

Characteristics of metal enrichment in Deep Bay, Hong Kong

LIU Wen-xin^{1,2}, LI Xiang-dong^{1,*}, LI Yok-sheung¹, WAI Wing-hong Onyx¹, O. W. H. Wai¹

(1. Department of Civil & Structural Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong. E-mail: cexdli@polyu.edu.hk; 2. SKLEAC, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China. E-mail: wxliu@urban.pku.edu.cn)

Abstract: Sediment cores, suspended particles and overlying water were collected in Deep Bay, Hong Kong. Enrichment of Zn in surface sediments in the landward direction and the decreasing of exchangeable Cd, Ni and Zn in sediment from the inner bay to the outer bay indicated the influence of anthropogenic pollutants discharged from the riparian runoffs.

Keywords: metal enrichment; sediments; overlying water; suspended particles; Deep Bay.

Introduction

Estuaries, as the fertile marine ecosystems, are crucial to the life cycle of many aquatic organisms. However, rapid industrialization and urbanization in recent years have led to widespread contamination of heavy metals in the coastal and estuarine sediments, and impose direct threat or potential risk on the local ecosystem (Chapman, 2001). Therefore, detailed studies on the biological and ecological significance of metal contamination in sediments are urgently required. Since the acute and chronic impacts of heavy metals are usually dependent on the existing chemical forms rather than total concentrations, extra attention must be paid on metal speciation when evaluating the environmental implications (Förstner, 1993).

The hydrodynamic conditions in Deep Bay, a semi-enclosed bay, are different from the adjacent Pearl River Estuary (PRE) in South China. In recent years, the local environment faces great pressure due to the increasing discharges of industrial effluents, domestic sewage and livestock wastewater via runoffs along the bank (Hills, 1998; Lau, 2000). The objective of the present study is to investigate the current distribution and associations of heavy metals in the overlying water, bottom sediments and suspended particles.

1 Materials and methods

1.1 Sediment and water sampling

Three sediment cores together with overlying waters, designated as site 1, 2 and 3 from the inner to the outer bay (Fig. 1), were collected by a gravity corer with automatic clutch and reversed catcher.

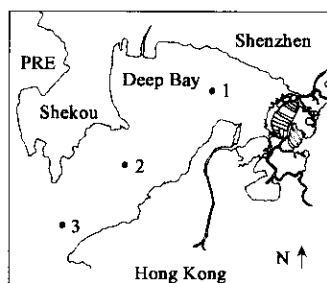


Fig. 1 Map of sampling locations

1.2 Chemical analysis

Dissolved organic carbon (DOC) and salinity were measured using TOC-analyzer (TOC 5000, Shimadzu) and conductivity meter (ES-14E, HORIBA), respectively. The overlying water was filtered through a pre-cleaned 0.45- μm membrane. The filters with retained suspended particles were dried up in the oven at 105°C over night. Sediment sections were sliced at an interval of 2 cm. After dried at 105°C and ground to pass a 74- μm sieve, each homogenized section was weighted in a tube and digested with a mixture of concentrated HNO₃ and HClO₄ at 90–190°C for 16 h (Li, 2000). A similar digestion procedure was applied to the suspended particles. Trace and major elements were determined using ICP-AES (Perkin Elmer Optima 3300DV). International standard reference material (SRM 1646a, NIST) was utilized to verify the accuracy of metal analysis. All the recovery rates of heavy metals in SRM were around 80%–115%. The deviations in replicates of the standard reference materials and actual samples were generally lower than 10%.

The soluble and exchangeable forms of heavy metals are usually regarded as more mobile and bioavailable (Förstner, 1983). The exchangeable metals extracted by 1.0 mol/L MgCl₂ for 1 h was also analyzed using the method developed by Tessier *et al.* (Tessier, 1979).

2 Results and discussion

2.1 Metals in overlying water and suspended particles

Physicochemical properties, dissolved metal concentrations of overlying water, and heavy metal concentrations of suspended particles, are summarized in Table 1.

The increase in dissolved concentrations of Cu, Ni and Zn from site 3 (outer bay) to site 1 (inner bay) revealed, to some extent, the influence of contaminant input from land sources. Since the different metal contents lie in the range of Grade I or Grade II of the National Seawater Quality Standards (WQS; China EPA, 1997), the current water quality of Deep Bay is good on the whole. The metal concentrations of suspended particles are usually affected by the quantity and adsorption capacity of suspended particles, both of which involve many factors, e. g., hydrodynamics and surface properties. As a result, the metal concentrations of suspended particles varied in a wide range among the sampling sites.

