

# Metal concentrations and mobility in marine sediment and groundwater in coastal reclamation areas: A case study in Shenzhen, China

Kouping Chen\*, Jiu J. Jiao

*Department of Earth Sciences, The University of Hong Kong, Pokfulam Road, Hong Kong, China*

Received 31 October 2006; received in revised form 29 March 2007; accepted 8 April 2007

*Metals in coastal groundwater and marine sediment are affected by land reclamation.*

## Abstract

The concentrations of metals in the buried marine sediment and groundwater were differently affected by land reclamation. Nine metals (V, Cr, Mn, Co, Ni, Cu, Zn, Cd and Pb) in sediment and coastal groundwater from reclamation areas in Shenzhen were examined. The gradually decreased concentrations (V, Cr, Mn, Ni, Cu, Zn) in sediment and relatively higher concentrations (V, Cr, Mn, Co, Ni, Cu and Cd) in groundwater within reclamation areas were observed. The increase of V, Cr, Mn, Ni, Cu and Cd concentrations in groundwater within reclamation areas subsequently after land reclamation should be resulted from the mobilization of these metals accumulated in the sediment. These metals appear to be easily mobilized from solid phase to solution phase after reclamation. The physico-chemical changes such as reduction in pH and salinity in water environment induced by land reclamation appear to be responsible for metal mobility in the sediment–groundwater system.  
© 2007 Elsevier Ltd. All rights reserved.

*Keywords:* Marine sediment; Coastal groundwater; Land reclamation; Metal mobility; Shenzhen

## 1. Introduction

The rapid urban and industrial development in coastal areas in Shenzhen, China during the past 20 years has led to a sharp increase in the demand for usable land, which has resulted in extensive coastal land reclamation. Land reclamation is carried out by dumping fill materials such as decomposed granite rock from nearby hills onto the seabed of marine sediment. Although a number of general investigations on the effects of reclamation on the marine environment have been carried out (Pagliai et al., 1985; Hall, 1989; Smith et al., 1995), however, it has not yet been recognized that there may be various chemical reactions in the pore water–sediment system in the reclamation site and that these reactions may have certain negative effect on the coastal environment.

There are many studies on the chemical and physical processes in the water–sediment system in coastal or estuarine environment. Marine sediment is widely believed to act as a filter for many metals passing from terrestrial to the marine setting (Schubel and Kennedy, 1984; Tam and Wong, 2000; Yu et al., 2000; Morillo et al., 2004) and to accumulate some metals within marine water bodies. Most previous studies concentrated on the contaminated sediment with the objective of describing metal concentrations and/or identifying sources of contamination (Daskalakis and O'Connor, 1995; Schneider and Davey, 1995; Angelidis and Aloupi, 1997; Power et al., 1999; Owen and Sandhu, 2000; Chen et al., 2001; De Carlo and Anthony, 2002). However, in discussing the metal filtration process of marine sediment, one must consider both the sediment and the water environment. Metals may be mobilized as a result of natural processes (e.g. weathering and erosion of geological formations) as well as by anthropogenic activities.

The accumulation of metals in marine sediment could pose problems because such metals may act as a source of

\* Corresponding author. Tel.: +86 852 2857 8250; fax: +86 852 2517 6912.  
E-mail address: [kpchen@hkusua.hku.hk](mailto:kpchen@hkusua.hku.hk) (K. Chen).

contamination when the physico-chemical characters of environment are changed. Markiewicz-Patkowska et al. (2005) conducted laboratory-based experiments of the sorption and release of metals from soil materials and observed the migration of metals from soil materials to solution. Simpson et al. (2004) carried out laboratory experiments on metal behavior in estuarine sediment and showed that pH and salinity of the overlying water played an important role controlling the mobility of metals across the sediment–water interface. The results of their research also showed that some metal mobility increased as the groundwater pH decreased and as the exposure duration increased and that man-made changes in external parameters (e.g. pH, Eh, salinity) may cause a mobilization of the accumulated metals in the estuarine sediment.

It was recognized that land reclamation and subsequent processes can severely alter physical, chemical and biological properties of sediment and may result in some remobilization of metals between the water and sediment in an estuarine environment (Hall, 1989). However, information regarding the changes of the physico-chemical properties of water and marine sediment induced by land reclamation, as well as possible metal remobilization in the sediment–water system is not well reported in the literature.

