

Chapter 5

Heavy Metal Mobility and Aquatic Biogeochemical Processes at Mai Po Marshes Nature Reserve, Hong Kong

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Abstract. Mai Po Marshes is a sub-tropical estuarine wetland in Hong Kong, which is a complex, dynamic and unique ecosystem. The main objective of the present study is to explore heavy metal mobility in the sediments as a function of biogeochemical conditions in the aquatic environment in Mai Po Marshes. Samples of sediments and water were collected monthly from eight sites during July–September 1997. Heavy metal (Cd, Cr, Cu, Ni, Pb, Zn) concentrations in the sediments and their associations with aquatic physicochemical properties were examined. Aquatic biogeochemical processes appear to be different between landward and seaward sides. Heavy metal mobility seems to be closely associated with organic matter degradation on the landward side, while water quality and changes in redox conditions appear to be the major processes responsible for heavy metal mobility on the seaward side. At Mai Po Marshes, whereas organic enrichment benefits bird conservation as previous studies indicated, the results of this present study suggest that organic dynamics associated with heavy metal mobility and toxicity may also be taken into consideration for organic matter management.

5.1. Introduction

The Mai Po Marshes Nature Reserve, one among the 21 *Ramsar* sites in China, is located on the eastern shore of Deep Bay (part of the Pearl River estuary) in Hong Kong (Fig. 1). Its ecological importance has been extensively described (Hodgkiss, 1986; Irving & Morton, 1988). The reserve serves as an important winter ground for 24% of the world population of the endangered species, the black-faced spoonbill (*Platalea minor*) (Young, 1995). The major ecosystems at Mai Po Marshes include mangrove swamps, inter-tidal mudflats, shrimp shallow

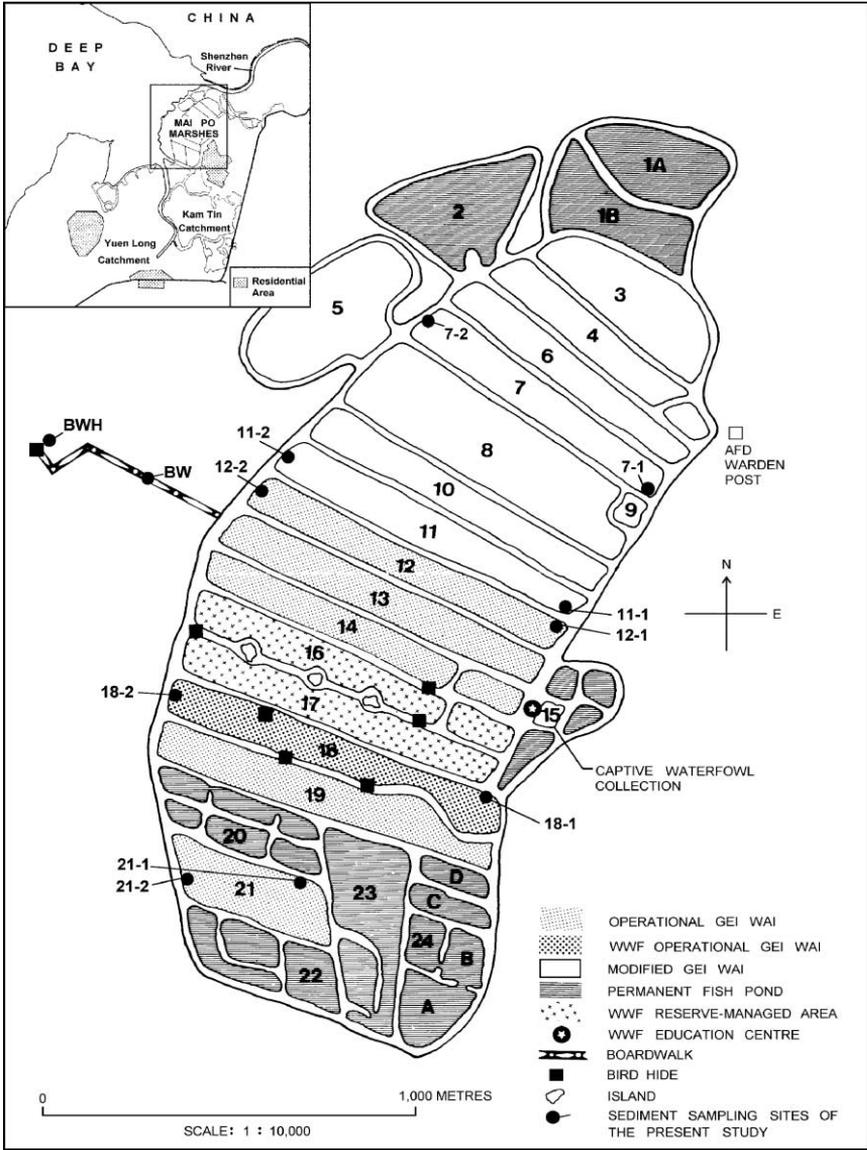


Figure 1: Map of the study sites showing the sampling locations.

ponds (local name *gei wais*) (Li & Lee, 1998) and freshwater fishponds. They are important nursery grounds for a number of migratory birds (Young, 1995).

Due to the discharges of domestic sewage, livestock wastewater and industrial effluent into Deep Bay from the Pearl River, Shenzhen River and Shan Pui River,

Mai Po Marshes have been facing increasing pressure due to heavy metals pollution in the recent years. As to the inter-tidal mudflats, trace metals (Cd, Cr, Cu, Fe, Pb and Zn) were 4–25% more enriched in the upper 0–10 cm of the topsoil compared to that in the 21–30 cm core of the sediments, which indicates an increased anthropogenic input of metals in the sediments (Tam & Wong, 2000). In mangrove swamps, the surface sediments were seriously polluted by heavy metals (Cd, Cu, Ni, Pb and Zn) (Tam & Wong, 2000). As to *gei wais*, topsoil enrichment of Zn was revealed in the upper 0–8 cm compared with the bottom 8–16 cm, which indicates an increasing pollution in *gei wais* (Lau & Chu, 2000). Among the three ecosystems at Mai Po Marshes that have been studied, mudflats, which are the closest to Deep Bay, have the greatest levels of trace metals in the sediments, suggesting that the increasing heavy metal input most possibly comes from Deep Bay.