Table 1 Physicochemical properties and dissolved metal concentrations in overlying waters, national seawater quality standards(WQS, GB 3097—1997) and heavy metal contents in suspended particles

Overlying waters	pH	Salinity,‰	DOC,mg C/L	Cd,μg/L	Co,μg/L	Cu,μg/L	Ni,μg/L	Pb,μg/L	Zn,μg/L
Site 1	7.5	32.1	2.9	ND	0.4	5.8	9.7	ND	20.7
Site 2	7.4	32.4	3.4	ND	0.8	3.5	5.4	ND	12.7
Site 3	7.6	33.9	1.9	ND	0.3	0.6	3.0	ND	10.5
Grade I ^a of WQS				≤1		≤5	≤5	≤1	≤20
Grade II ^b of WQS				1—5		5—10	5—10	1—5	20—50
Suspended particles				Cd,μg/L	Co,μg/L	Cu,μg/L	Ni,μg/L	Pb,μg/L	Zn,μg/L
Site 1				2.5	45.3	219.3	135.4	341.8	1004.4
Site 2				1.6	30.3	137.7	89.3	451.1	701.7
Site 3				4.8	53.9	245.5	171.0	319.7	1365.5
Suspended particles				Cd,mg/kg	Co,mg/kg	Cu,mg/kg	Ni,mg/kg	Pb,mg/kg	Zn,mg/kg
Site 1				0.7	9.6	48.0	31.9	84.2	230.2
Site 2				1.1	14.6	68.8	50.4	264.9	380.8
Site 3				1.3	12.2	56.6	42.2	82.5	330.1

Notes: ND. Not detected; a. Grade I is applied to marine fishery; b. Grade II is applied to aquaculture practice and bathing beaches(China EPA, 1997)

2.2 Metals in sediment profiles

The metal concentrations in the sediment cores are shown in Fig.2. Cd and Co concentrations were low and stable throughout the entire profile. The vertical variations in Cu, Ni and Pb levels were relatively small, whereas there was a slight increase from the outer bay to the inner

bay. In the case of Zn, a significant enrichment in the profile could be observed, and the Zn concentration at the top layer also increased from site 3 to site 1.

The correlation coefficients and the principal component (PC) loadings of heavy metals are listed in Table 2(upper panel) and depicted in Fig. 3, respectively. Three groups can be identified based on loading distribution and associations of metal variables: (1) Cu, Pb and Zn; (2) Cd, Co, Ni and Fe; and (3) Mn.

Table 2 Pearson correlation coefficients for total metal concentrations($n = 63$) and for exchangeable metals in sediments ($n = 18$)

Total metal	Cd	Co	Cu	Ni	Pb	Zn	Fe	Mn
Cd	1.00							
Co	0.79	1.00						
Cu	0.69	0.58	1.00					
Ni	0.93	0.79	0.79	1.00				
Pb	0.80	0.65	0.88	0.85	1.00			
Zn	0.72	0.53	0.98	0.80	0.90	1.00		
Fe	0.90	0.92	0.64	0.91	0.75	0.63	1.00	
Mn	0.31 ^a	0.47	0.31 ^a	0.42	0.33	0.26 ^a	0.45	1.00
Exchangeable metal	Cd ^b	Co	Cu	Ni	Pb ^c	Zn		
Cd	1.00							
Co	0.92	1.00						
Cu	0.81	0.77	1.00					
Ni	0.89	0.95	0.88	1.00				
Pb ^c					1.00			
Zn	0.85	0.97	0.67	0.90		1.00		

Notes: a. The values are statistically significant at $P < 0.05$, others are statistically significant at $P < 0.01$; b. Actual data on Cd below the detection limit in this study are regarded as 0.0; c. The correlation coefficients of Pb with other metals are neglected due to many values lower than the detection limit

In comparison with the local backgrounds and sediment quality values (Table 3), except Cd with slightly excessive levels, the concentrations of other studied metals were generally below the low values of the interim sediment quality values(ISQVs) for Hong Kong(Chapman, 1999). However, it should be noted that the concentrations of Cu, Ni, Pb and Zn still exceed the regional backgrounds. The increasing trend of metal concentrations from the outer bay to the inner bay exhibits the influences of riparian anthropogenic activities in the inner bay area. Hills *et al.* (Hills, 1998) showed that the main local sources of heavy metals

