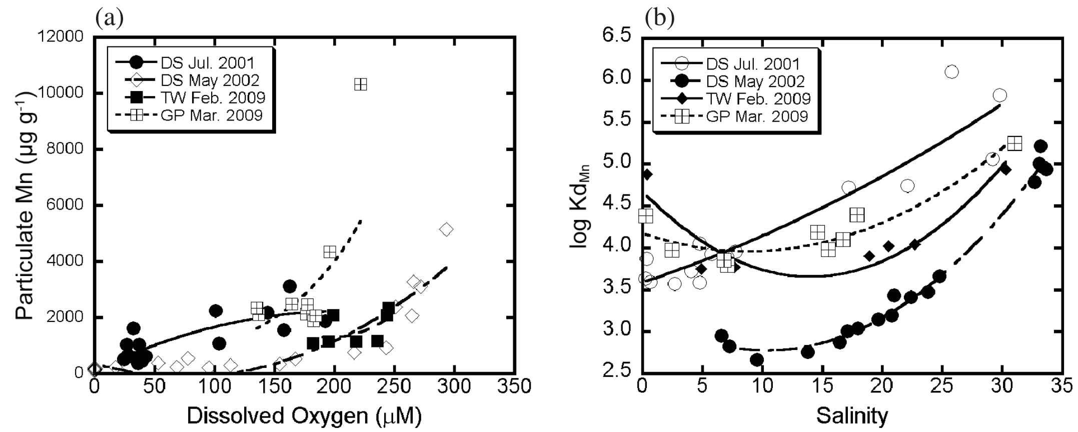

Fig. 5 (a) Relationship between particulate Mn (in SPM) and dissolved oxygen concentration and (b) distribution coefficient (K_d) for Mn along salinity gradients in the three estuaries studied. Because dissolved and particulate phases do not behave the same, distribution patterns at times do not show typical estuarine behavior. Therefore, the fitted curves displayed in the figures are for visual purposes.

oxygen-deplete upper DS Estuary (Fig. 2), reduced sulfur species have been reported to be as high as ~500 μM (Jiann et al. 2005), a concentration so high that would lead to saturation with respect to metal sulfide complexes, including those of Cd. Samples measured for total dissolved sulfide concentrations in the anoxic waters collected in May 2002 were also high (100 - 300 μM range, not shown). Cd sulfide would be in the colloidal size range when first formed (Jiann et al. 2005). However, this would result in a large proportion of Cd ending up in the particulate phase in the upper DS Estuary followed by substantial removal of dissolved Cd (Fig. 3) due to fast coagulation (colloidal pumping) processes (Honeyman and Santschi 1991; Wen et al. 1997). The extent of removal is more significant during the dry season when dissolved sulfides are present at hundred-μM range (Jiann et al. 2005). Because of the high stability of metal sulfide minerals, this removal is not reversible in the time scale of days (common residence time of water in small estuaries) when oxygen is supplied from coastal water intrusion into the estuary (Simpson et al. 2000).

Owing to the anoxic characteristics of the upper DS Estuary, Mn oxide formation is not favored until very close to the coastal region. This is indicated by the comparably low particulate Mn concentrations compared to those of dissolved Mn concentrations, until reaching the lower estuary and coast (Fig. 4). Therefore, Cd adsorption onto Mn oxides is limited in the DS Estuary because of two different effects: (1) insignificant Mn oxide formation in the upper estuary, and (2) competition from chloride in the lower estuary. As a result, nearly all Cd in the lower DS estuarine waters (S > 20) are present in the dissolved phase (Fig. 3).

In both the TW and GP Estuaries, which drain high slope, mountainous river systems, the salt wedge estuary type character produced some mildly under-saturated DO conditions. Contrary to the Cd mixing behavior in the DS Estuary, higher particulate Cd concentrations (relative to those in the lower estuaries) in the upper TW and GP Estuaries were concomitantly observed with high particulate Mn concentrations (Figs. 3 - 4). The waters in these two estuaries were not in anoxic condition and the formation of Mn oxides was evidenced by the presence of high particulate Mn concentrations (Fig. 4) in the upper- and mid-estuaries, thus providing adsorption carriers for Cd. The mixing behavior of dissolved Cd in the TW Estuary was thus likely the result of Cd adsorption onto Mn oxides in the upper estuary and subsequent desorption in the lower estuary where chloride can compete for Cd adsorbed onto Mn oxides.