On the other hand, organic matter enrichment in Deep Bay may be essential for shorebird conservation. Anthropogenic input of organic matter is an important carbon source (up to 50%) for shorebirds (Li & Lee, 1998), and local catchments, such as Shenzhen River and Shan Pui River, provide the major nutrients for shorebirds at Deep Bay (Lee, 2000).

It is generally accepted that organic matter is one of the major controlling factor for heavy metal transportation in the sediment (Förstner, 1995; Schulin et al., 1995; Sauvé et al., 2000; Cantwell & Burgess, 2001; Chapman & Wang, 2001). Biological processes in the aquatic environment, such as organic degradation, nitrification and algal growth, play key roles in adjusting pH and Eh as well as in organic decomposition and formation (Wetzel, 2001). At Mai Po Marshes, it has been shown that the reduction of Mn (hydr)oxides was the major remobilization mechanism for metals such as Cd, Cr, Cu, Pb, Zn, Fe and Mn (Yu et al., 2000), but few studies have addressed the relationships between organic matter related processes and heavy metal mobility.

The main objective of the present study is to investigate heavy metal mobility and its associations with aquatic biogeochemical processes in water and sediments in *gei wais* at Mai Po Marshes. Six heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) were selected because they have been the most studied anthropogenic pollutants (Ong Che & Cheung, 1998; Tam & Wong, 2000; Yu et al., 2000). Two locations in *gei wais* (landward and seaward sides) including four sites at each location were selected. Based on our field observation, sampling sites at the landward side had shallower and static overlying water (<0.5 m) above the sediments with more mangrove tree coverage, while those at the seaward side had deeper and flowing overlying water (1–1.5 m) with less mangrove trees. Through comparisons between the two locations, the major aquatic biogeochemical factors that influence heavy metal mobility will be identified. Information from the study may help further explore the mechanisms of heavy metal mobility and toxicity as well as organic matter management at Mai Po Marshes.

5.2. Materials and Methods

Detailed descriptions of the study site (Fig. 1) can be referred to in Liang et al. (1999). Monthly water and sediment samples were collected from the landward sites (7-1, 11-1, 12-1, 18-1) and the seaward sites (7-2, 11-2, 12-2, 18-2) during July–September 1997. Detailed methods of physicochemical analysis of water and sediments, as well as the total metal contents in the sediments, are described by Liang & Wong (2003). In general, besides water temperature ($^{\circ}\text{C}$), pH, dissolved oxygen (DO) (mg l^{-1}) and salinity (%), four groups of parameters indicating biological processes in the overlying water were measured (APHA, 1985). These included: (1) organic matter metabolism related: biochemical oxygen demand (mg l^{-1}) (BOD) and dissolve organic carbon (mg l^{-1}) (DOC); (2) N metabolism related: $\text{NH}_3\text{-N}$ (mg l^{-1}), $\text{NO}_2\text{-N}$ (mg l^{-1}) and $\text{NO}_3\text{-N}$ (mg l^{-1}); (3) P metabolism related: *ortho*-P ($\text{PO}_4^{3-}\text{-P}$) (mg l^{-1}) and total P (TP) (mg l^{-1}); and (4) biomass or particulate organic matter in water related: volatile suspended solids (VSS) (g l^{-1}) and total suspended solids (TSS) (g l^{-1}). Parameters representing major factors in the sediments influencing heavy metal mobility were measured, which included pH, redox potential (Eh) (mV), total organic matter (TOM) (%) and electrical conductivity (EC) (mS cm^{-1}).

Sequential extraction for heavy metal speciation analysis was performed according to the scheme proposed by Stover et al. (1976). The extracted heavy metal phases, reagent strength, extraction duration and solution to solid ratios are summarized in Table 1. Three replicates were carried out for each sediment sample. The filtrates of each phase were analyzed for heavy metals using Flame Atomic Absorption Spectrometry (Varian SpectrAA-20 model).

Statistical Analysis System for windows V8 was used for all statistical analyses. PROC ANOVA procedure was used for analysis of variance (ANOVA). PROC

Table 1: Summarized sequential extraction of heavy metals in the sediments.

Speciation phases	Extractants	Reagent strength (M)	Extraction duration	Solution to solid ratio
Exchangeable (Me1)	KNO_3	1	16 h, 200 rpm	50 ml:1 g
Adsorbed (Me2)	KF	0.5	16 h, 200 rpm	80 ml:1 g
Organic matter (Me3)	$\text{Na}_4\text{P}_2\text{O}_7$	0.1	16 h, 200 rpm	80 ml:1 g
Carbonates (Me4)	Na_2EDTA	0.1	8 h, 200 rpm	80 ml:1 g
Sulfides (Me5)	HNO_3	6	16 h, 200 rpm	50 ml:1 g

Stover et al. (1976).

CORR procedure was used for Pearson correlation analysis. PROC REG procedure was used for regression analysis.

5.3. Results and Discussion

5.3.1. Comparisons of Physicochemical Properties of the Water and Sediments Between the Landward and Seaward Sides in Gei Wais at Mai Po Marshes

Physicochemical properties of water and sediments in *gei wais* are shown in Table 2. One-way ANOVA results indicate that the landward side had significantly ($p < 0.05$) higher organic matter (TOM) contents in the sediments (12.7%) than the seaward side (8.16%). Mangrove plants such as *Kandelia candel* and *Phragmites australis* are major producers in *gei wais*, contributing more than 95% of organic matter (t C yr^{-1}) production (Li & Lee, 1998). It is suggested that the uneven distribution of mangrove trees in *gei wais* caused the difference of organic matter in the sediments. Therefore, the higher TOM contents in the sediments of the landward side may be due to the more densely populated mangrove trees at the landward side. The significantly ($p < 0.05$) lower water temperature (29.4°C) at the landward side compared with that at the seaward side (30.5°C) might also possibly be the result of the more mangrove tree canopy at the landward side.

Due to the release of organic acids such as humic acid, pH levels can be reduced during the process of organic matter decomposition (Wetzel, 2001). The higher organic matter contents in the sediments at the landward side may be responsible for the significantly ($p < 0.05$) lower levels of pH (sediments: 6.99; water: 6.97) compared to those at the seawards side (sediments: 7.75; water: 7.48).