The impact of land reclamation on coastal groundwater flow systems has been studied by Jiao et al. (2001) and Jiao (2002). The sediment, which was originally under seawater, would be gradually surrounded by groundwater after land reclamation. It is hypothesized that the change of the water environment may cause some chemical and physical changes of the sediment. Fig. 1 presents conceptual models about the hydraulic and chemical processes in a coastal reclaimed site. This figure demonstrates the possible physico-chemical interaction between marine sediment, decomposed granite rock fill, groundwater and seawater. Within the reclaimed land the original seawater at the site would be gradually replaced by terrestrial groundwater, and the marine sediment, which was originally present under alkaline and anoxic conditions, may be flushed by acidic groundwater with high dissolved oxygen. A number of chemical reactions, including release of metals from the sediment, may therefore take place.

Using land reclamation areas in Shenzhen as a case study, this paper aims to determine the concentrations and distribution of nine metals (V, Cr, Mn, Co, Ni, Cu, Zn, Cd and Pb) in the coastal areas and examine potential metal release from the sediment and potential mobility within the sediment–groundwater system inside the reclamation areas. An understanding of these processes will improve knowledge on variability of metal concentrations in marine sediment and groundwater which may occur within existing or proposed reclamation schemes.

## 2. The study area

The study area is located in the southwest of Shenzhen City, China (Fig. 2). This area was reclaimed from the sea in different years since 1983. Before land reclamation, temporal dikes around the coastal sea area to be reclaimed were

constructed. The seawater in the closed area was pumped out to lower the water level and the sediment at the bottom was exposed to the air and partially dried. This air-dried process is a geotechnical measure to speed up the consolidation of the sediment. Eventually the fill materials, which were decomposed granitic soil or rock fragments collected from nearby hills were dumped to the site and the final ground elevation is about 5–7 m above the sea level.

Like most of the southern areas in China, the study area has humid subtropical climates, with hot, wet summers and mild, dry winters. The coastal sea around the reclaimed area is dominated by a tidal condition with a typical tidal range of –0.13 to 2.49 m. The tidal water dynamics in this area allows the accumulation of fine-grained sediment, in which the clay fraction is high. Before reclamation, the marine sediment was in the anoxic conditions and iron sulfides can be stable and also the small grain size characteristics provided the marine sediment with great adsorption capacity of metals dissolved in the water. The marine sediment buried by the fill materials in the reclamation area was mainly derived from alluvial origin and had similar lithological sources.

## 3. Sampling and analytical methods

### 3.1. Sampling design

As conceptualized in Fig. 1, there may be some chemical and physical changes in the sediment after being buried by fill materials. A sampling scheme was carried out in 2004 to investigate the possible changes. The details of the samples are presented in Table 1 and the purposes of the sampling are as follows.

1. Marine sediment samples from Sites A, B and C. The three sites were reclaimed in 2003, 1998 and 1996, respectively. By the time of the sampling in 2004, the sediment was buried, respectively, for 1, 6 and 8 years. The samples from these three sites can provide information on the changes of the metal concentrations in the sediment with time after it was buried.
2. Groundwater samples from Site A after reclamation. These samples, together with the sediment samples from the same site, can provide information on the chemical exchange between the sediment and the pore water. The groundwater samples can also provide information on the aqueous chemical environment of the sediment after reclamation.
3. In-situ seawater testing along the coastline on the east. The marine sediment below the reclamation site was under seawater before reclamation. In-situ testing of pH, temperature, EC, and salinity can provide information on the chemistry of the seawater overlying the sediment before reclamation.
4. Groundwater samples from the original coastal areas to the north and west of the reclamation area. These samples are used to compare with those inside the reclamation area.