The association between particulate Mn and Cd adsorption was further displayed in a positive linear correlation, as illustrated in Fig. 6b, between exchangeable Cd and exchangeable Mn concentrations. Both Cd and Mn appeared mostly in the exchangeable fractions (> 80%) in the two sample sets (February and March, 2009). In the DS Estuary samples in which only total particulate Cd and Mn concentrations were determined, an inverse correlation between Cd and Mn was found (Fig. 6a), with some exceptions due to re-suspension of bottom sediments (high SPM concentrations, Fig. 2) that contained lower particulate Cd concentrations in the July 2001 samples (values provided below). Contributions from re-suspended sediments toward the addition of dissolved Cd was considered limited in the DS and TW Estuaries owing to the facts that (1) the particulate Cd load in the TW Estuary was clearly much lower than the dissolved Cd concentrations (Fig. 3), and (2) Cd concentrations in TW Estuary sediments (0.05 - 0.1 μg g^{-1}) were lower or comparable to particulate Cd concentrations and much lower in the DS Estuary (Jiann et al. 2005).

Plotting the composite data from all three estuaries (Fig. 7), it can be seen that particulate Cd concentrations decreased with increasing dissolved oxygen concentration because of: (1) sulfides were only present in anoxic, upper DS estuarine waters; and (2) desorption of Cd from mostly

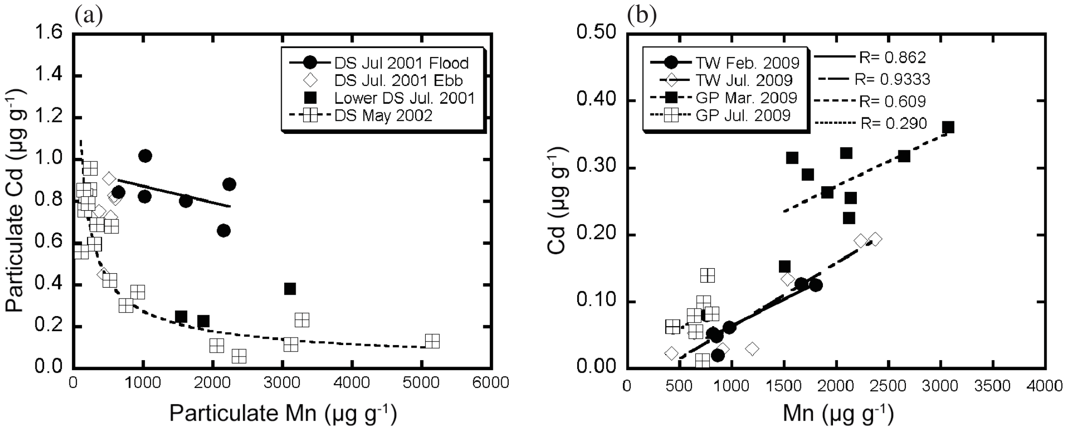

Fig. 6 Relationship between (a) particulate Cd and Mn (in SPM) concentration in the DS Estuary and (b) exchangeable Cd and exchangeable Mn concentrations in the TW and GP Estuaries. Because dissolved and particulate phases do not behave the same, distribution patterns at times do not show typical estuarine behavior. Therefore, the fitted curves displayed in the figures are for visual purposes.