Compared with the landward side (TSS: 0.0229 g l^{-1} ; $\text{PO}_4^{3-} - \text{P}$: 0.0972 mg l^{-1}), the seaward side had significant higher turbidity and *ortho*-P (TSS: 0.0469 g l^{-1} ; $\text{PO}_4^{3-} - \text{P}$: 0.253 mg l^{-1}). Extremely high sedimentation (1.7 cm yr^{-1}) in *gei wais* (Lee, 1990) has been reported, and the tidal water from Deep Bay has been the major source of suspended solids and organic matter input to *gei wais* (Li & Lee, 1998). Besides the tidal water, potentially higher resuspension of sediments at the seaward side may possibly cause the higher TSS in the overlying water, since the seaward side is both the inlet and outlet of water flux in the *gei wais*.

5.3.2. Comparisons of Aquatic Biological Processes Between the Landward and Seaward Sides in Gei Wais at Mai Po Marshes

The correlations among aquatic physicochemical variables in *gei wais* are shown in Table 3. At the landward side, the correlation results suggest that organic matter

Table 2: Summary of physicochemical properties of the water and sediments in *gei wais* at Mai Po Marshes.

	Landward			Seaward		
	Mean \pm SD	Min	Max	Mean \pm SD	Min	Max
Sediments						
pH	6.99 \pm 0.438*	6.22	8.00	7.75 \pm 0.417	6.98	8.28
EC (mS cm ⁻¹)	-114 \pm 44.4	-165	-44.4	-120 \pm 45.2	-178	-52.7
Eh (mV)	2.46 \pm 1.54	1.21	6.76	2.32 \pm 2.52	0.750	8.20
TOM (%)	12.7 \pm 4.44*	6.54	21.7	8.16 \pm 2.33	5.26	12.4
Water						
Temp (°C)	29.4 \pm 0.716*	28.2	30.3	30.5 \pm 1.25	28.7	32.9
pH	6.97 \pm 0.342*	6.10	7.39	7.48 \pm 0.495	6.87	8.44
Salinity (%)	0.163 \pm 0.0664	0.090	0.300	0.158 \pm 0.0832	0.0700	0.310
DO (mg l ⁻¹)	7.90 \pm 0.513	6.91	8.63	7.94 \pm 0.232	7.43	8.29
BOD (mg l ⁻¹)	5.44 \pm 2.47	2.69	9.84	6.98 \pm 3.69	1.87	13.8
DOC (mg l ⁻¹)	9.31 \pm 3.95	3.61	18.3	4.26 \pm 2.04	0.510	6.49
TSS (g l ⁻¹)	0.0229 \pm 0.00833*	0.0063	0.0369	0.0469 \pm 0.0221	0.0173	0.0760
VSS (g l ⁻¹)	0.0143 \pm 0.00317	0.0089	0.0189	0.0160 \pm 0.00350	0.0119	0.0232
NH ₃ -N (mg l ⁻¹)	0.283 \pm 0.239	0.0133	0.709	1.56 \pm 2.15	0.0100	5.21
NO ₂ ⁻ -N (mg l ⁻¹)	0.0310 \pm 0.0687	0.000	0.244	0.113 \pm 0.138	0.0041	0.423
NO ₃ ⁻ -N (mg l ⁻¹)	0.0620 \pm 0.112	0.0029	0.365	0.196 \pm 0.210	0.0023	0.770
PO ₄ ³⁻ -P (mg l ⁻¹)	0.0972 \pm 0.0896*	0.0013	0.255	0.253 \pm 0.136	0.0371	0.459
TP (mg l ⁻¹)	0.203 \pm 0.143	0.000	0.492	0.372 \pm 0.289	0.0072	0.868

Data from monthly sampling in July, August, September 1997 from landward side and seaward side, $n = 12$.

*One-way ANOVA results showed significant difference between landward and seaward sides ($p < 0.05$).

Table 3: Correlation matrices of physico-chemical variables of the water and sediments in *gei wais* at Mai Po Marshes (data from monthly sampling in July, August, September 1997 from landward side and seaward side, $n = 12$).

	pH (sediments)	Eh	EC	TOM	Temp	pH (water)	Sal	DO	BOD	DOC	TSS	VSS	NH4	NO2	NO3	PO4	TP
Landward																	
(r)																	
pH	1.000																
(sediments)																	
Eh	-0.141	1.000															
EC	0.014	-0.551	1.000														
TOM	-0.307	-0.175	-0.074	1.000													
Temp	0.229	0.132	-0.559	0.073	1.000												
pH (water)	-0.674*	0.100	0.191	0.035	-0.073	1.000											
Sal	-0.051	0.090	-0.399	-0.223	0.566	0.301	1.000										
DO	-0.128	-0.382	-0.396	0.401	0.192	-0.173	0.276	1.000									
BOD	0.097	-0.369	0.427	0.117	0.117	0.467	0.329	-0.229	1.000								
TOC	-0.273	-0.318	0.335	0.244	-0.405	0.365	-0.271	-0.006	0.350	1.000							
TSS	0.419	-0.388	0.290	-0.381	0.297	0.162	0.538	0.050	0.556	-0.230	1.000						
VSS	0.236	-0.477	0.431	-0.074	0.131	0.304	0.493	0.080	0.758**	0.195	0.836***	1.000					
NH4	-0.068	-0.146	0.540	-0.152	-0.871***	-0.099	-0.467	-0.126	-0.242	-0.045	-0.094	-0.113	1.000				
NO2	-0.559	-0.087	0.021	0.135	-0.479	0.064	-0.155	0.345	-0.403	-0.041	-0.389	-0.437	0.536	1.000			
NO3	-0.525	-0.025	-0.040	0.224	-0.319	0.105	-0.214	0.309	-0.402	-0.152	-0.371	-0.511	0.431	0.940***	1.000		
PO4	-0.095	0.527	-0.097	0.164	0.055	0.226	0.190	-0.332	0.332	0.174	-0.096	0.202	-0.264	-0.378	-0.451	1.000	
TP	-0.283	0.231	0.392	-0.124	-0.390	0.541	0.120	-0.403	0.443	0.320	0.171	0.433	0.196	-0.141	-0.279	0.741**	1.000
Seaward																	
(r)																	
pH	1.000																
(sediments)																	
Eh	-0.712**	1.000															
EC	-0.160	0.094	1.000														
TOM	-0.190	-0.072	0.104	1.000													
Temp	-0.180	0.322	0.242	-0.116	1.000												
pH (water)	-0.349	0.117	0.106	0.443	0.295	1.000											
Sal	-0.399	0.210	0.607*	0.517	0.585*	0.678*	1.000										
DO	0.144	-0.058	-0.003	0.262	0.317	0.482	0.253	1.000									
BOD	-0.267	0.444	0.186	-0.242	0.934***	0.112	0.416	0.309	1.000								
TOC	-0.062	0.253	0.399	-0.327	0.842***	0.036	0.375	0.168	0.781**	1.000							
TSS	0.000	0.068	-0.053	0.292	-0.111	-0.316	0.025	0.083	0.029	-0.151	1.000						
VSS	0.107	-0.047	-0.388	0.173	-0.473	-0.332	-0.343	-0.003	-0.306	-0.520	0.813**	1.000					
NH4	-0.404	0.383	0.803***	0.155	0.679*	0.423	0.830***	0.150	0.591*	0.637*	-0.208	-0.571	1.000				
NO2	-0.247	0.127	0.643**	0.295	0.559	0.132	0.712**	0.204	0.485	0.551	0.306	-0.257	0.648*	1.000			
NO3	-0.505	0.679*	0.070	0.075	0.793**	0.465	0.497	0.386	0.792**	0.562	-0.212	-0.413	0.613*	0.286	1.000		
PO4	-0.499	0.499	0.715**	0.236	0.326	0.330	0.625*	0.207	0.377	0.276	0.012	-0.355	0.767**	0.540	0.464	1.000	
TP	-0.527	0.440	0.731**	0.382	0.438	0.407	0.738**	0.161	0.404	0.359	-0.181	-0.526	0.886***	0.571	0.582*	0.903***	1.000