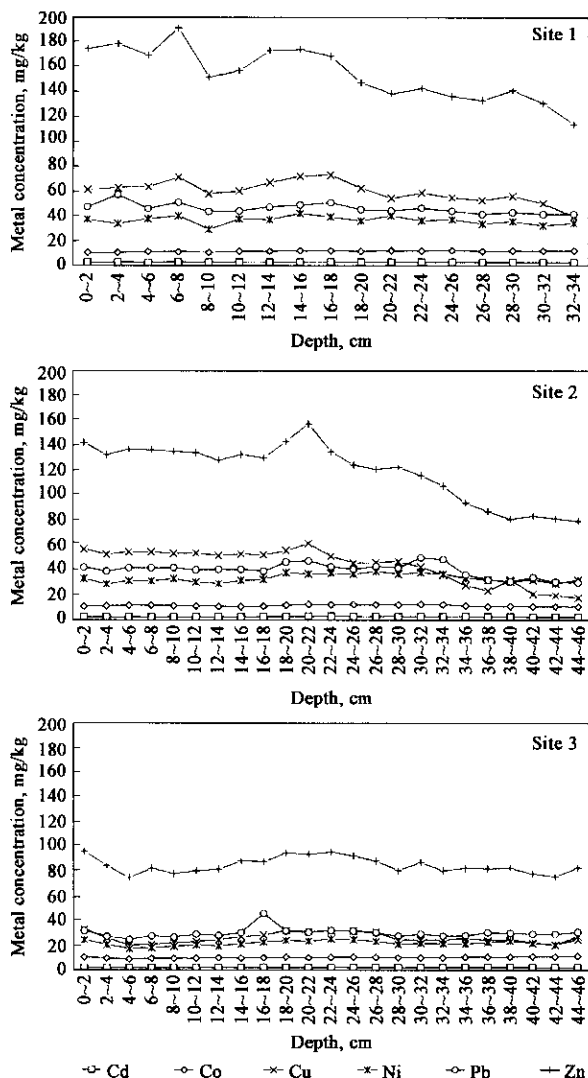


Fig.2 Concentrations of heavy metals in sediment cores

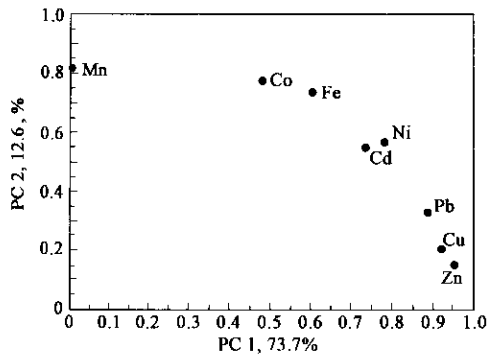


Fig.3 Principal component loadings of heavy metals in the sediment cores. The percentage of explained variance by each principal component is shown in parentheses

in sediments could be attributed to the inputs of industrial wastewater through Shenzhen River and other discharging points in the inner bay area. The monitoring records indicated that, in the normal season, the concentrations of Cu, Pb and Zn at the mouth of Shenzhen River were 61, 17 and 231 $\mu\text{g/L}$, respectively (Peking University, 1994). These values were much higher than the range of Grade I and Grade II of the National WQS (Table 1).

2.3 Exchangeable metals

The concentrations of exchangeable metals in the top layer and the

Table 3 Comparison of total concentrations in surface sediments with regional backgrounds, interim sediment quality values and monitoring results in the neighboring area (mg/kg)

Type	Cd	Cu	Ni	Pb	Zn	Sources
Coastal background in South Sea of China	30	25	80			Zheng, 1992
Background in the Pearl River Estuary	10	15	29	70		Tanner, 2000
Local background in Hong Kong	7	10	19	40		Lau, 1993
Target ^a	20	20	35	75		<i>Idem</i>
Trigger ^b	55	35	65	150		<i>Idem</i>
Action ^c	65	40	75	200		<i>Idem</i>
Low value in the ISQV ^d for Hong Kong	1.5	65	40	75	200	Chapman, 1999
Average in the Pearl River Estuary (0—5 cm)	1.7	41	33	60	115	Li <i>et al.</i> , 2000
Site 1 (0—2 cm)	2.8	61	38	48	174	This study
Site 2 (0—2 cm)	2.5	56	33	42	142	<i>Idem</i>
Site 3 (0—2 cm)	2.3	34	25	32	96	<i>Idem</i>