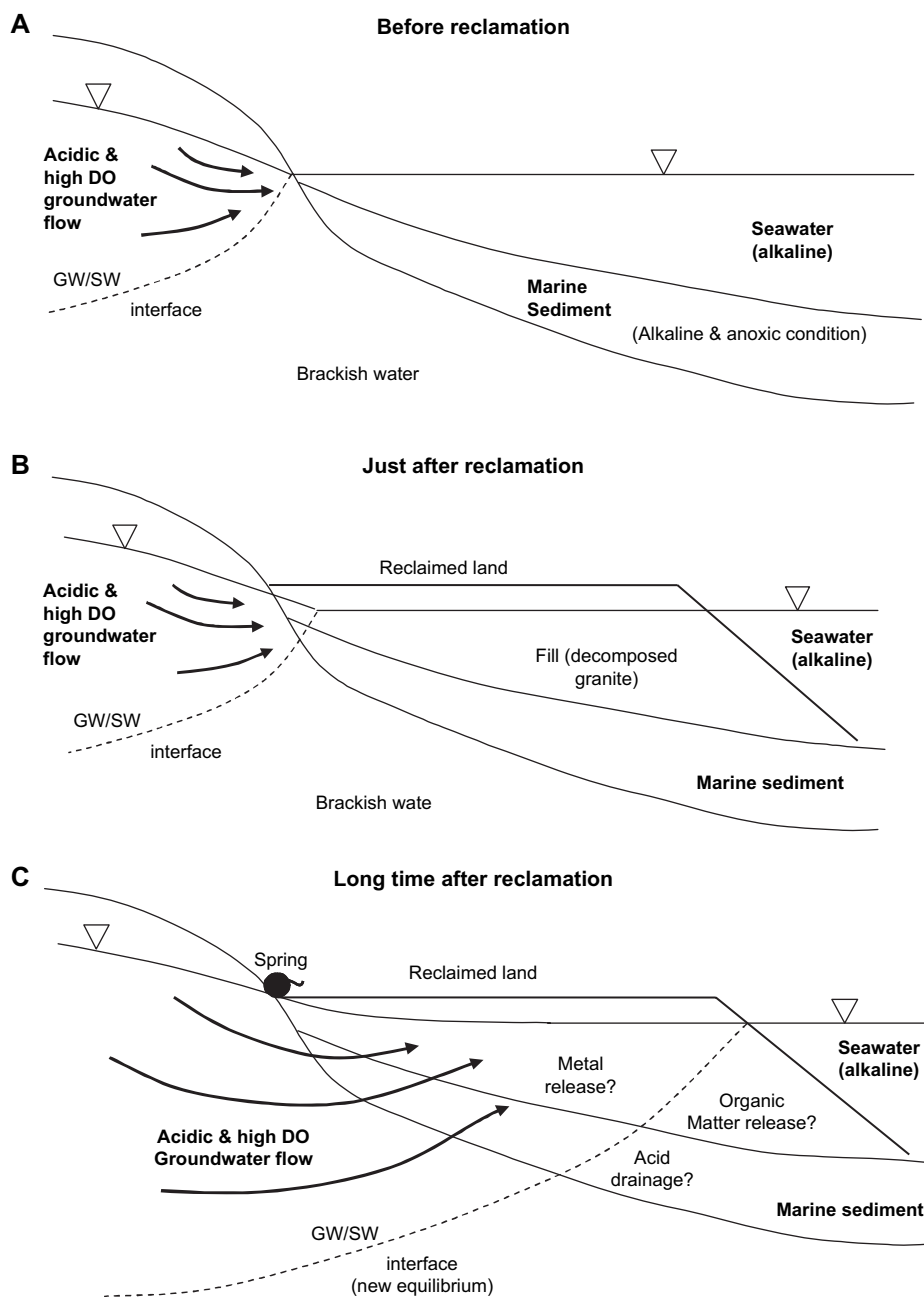


Fig. 1. Conceptual models of land reclamation and possible chemical processes (Jiao et al., 2005).

### 3.2. Sample collection

The locations at which samples were taken are shown in Fig. 2. Site A was the construction site at the western end of the so-called the Hong Kong–Shenzhen Western Corridor, a cross-bay highway. This site was an elongated area with the dimension of about  $2.2 \times 0.7 \text{ km}^2$ . Sites B and C were comparatively much smaller building construction sites. Boreholes were drilled at Sites A and C for site investigation. Sediment samples (22 and 6) were collected from the soil cores of the boreholes in Site A and C, respectively. Superficial soil was removed and only the soil inside the cores was sampled to avoid possible contamination. Eleven

samples of fill materials were also collected from Site A. Site B was a deep and open excavation site and six sediment samples were collected directly from the sediment layer under excavation. All sediment samples were stored in polyethylene bags and then transported to the laboratory where they were stored at  $4^\circ\text{C}$  until further chemical analysis.