$p < 0.05^*$; $p < 0.01^{**}$; $p < 0.001^{***}$.

degradation may dominate the interactions between the water and the sediments. Organic acids produced during organic matter decomposition contribute to low pH levels, while nutrients released from organic matter decomposition may promote algal growth in water, which may, in turn, lead to high water pH levels (Wetzel, 2001). The negative correlations ($p < 0.05$) between water pH and sediment pH may possibly result from organic matter degradation in the sediments. In the water column, heterotrophic bacteria promotion by organic matter (Wetzel, 2001) seems to explain the positive correlations ($p < 0.05$) between BOD and VSS. Moreover, the negative relationship ($p < 0.05$) between temperature and $\text{NH}_3\text{-N}$ suggests that temperature affects $\text{NH}_3\text{-N}$ metabolism (assimilation by bacteria or algae, or transformation by nitrobacteria) (Wetzel, 2001), that more $\text{NH}_3\text{-N}$ was removed under higher water temperature.

At the seaward side, change in redox seems to be the major factor controlling the interactions between water and the sediments. It has been revealed that the oxidation of FeS_2 (and other sulphide minerals) to sulphate and $\text{NH}_3\text{-N}$ to $\text{NO}_3^- \text{-N}$ leads to the production of H^+ and low pH levels (Bourg & Loch, 1995). The negative correlations between pH and Eh in the sediments ($p < 0.01$) reflect this redox change in response to the electron-accepting reactions in aquatic systems. This result confirms the relationships between Eh and pH at the seaward side as previously reported (Lau, 2000). On the other hand, the close relationship between EC and salinity seems to imply possible sediment resuspension at the seaward side. Temperature has been shown to promote N and P release from the sediments in *gei wais* (Lau & Chu, 1999), while temperature is the key in governing microbial activities in the water (Wetzel, 2001). The close correlations among water temperature, organic matter (BOD, TOC) and nutrients (N, P) in the water possibly reflect the importance of temperature in the aquatic biological and physicochemical processes.

5.3.3. Relationships Between Heavy Metal Concentrations in the Sediments and Aquatic Physicochemical Properties in Gei Wais at Mai Po Marshes

The concentrations of total heavy metal and heavy metal speciations in the sediments are shown in Table 4. The distributions of heavy metals in different speciation fractions in the sediments from both locations are similar, except for the significant differences ($p < 0.05$) of Cr in the organic matter phase (Cr3) (landward: $2.81 \mu\text{g g}^{-1}$; seaward: $1.44 \mu\text{g g}^{-1}$) and Ni in the sulfide phase (Ni5) (landward: $16.6 \mu\text{g g}^{-1}$; seaward: $19.7 \mu\text{g g}^{-1}$). Cr has been shown to have greater humic acid sorption ability, compared with Cd, Zn and Ni (Sposito, 1986), but it has low mobility under acidic conditions (Reimann & De Caritat, 1998). It seems that more TOM input might provide more binding

Table 4: Summary of heavy metal concentrations ($\mu\text{g g}^{-1}$) (total and speciation) in the sediments in *gei wais* at Mai Po Marshes.