Notes: a. Desired quality for fairly clean sediment; b. moderate pollution; c. heavy pollution; d. interim sediment quality values (ISQVs)

percentages of exchangeable metals in the upper sections to the corresponding total contents are presented in Table 4. In general, the exchangeable species of heavy metals are considered to be more migratory and bioavailable (Förstner, 1983). Therefore, the elevating trend of exchangeable Cd, Ni and Zn from the outer bay to the inner bay implied that the activity and potential risk of sediment-bound Cd, Ni and Zn enhanced, though the contribution of exchangeable forms were quite low (less than 6%).

Table 4 Concentrations of exchangeable metals in the top layer and contribution of exchangeable form to the total concentration in sediment profiles (depth: cm)

Metal	Cd, mg/kg	Co, mg/kg	Cu, mg/kg	Ni, mg/kg	Pb, mg/kg	Zn, mg/kg
Depth	Site 1/2/3	Site 1/2/3	Site 1/2/3	Site 1/2/3	Site 1/2/3	Site 1/2/3
0—2	0.1/0.0/ND	0.2/0.1/0.1	0.8/1.0/0.4	0.5/0.2/0.1	0.1/ND/0.2	9.0/0.5/0.2
Metal	Cd, %	Co, %	Cu, %	Ni, %	Pb, %	Zn, %
Depth	Site 1/2/3	Site 1/2/3	Site 1/2/3	Site 1/2/3	Site 1/2/3	Site 1/2/3
0—2	3.5/1.3/ND	2.3/0.8/0.7	1.4/1.7/1.3	1.4/0.7/0.4	0.3/ND/0.5	5.1/0.4/0.2
2—4	3.6/0.9/ND	1.9/0.9/0.6	1.5/1.4/1.3	1.4/0.8/0.7	0.0/0.2/0.9	3.5/0.5/0.3
4—6	3.0/1.4/ND	1.8/0.9/0.8	1.4/1.0/1.3	1.0/0.7/0.3	ND/ND/0.5	3.0/0.7/0.3
8—10	3.1/0.7/ND	1.6/0.9/0.7	1.5/1.1/0.9	1.2/0.7/0.2	0.1/0.2/0.2	2.0/0.4/0.4
12—14	4.3/0.1/ND	1.5/0.9/0.8	1.4/1.0/0.8	0.9/0.7/0.2	ND/ND/ND	2.6/0.4/0.3
16—18	4.0/1.1/ND	1.5/0.8/0.8	1.1/1.0/0.9	1.0/0.5/0.3	ND/ND/ND	2.2/0.5/0.3

Note: ND, not detected (the detection limits for Cd and Pb are 1 $\mu\text{g/L}$ in this study)

The correlation coefficients of exchangeable metals are given in Table 2. Close relationship occurred between Cd, Co, Ni and Zn, however, association between exchangeable Cu and Zn was less significant, with respect to that of total Cu and Zn, possibly due to their different chemical forms in sediments.

3 Conclusions

More enrichment of Cu, Pb and Zn in the surface sediments in the inner bay area and the decreasing trend of bioavailability of Cd, Ni and Zn from the inner bay to the outer bay reflected the influences from the coastal anthropogenic activities in Deep Bay.

Acknowledgements: The authors are grateful to Dr. X. P. Huang and Dr. D. C. Wang for their help on the sampling program.

References:

Chapman P M, Allard P J, Vigers G A, 1999. Development of sediment quality

values for Hong Kong Special Administrative Region: A proposal model for other jurisdictions[J]. *Mar Pollut Bull*, 38: 161—169.

Chapman P M, Wang F Y, 2001. Assessing sediment contamination in estuaries [J]. *Environ Toxic Chem*, 20: 3—22.

China EPA, 1997. National quality standards of marine water in P. R. China (GB 3097—1997) [S].

Förstner U, 1983. Assessment of metal pollution in rivers and estuarine[M]. In: *Applied environmental geochemistry* (Thornton I. ed.). London: Academic Press. 395—423.