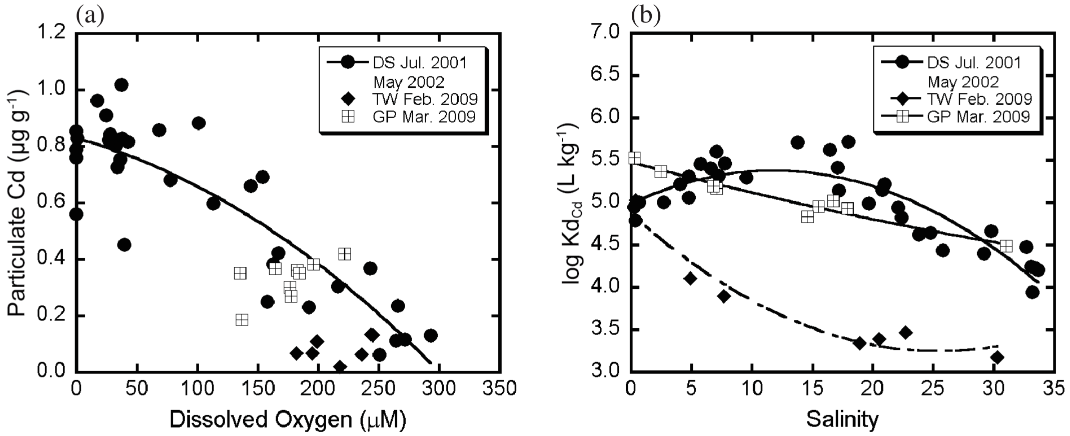

Fig. 7 (a) Relationship between particulate Cd (in SPM) and dissolved oxygen concentration and (b) distribution coefficient for Cd along salinity gradients in the three estuaries studied. Because dissolved and particulate phases do not behave the same, distribution patterns at times do not show typical estuarine behavior. Therefore, the fitted curves displayed in the figures are for visual purposes.

non-sulfidic particulate matter, including Mn oxides formed in oxygen-replete lower estuarine waters (> 150 - 200 μM, Fig. 4), as chloride concentrations increased allowing them to compete for Cd. An apparent inverse correlation was observed in the partly anoxic DS Estuary for the redox condition (DO concentration) effect on Cd partitioning and no clear trends were found in the suboxic TW/GP systems (Fig. 7). This observation is in agreement with the distinctively different sulfur and Mn chemistry controlling for Cd behavior in the waters under anoxic and suboxic conditions. The low-DO, high-particulate Cd concentrations in the upper (anoxic) DS Estuary were caused by sulfides being produced to form sulfide minerals of Cd.

As a result of decreasing particulate Cd and increasing dissolved Cd concentrations in the lower estuaries which gave results that are contrary to many other studies (Chiffoleau et al. 2001; Garnier and Guieu 2003; Wen et al. 2008b), distribution coefficient (K_d) between particulate and dissolved phases of Cd displayed substantial decreases along salinity gradients in all three estuaries (Fig. 7b). The slightly elevated K_d values in the upper DS Estuary were due to the formation of Cd sulfide minerals in the water, as reported earlier (Jiann et al. 2005). The changes in Cd concentrations in SPM and the corresponding K_d variation in the GP systems were minimal compared to the DS and TW Estuaries. Ultimately, variations in Cd solid-solution partitioning coefficients resulted from its association with Mn oxides, sulfides and/or Cl (salinity) in different parts of the estuaries.

4. CONCLUSIONS

Mixing behavior of Cd in estuarine waters is a result of the interplay between redox conditions and salinity (chloride concentration). In highly urbanized estuaries or river segments where oxygen can be completely consumed due to high domestic and industrial wastewater discharges, the presence of sulfides leads to the formation of Cd sulfide minerals that are initially colloidal in size but contribute rapidly to elevated Cd concentrations in suspended particles. The CdS minerals are stable within the average flushing time scales of estuaries and ultimately settle out and deposit into bottom sediments through flocculation processes. In suboxic waters the Mn(II) produced in the water and diffusing from bottom sediments will be oxidized to form Mn oxides onto which Cd can adsorb reversibly. This reversible Cd adsorption process onto oxides is reversed in the lower estuaries when salinity increases, as the strong affinity between Cd and chlorides results in elevated dissolved Cd concentrations from Cd desorption in the lower estuaries and coastal regions. These above mentioned processes create Cd being possibly removed and remobilized in the same estuary, depending on DO and salinity. The Cd sulfidic minerals can cause elevated sedimentary Cd concentrations (along with other trace metals) until they are exposed to the air over a long period of time (dredging and disposal), while the remobilization of Cd from adsorbed particulate matter will enhance the Cd fluxes being transported to the ocean.

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