	Landward			Seaward		
	Mean \pm SD	Min	Max	Mean \pm SD	Min	Max
Cd						
HNO ₃ + H ₂ SO ₄ (total, Cd)	0.574 \pm 0.441	0.000	1.27	0.992 \pm 0.817	0.040	2.28
KNO ₃ (exchangeable, Cd1)	0.078 \pm 0.107	0.000	0.250	0.0508 \pm 0.0769	0.000	0.200
KF (adsorbed, Cd2)	0.001 \pm 0.003	0.000	0.010	0.0717 \pm 0.139	0.000	0.420
Na ₄ P ₂ O ₇ (org matter, Cd3)	0.136 \pm 0.218	0.000	0.650	0.168 \pm 0.252	0.000	0.800
Na ₂ EDTA (carbonates, Cd4)	0.057 \pm 0.089	0.000	0.230	0.109 \pm 0.155	0.000	0.500
HNO ₃ (sulfides, Cd5)	0.085 \pm 0.148	0.000	0.500	0.226 \pm 0.369	0.000	1.30
Cr						
HNO ₃ + H ₂ SO ₄ (total, Cr)	20.5 \pm 4.81	13.4	29.7	17.2 \pm 3.85	10.9	22.2
KNO ₃ (exchangeable, Cr1)	0.878 \pm 0.520	0.230	2.01	0.670 \pm 0.485	0.040	1.50
KF (adsorbed, Cr2)	1.23 \pm 1.20	0.230	4.24	0.999 \pm 0.842	0.200	2.80
Na ₄ P ₂ O ₇ (org matter, Cr3)	2.81 \pm 1.42*	0.600	4.68	1.44 \pm 1.02	0.000	3.20
Na ₂ EDTA (carbonates, Cr4)	2.78 \pm 1.15	1.23	5.20	2.58 \pm 1.15	0.380	4.22
HNO ₃ (sulfides, Cr5)	9.58 \pm 3.21	3.83	16.9	8.03 \pm 1.87	5.18	10.3
Cu						
HNO ₃ + H ₂ SO ₄ (total, Cu)	38.7 \pm 12.1	24.8	58.6	34.0 \pm 10.5	21.5	58.9
KNO ₃ (exchangeable, Cu1)	0.804 \pm 0.373	0.180	1.53	0.517 \pm 0.317	0.000	0.990
KF (adsorbed, Cu2)	2.51 \pm 1.02	1.16	4.41	2.01 \pm 0.895	0.480	3.20
Na ₄ P ₂ O ₇ (org matter, Cu3)	6.70 \pm 4.40	2.78	16.3	5.03 \pm 1.61	3.02	8.96
Na ₂ EDTA (carbonates, Cu4)	9.20 \pm 4.74	2.81	20.5	7.23 \pm 2.25	3.76	11.7
HNO ₃ (sulfides, Cu5)	12.3 \pm 3.77	6.29	19.8	11.5 \pm 3.89	6.52	19.5

(continued)

Table 4: Continued.

	Landward			Seaward		
	Mean \pm SD	Min	Max	Mean \pm SD	Min	Max
Ni						
HNO ₃ + H ₂ SO ₄ (total, Ni)	36.2 \pm 6.30	28.4	47.2	38.3 \pm 8.30	21.9	50.3
KNO ₃ (exchangeable, Ni1)	1.60 \pm 1.33	0.080	4.33	1.95 \pm 1.36	0.140	4.34
KF (adsorbed, Ni2)	2.53 \pm 1.63	0.240	5.23	1.77 \pm 1.24	0.600	5.01
Na ₄ P ₂ O ₇ (org matter, Ni3)	3.71 \pm 1.42	1.68	6.42	3.59 \pm 1.91	0.640	6.63
Na ₂ EDTA (carbonates, Ni4)	5.05 \pm 1.94	1.68	8.22	5.42 \pm 1.95	2.58	9.71
HNO ₃ (sulfides, Ni5)	16.6 \pm 2.16*	13.3	20.1	19.7 \pm 4.42	13.8	29.0
Pb						
HNO ₃ + H ₂ SO ₄ (total, Pb)	56.0 \pm 9.58	36.8	67.6	51.8 \pm 11.2	33.0	72.4
KNO ₃ (exchangeable, Pb1)	1.90 \pm 1.16	0.350	4.05	1.54 \pm 1.04	0.200	3.20
KF (adsorbed, Pb2)	1.60 \pm 1.00	0.320	3.83	1.99 \pm 2.12	0.310	8.12
Na ₄ P ₂ O ₇ (org matter, Pb3)	6.50 \pm 4.39	0.920	13.5	4.95 \pm 3.84	0.740	13.2
Na ₂ EDTA (carbonates, Pb4)	16.6 \pm 7.66	2.76	29.7	21.2 \pm 10.6	5.53	37.8
HNO ₃ (sulfides, Pb5)	17.4 \pm 6.84	5.75	26.5	13.9 \pm 6.36	4.40	28.2
Zn						
HNO ₃ + H ₂ SO ₄ (total, Zn1)	129 \pm 27.4	76.2	162	121 \pm 27.2	74.1	174
KNO ₃ (exchangeable, Zn2)	0.912 \pm 0.775	0.030	2.36	0.500 \pm 0.658	0.010	2.18
KF (adsorbed, Zn3)	1.13 \pm 2.04	0.010	7.22	0.580 \pm 0.776	0.000	2.60
Na ₄ P ₂ O ₇ (org matter, Zn3)	16.4 \pm 6.08	10.3	27.4	18.2 \pm 9.91	8.68	39.4
Na ₂ EDTA (carbonates, Zn4)	23.7 \pm 5.88	14.7	32.5	25.1 \pm 5.91	15.5	39.1
HNO ₃ (sulfides, Zn5)	48.0 \pm 11.2	23.0	59.6	42.8 \pm 9.12	26.1	60.7

Data from the monthly sampling in July, August and September 1997 from landward and seaward sides, $n = 12$.

*One-way ANOVA results showed significant difference between landward and seaward sides ($p < 0.05$).

sites for Cr, which led to a higher retention of Cr³⁺ in the sediments at the landward side.

Percentage distributions of heavy metal speciation are shown in Fig. 2. Heavy metal sulfide phases (Me5) (landward: 31.9–47.2%; seaward: 28.0–52.5%) and carbonate phases (Me4) (landward: 13.7–29.1%; seaward: 14.1–39.3%) accounted for most of the total metal contents of each heavy metal, except for Cd. The exchangeable (Me1) (landward: 0.767–3.69%; seaward: 0.406–5.00%) and adsorbed phases (Me2) (landward: 0.836–7.42%; seaward: 0.511–6.66%) had the least percentage. Large variations were detected for Cd distribution in different speciation fractions.

The relationships between total heavy metal contents and aquatic physicochemical properties were revealed through regression analysis (Fig. 3). Among the six heavy metals, total Cd and Pb in the sediments seem to be closely associated with aquatic environmental factors at both the landward and seaward sides, while no significant relationships ($p < 0.05$) were revealed for total Zn or Ni. The results demonstrate that high water pH levels caused high Pb and Cr precipitation and retention in the sediments. Cu may dissolve from the sediments by Cl⁻ complexation at high salinity (Lydersen et al., 2002), but the results of the present study showed that high Cu retention in the sediments occurred under high water salinity. Future studies are necessary in order to pinpoint the proper mechanisms. On the other hand, our result indicating that high suspended solids (TSS, VSS) increased Cd in the sediments also cannot be easily explained. Further investigations on the suspended particles are needed to elucidate these problems.