Hills P, Zhang L, Liu J H, 1998. Transboundary pollution between Guangdong Province and Hong Kong: Threats to water quality in the Pearl River Estuary and their implications for environmental policy and planning[J]. *J Environ Planning Manage*, 41: 375—396.

Lau M M, Rootham R C, Bradley G C, 1993. A strategy for the management of contaminated dredged sediment in Hong Kong[J]. *J Environ Manage*, 38: 99—114.

Lau S S S, Chu I. M, 2000. The significance of sediment contamination in a coastal wetland, Hong Kong, China[J]. *Water Res*, 34: 379—386.

- Li X D, Wai O W H, Li Y S *et al.*, 2000. Heavy metal distribution in sediment profiles of the Pearl River Estuary, South China[J]. *Appl Geochem*, 15: 567—581.
- Peking University, 1994. Environmental impact assessment study on Shenzhen River regulation project: preliminary study report[R]. Beijing. 1—200.
- Tanner P A, Leong L S, Pan S M, 2000. Contamination of heavy metals in marine sediment cores from Victoria Harbor, Hong Kong[J]. *Mar Pollut Bull*, 40: 769—779.
- Tessier A, Campbell P G C, Bisson M, 1979. Sequential extraction procedure for the speciation of trace metals[J]. *Anal Chem*, 51: 844—851.
- Zheng Q H, Liang Z Q, He Y Q *et al.*, 1992. Geochemical behavior of the pollutants in surface sediments of Daya Bay[J]. *China Tropical Oceanology*, 11: 65—71.

(Received for review September 20, 2002. Accepted October 21, 2002)

About the Department of Atmospheric Chemistry and Air Pollution Control Technology, The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences

The research program focuses on environmental catalysis and related surface/interface sciences. From a practical viewpoint, it is important to understand the relationship between surface structures of catalysts and the rates of individual reaction steps as well as overall catalytic reaction pathways. Molecular structures and reaction intermediates on surfaces are characterized by in situ Diffuse Reflectance Infra-red Fourier Transform Spectroscopy(DRIFTS), TPD/R, XPS, UPS, and by detailed computer-modeling based on ab initio theory.

Specific research projects include:

- 1) Fundamental research on the selective catalytic reduction of NO_x
- 2) Catalytic cleaning of NO_x for diesel engine exhaust
- 3) Low temperature oxidation of VOCs
- 4) Selective oxidation of CO in H₂
- 5) Catalytic oxidation of carbonyl sulfide over atmospheric particles

The up-to-the-minute achievements:

- 1) H. He, J. Wang, Q. Feng, Y. Yu, K. Yoshida, *Appl. Catal. B* (in press).

A novel palladium promoted Ag/Al₂O₃ catalyst has been developed for selective catalytic reduction of NO by C₃H₆. The Ag-Pd/Al₂O₃ shows a higher NO_x conversion than Ag/Al₂O₃, especially at the temperatures

ranging from 300 to 450 °C. The addition of a small amount of Pd (0.01 wt %) to Ag/Al₂O₃ is considered to be favorable for the partial oxidation of C₃H₆. In-situ DRIFT spectra suggest that the presence of Pd catalyzes the formation of enolic species which is converted from C₃H₆. The enolic species is very active towards NO₂ and NO₃⁻, resulting in the formation of -NCO species which is the key reaction intermediate in selective catalytic reduction of NO.

- 2) Y. Yu, H. He, Q. Feng *J. Phys. Chem. B* (accepted).

Exposing of Ag/Al₂O₃ to CH₃CHO/C₂H₅OH/C₃H₆ + O₂ in a steady state leads to form two kinds of partial oxidation products: acetate and novel enolic surface species. Peaks at 1633, 1416, and 1336 cm⁻¹ are assigned to an adsorbed enolic species. The adsorbed enolic species is more active to react with NO + O₂ on Ag/Al₂O₃ than acetate, and plays a crucial role in the formation of NCO which is a key intermediate during selective catalytic reduction of NO. Research Center for Eco-Environmental Sciences

Professor Hong He

The Research Center for Eco-Environmental Sciences, the Chinese Academy of Sciences, Beijing 100085, China

Tel: + 86-10-6284-9123 (O) + 86-10-6284-9121 (O)

E-mail: honghe@mail.rcees.ac.cn or honghe7@hotmail.com