Large-diameter wells were constructed in the reclamation site to drain the pore water from the sediment and speed up consolidation of the soil. Twenty-two groundwater samples were taken from these wells in Site A during wet and dry seasons in 2004. During the same period, groundwater samples were collected from 16 private water wells in the

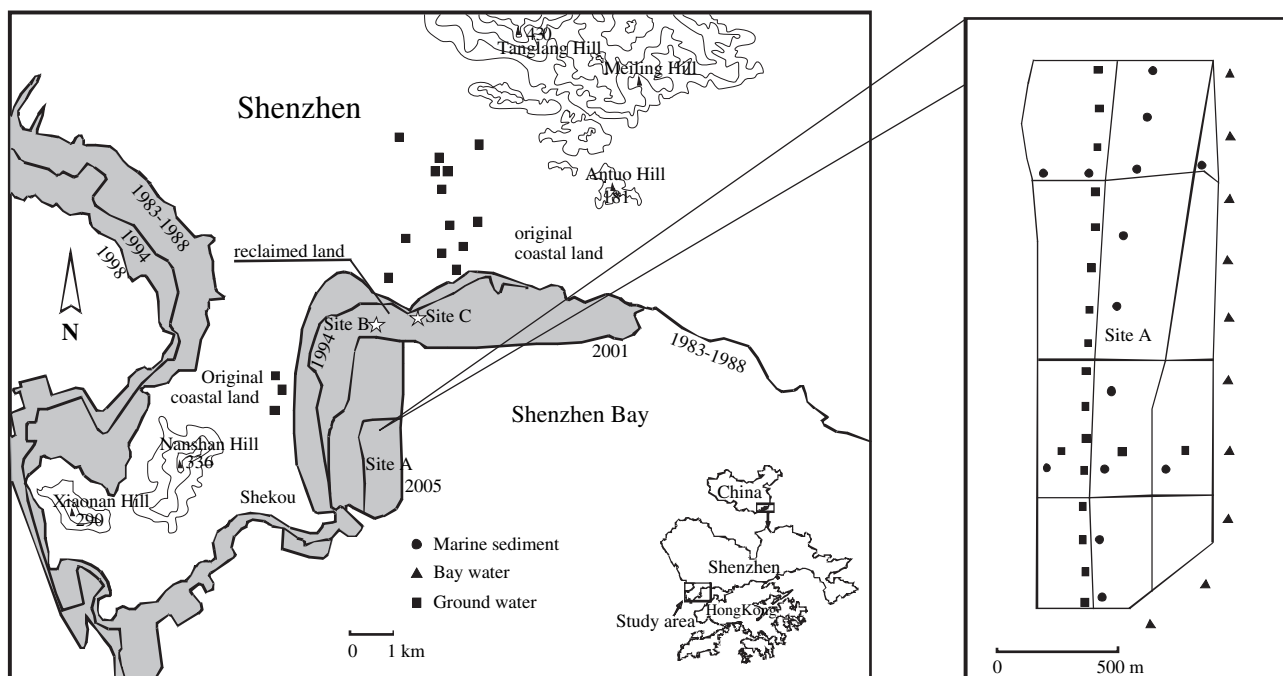


Fig. 2. A sketch map of locations of the study area. The shaded are the reclamation areas. The area to the north and west of the reclamation area is the original coastal area. Sampling Sites A, B and C were reclaimed in 2003, 1998 and 1996, respectively.

original coastal area to the north and west of the reclamation land. Water samples were collected into a 125 ml polyethylene narrow-mouth bottle with screw cap. Special care was taken to avoid contamination during sampling. Before sample collection, the bottle was rinsed at least three times with water filtered through 0.45-µm mixed cellulose ester membrane (Advantec MFS, USA). After collection, each sample was immediately acidified to pH < 2 with ultrapure nitric acid and then stored at approximately 4 °C before chemical analysis. Water temperature, pH, electric conductivity and salinity were all measured in the field with portable electronic instruments. During both wet and dry seasons, water temperature, pH, electric conductivity and salinity of the near shore seawater were also measured. These measurements can provide an indication of the local environment of the marine sediment in pre-reclamation condition. Table 2 lists the physico-chemical parameters of the local shallow

seawater and those of groundwater within and peripheral to the reclamation areas.

### 3.3. Analysis of metals in marine sediment and groundwater samples

The collected marine sediment samples were oven-dried at 80 °C for 2 days, then ground using an agate mortar and pestle to obtain homogenous powder. The prepared samples were analyzed for metal concentrations using an acid digestion (HNO<sub>3</sub> and HF) method (Tam and Yao, 1999). In this method, each sample (0.05 g) was digested using a 2 mL mixture of ultrapure HNO<sub>3</sub>:HF (1:1) in a sealed PTFE bomb heated at 190 °C in an electric oven for 24 h. After cooling, the bombs were opened and placed on a hot plate (at around 150 °C) until the solutions were evaporated to dryness. The final residue was re-dissolved by adding 2 mL ultrapure HNO<sub>3</sub> and 4 mL deionized water. At the same time, 1 mL of 500 ng/mL Rh solution was added as an internal standard. The resealed bombs were returned to the electric oven and heated to 140 °C for 4 h. After cooling, the final was made up to 50 mL solution by the addition of deionized water and stored in a PVC bottle at 4 °C prior to analysis by Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) (Model VG EXCELL). The reagent blanks were treated the same as the marine sediment samples.