The relationships between the concentrations of fractionated speciations of heavy metals and aquatic physicochemical properties are presented in Table 5. At the landward side, organic matter and biological activities appear to influence heavy metal mobility. It is suggested that the negative regressions of temperature on the organic phases of Cu (Cu3) and Cd (Cd3) may result from reduced pH levels in the sediment due to increased organic matter degradation under higher temperature (Wetzel, 2001). Natural organic matter has been shown to compete for the adsorption of heavy metals over clay minerals (Schmitt et al., 2002). It is likely that the increase of particulate organic matter (indicated by TSS and VSS) led to the decreased Cu adsorption to clay minerals, which reduced the fractions of the adsorbed phase of Cu (Cu2). The negative correlations ($p < 0.01$) between the exchangeable phase of Cu (Cu1) and water salinity may possibly be explained by the effects of Cl⁻ complexation of Cu (Lydersen et al., 2002).

At the seaward side, variations in redox condition seem to play an important role in heavy metal mobility. The results indicate that adsorbed phases of heavy metals (Cr2, Cu2 and Zn2) are closely associated with water salinity, NH₃-N, TP, PO₄³⁻-P, temperature, and sediment pH and EC (Table 5), which is in agreement

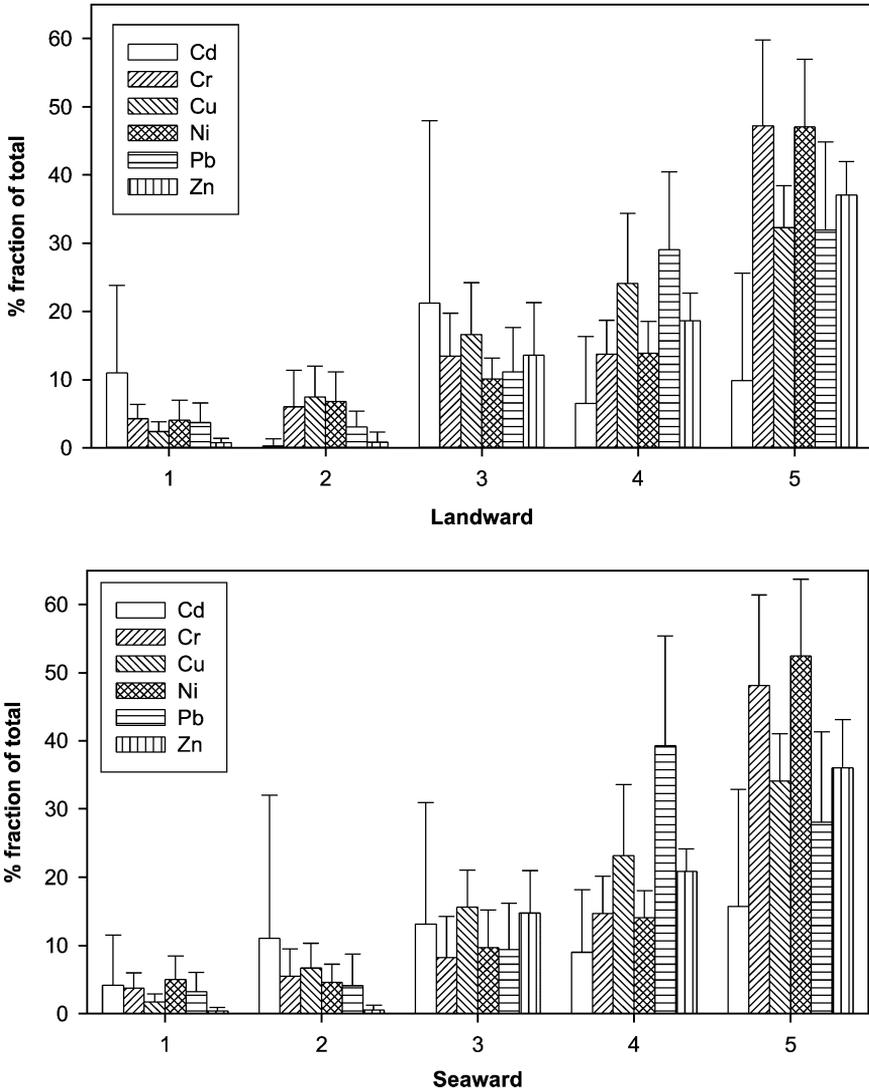


Figure 2: Percentage distribution of metal speciations relative to total metal concentrations season. Phases: 1— KNO_3 extracted, exchangeable; 2— KF extracted, absorbed; 3— $\text{Na}_4\text{P}_2\text{O}_7$ extracted, organic matter bond; 4— Na_2EDTA extracted, carbonates; 5— HNO_3 extracted, sulfides). Errors bars represent one standard deviation about the mean.

with Yu et al. (2000) who found that Mn (hydr)oxides were responsible for the mobility of Cr, Cu and Zn in the sediments at Mai Po Marshes.

It is noticed that total Pb in the sediments of the seaward side was well predicted by TOM in the sediments ($p < 0.01$) (Fig. 3). Pb has much stronger affinity for

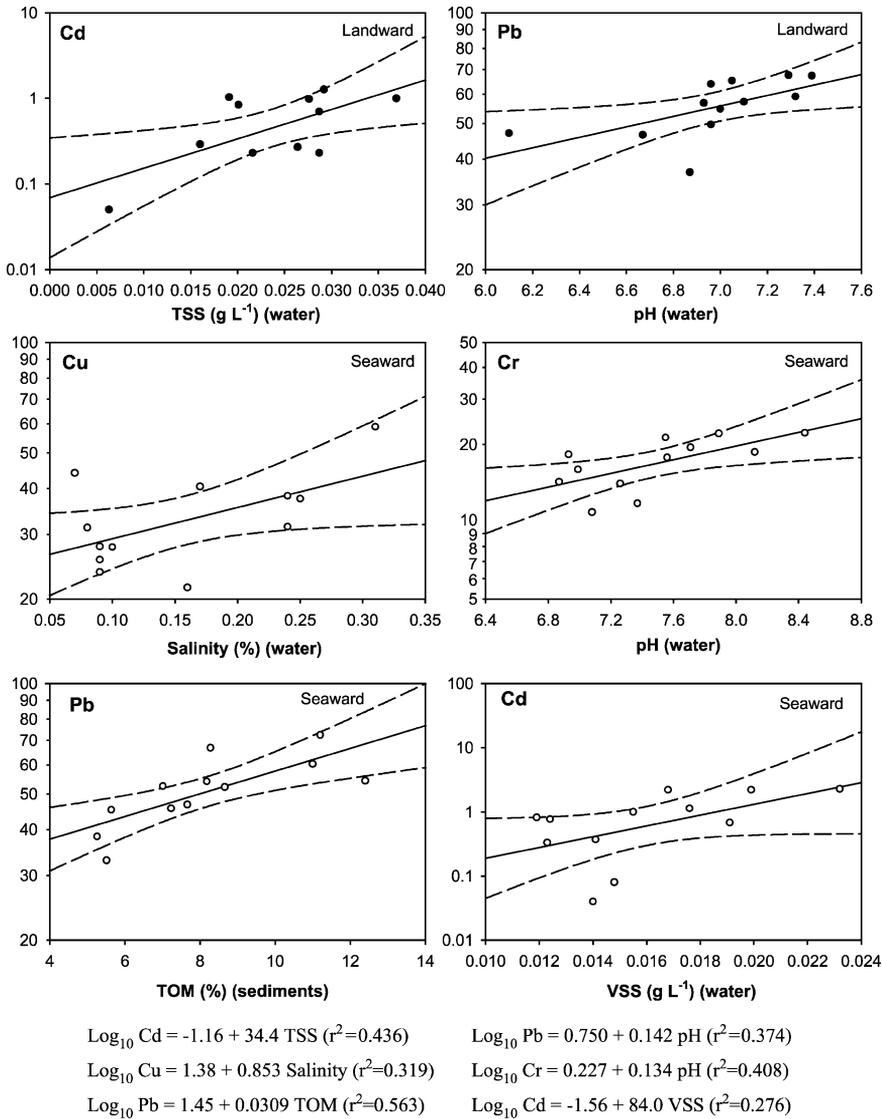


Figure 3: Significant regression ($p < 0.05$) (95% confidence intervals) between heavy metals in the sediments ($\mu\text{g g}^{-1}$) and physico-chemical parameters at Mai Po Marshes.

sediment surface sorption and organic complexation over other heavy metals (Sposito, 1986; Calmano et al., 1994). It seems that during the sediment disturbance, Pb may have an advantage over other heavy metals in the formation of carbonated Pb, or complexes with the organic matter. Our heavy metal

Table 5: Significant linear regressions between heavy metal concentrations in the sediments (total and speciation) and physicochemical variables of the water and sediments in *gei wais* at Mai Po Marshes.

Landward					Seaward				
Variables	Metals	Slopes	R^2	p value	Variables	Metals	Slopes	R^2	p value
TSS	Cu2	-0.006	0.583	0.0039	EC (sediments)	Cu2	-2.074	0.541	0.0064
VSS	Cu1	-0.007	0.624	0.0022		Pb3	0.522	0.630	0.0021
	Cu2	-0.002	0.583	0.0038	Sal	Cu2	-0.075	0.646	0.0016
Temp	Cu3	-0.121	0.549	0.0058		Pb3	0.017	0.622	0.0023
Sal	Cu1	-0.135	0.574	0.0043		Pb4	0.006	0.529	0.0074
DO	Zn4	0.069	0.623	0.0023	NH4	Cu2	-2.211	0.845	0.0008
pH (sediments)	Cd3	1.489	0.550	0.0058		Pb3	0.500	0.794	0.0001
					TP	Cu2	-0.295	0.836	0.0001
						Pb3	0.057	0.575	0.0040
					PO4	Cu2	-0.127	0.694	0.0001
					Temp	Cr2	1.083	0.529	0.0074
					pH (sediments)	Zn2	-0.407	0.574	0.0043
					TOM (sediments)	Pb4	0.180	0.668	0.0012

Data from monthly sampling in July, August, September 1997 from landward and seaward sides, $n = 12$.

speciation results support this explanation, in that the organic matter complexed phase of Pb (Pb₃) was well predicted by EC, salinity and NH₃-N and TP ($p < 0.01$) (Table 5). On the other hand, one-way ANOVA results showed that TOM was higher at the landward side ($p < 0.05$) than the seaward side, but there were no significant differences ($p < 0.05$) for total Pb (Liang & Wong, 2003). Compositions as well as concentrations of TOM may possibly affect Pb retention in the sediment. However, more studies are necessary to trace the source of the organic matter and the mechanisms regarding Pb behavior in the sediments.

5.4. Conclusions

There seems to be a spatial difference as to heavy metal mobility and its associations with the local aquatic biogeochemical processes at Mai Po Marshes. Organic matter decomposition seems to be the major process that determines heavy metal (Cd, Cr, Cu, Pb) mobility at the landward side, while redox condition dynamics at the seaward side appears to be the controlling factor for heavy metal (Cr, Cu, Zn) mobility. It is suggested that the uneven distribution of mangrove trees in *gei wais* may determine the organic matter (litter) input to the sediments and water temperature. Sediment resuspension and changes in redox conditions seem to be typical characteristics in estuarine systems, and sites closer to the coast seem to have more dramatic sediment resuspension and redox change in *gei wais* at Mai Po Marshes.

Organic matter appears to play an important role in heavy metal (Cd, Cr, Cu, Pb) mobility. Organic matter appears to complex heavy metals directly, decrease pH by releasing organic acid, and increase pH through releasing nutrients and stimulating algal bloom, while pH determines heavy metal retention in the sediments. The results imply that organic matter management at Mai Po Marshes should also consider organic dynamics associated heavy metal mobility.

At Mai Po Marshes, water quality and salinity seem to be important factors influencing heavy metal (Cu, Pb) mobility. Seasonal salinity and temperature gradients in *gei wais* at Mai Po Marshes were revealed in our previous study (Liang & Wong, 2003). Further studies on predicting temporal heavy metal mobility based on water quality and salinity are necessary in the future.

Suspended solid material was shown to well predict total Cd in the sediments in *gei wais*. While information on the composition of the suspended particles and its associations with the turbidity in the inter-tidal water has not been available, more investigations should be conducted.

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References

- APHA. (1985). *Standard methods for the examination of water and wastewater*. American Public Health Association, Washington, 16th ed.
- Bourg, A. C. M., & Loch, J. P. G. (1995). Mobilization of heavy metals as affected by pH and redox conditions. In: W. Salomons, & W. M. Stigliani (Eds), *Biogeochemistry of pollutants in soils and sediments: risk assessment of delayed and non-linear responses*. Springer, Berlin.
- Calmano, W., Förster, U., & Hong, J. (1994). Mobilization and scavenging of heavy metals following resuspension of anoxic sediments from the Elbe River. In: C. N. Alpers, & D. W. Blowes (Eds), *Environmental Geochemistry of Sulfide Oxidation* (ACS Symposium Series 550, pp. 298–321). American Chemical Society, Washington, DC.
- Cantwell, M. G., & Burgess, R. M. (2001). Metal–colloid partitioning in artificial interstitial waters of marine sediments: influences of salinity, pH, and colloidal organic carbon concentration. *Environmental Toxicology and Chemistry*, **20**, 11, 2420–2427.
- Chapman, P. M., & Wang, F. (2001). Annual review: assessing sediment contamination in estuaries. *Environmental Toxicology and Chemistry*, **20**, 1, 3–22.
- Förstner, U. (1995). Non-linear release of metals from aquatic sediments. In: W. Salomons, & W. M. Stigliani (Eds), *Biogeochemistry of pollutants in soils and sediments: risk assessment of delayed and non-linear responses*. Springer, Berlin.
- Hodgkiss, I. J. (1986). Aspects of mangrove ecology in Hong Kong. *Memoirs of the Hong Kong Natural History Society*, **17**, 107–116.
- Irving, R., & Morton, B. (1988). *A geography of the Mai Po Marshes*. Hong Kong University Press, Hong Kong.
- Lau, S. S. S. (2000). The significance of temporal variability in sediment quality for contamination assessment in a coastal wetland. *Water Research*, **34**, 2, 387–394.
- Lau, S. S. S., & Chu, L. M. (1999). Contaminant release from sediments in a coastal wetland. *Water Research*, **33**, 4, 909–918.
- Lau, S. S. S., & Chu, L. M. (2000). The significance of sediment contamination in a coastal wetland, Hong Kong, China. *Water Research*, **34**, 2, 379–386.
- Lee, S. Y. (1990). Primary productivity and particulate organic matter flow in an estuarine mangrove-wetland in Hong Kong. *Marine Biology*, **106**, 453–463.
- Lee, S. Y. (2000). Carbon dynamics of Deep Bay, Eastern Pearl River Estuary, China. II: Trophic relationship based on carbon- and nitrogen-stable isotopes. *Marine Ecology Progress Series*, **205**, 1–10.

- Li, M. S., & Lee, S. Y. (1998). Carbon dynamics of Deep Bay, Eastern Pearl River Estuary, China. I: a mass balance budget and implications for shorebird conservation. *Marine Ecology Progress Series*, **159**, 275–284.
- Liang, Y., & Wong, M. H. (2003). Spatial and temporal organic and trace metal pollution at Mai Po Marshes Nature Reserve, Hong Kong. *Chemosphere*, **52**, 9, 1647–1658.
- Liang, Y., Wong, M. H., Shutes, R. B. E. and Revitt, D. M. (1999). Ecological risk assessment of PCBs contamination in Mai Po Marshes Nature Reserve, Hong Kong. *Water Research*, **33**, 6, 1337–1346.
- Lydersen, E., Löfgren, S., & Arnesen, R. T. (2002). Metals in Scandinavian surface waters: effects of acidification, liming, and potential reacidification. *Critical Reviews in Environmental Science and Technology*, **32**, 2/3, 73–295.
- Ong Che, R. G., & Cheung, S. G. (1998). Heavy metals in *Metapenaeus ensis*, *Eriocheir sinensis* and sediment from the Mai Po Marshes, Hong Kong. *The Science of the Total Environment*, **214**, 87–97.
- Reimann, C., & De Caritat, P. (1998). *Chemical elements in the environment: factsheets for the geochemist and environmental scientist*. Springer, Berlin, Germany.
- Sauvé, S., Hendershot, W., & Allen, H. E. (2000). Solid–solution partitioning of metals in contaminated soils: dependence on pH, total metal burden, and organic matter. *Environmental Science & Technology*, **34**, 7, 1125–1131.
- Schmitt, D., Taylor, H. E., Aiken, G. R., Roth, D. A., & Frimmel, F. H. (2002). Influence of natural organic matter on the adsorption of metal ions onto clay minerals. *Environmental Science & Technology*, **36**, 2932–2938.
- Schulin, R., Geiger, G., & Furrer, G. (1995). Heavy metal retention by soil organic matter under changing environmental conditions. In: W. Salomons, & W. M. Stigliani (Eds), *Biogeochemistry of pollutants in soils and sediments: risk assessment of delayed and non-linear responses*. Springer, Berlin.
- Sposito, G. (1986). Sorption of trace metals by humic materials in soils and natural waters. *CRC Critical Reviews in Environmental Control*, **16**, 2, 193–229.
- Stover, R. C., Sommers, L. E., & Silveira, D. J. (1976). Evaluation of metals in wastewater sludge. *Journal WPCF*, **48**, 9, 2165–2175.
- Tam, N. F. Y., & Wong, Y. S. (2000). Spatial variation of heavy metals in surface sediments of Hong Kong Mangrove Swamps. *Environmental Pollution*, **110**, 195–205.
- Wetzel, G. R. (2001). *Limnology: lake and river ecosystems*. Academic Press, New York, 3rd ed.
- Young, L. (1995). The biological importance of Deep Bay and the Mai Po Marshes. In: S. T. Chiu (Ed.), *Wetlands: Deep Bay and the Mai Po Marshes*, One day symposium. Institute of Biology (Hong Kong Branch), Hong Kong.
- Yu, K. T., Lam, M. H. W., Yen, Y. F., & Leung, A. P. K. (2000). Behavior of trace metals in the sediment pore waters of intertidal mudflats of a tropical wetland. *Environmental Toxicology and Chemistry*, **19**, 3, 535–542.