Stock solutions of commercially produced (Plasma Pure Standard Solutions) multi-element standard solutions (100 mg/L) in 10% HNO<sub>3</sub> were used to prepare appropriate elemental calibration curves for ICP-MS. All the reported values are mean values of three replicates of each analysis.

Table 1  
Details of the field sampling or testing in and around the reclamation area

Soil/water sample types	Location	Number of samples for testing	Source of sampling	Sampling/testing time
Sediment	Site A	22	Borehole	June–July, 2004
	Site B	6	Excavation site	July, 2004
	Site C	6	Borehole	July, 2004
Fill	Site A	11	Borehole	June–July, 2004
Groundwater	Site A	22	Borehole	July, November 2004
Seawater	Original coastal land	16	Private well or borehole	July, November 2004
	Along east coastline	10	Open seawater	July, November 2004

Table 2  
Physico-chemical parameters of water samples measured in-situ (mean  $\pm$  SD)

	Sampling period	pH	Temperature ( $^{\circ}$ C)	EC(mS $\text{cm}^{-1}$ )	Salinity (‰)
Bay water ( $n = 10$ )	July 2004	7.7 $\pm$ 0.1	30.1 $\pm$ 1.1	41.3 $\pm$ 1.3	26.5 $\pm$ 1.2
	November 2004	7.9 $\pm$ 0.1	23.2 $\pm$ 1.5	42.6 $\pm$ 1.6	27.9 $\pm$ 1.0
Groundwater in reclamation site A after reclamation ( $n = 22$ )	July 2004	7.2 $\pm$ 0.2	26.7 $\pm$ 1.0	5.7 $\pm$ 1.1	2.8 $\pm$ 0.6
	November 2004	7.0 $\pm$ 0.2	24.7 $\pm$ 1.1	6.8 $\pm$ 1.0	3.5 $\pm$ 0.5
Groundwater in original coastal land ( $n = 16$ )	July 2004	6.6 $\pm$ 0.2	25.9 $\pm$ 1.0	0.6 $\pm$ 0.1	–
	November 2004	6.5 $\pm$ 0.1	24.8 $\pm$ 1.1	0.6 $\pm$ 0.1	–

–, Below detection limit.

The completeness of the  $\text{HNO}_3$  and HF digestion technique in extracting metals from sediment was checked by digesting and analyzing two Certified Reference Materials GBW07313 and GBW07302 (Chinese national standard reference material) using the method described above. The analytical values of the two reference materials were within the range of the certified values except Zn in GBW07313 issued by National Research Center for Geoanalysis (Table 3) and the reagent blanks were found to be below the detection limits.

Analysis of metals in groundwater samples was conducted using ICP-MS. The international standard reference material (SRM 1640, Trace Elements in Natural Water, National Institute of Standards and Technology) was used in the quality control. The analytical precision obtained by ICP-MS was determined as the percentage of the relative standard deviation (RSD) of the three consecutive measurements of the standard reference solution. The recovery rates of the analyzed metals in the standard reference material were  $>90\%$ .

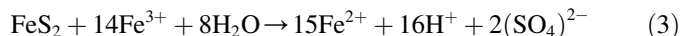
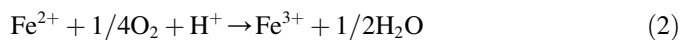
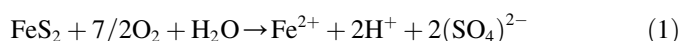
Three replicates of each analysis were performed and the mean values were used for calculations. The analytical results of metals in the sediment and groundwater samples are tabulated in Tables 4 and 5. The metal concentrations in sediment samples are expressed in terms of  $\text{mg kg}^{-1}$  dry weight; concentrations of metals in groundwater samples are reported as  $\mu\text{g L}^{-1}$ .

## 4. Results and discussion

### 4.1. Changes of water environment surrounding sediment

Before reclamation, the marine sediment was overlain by seawater; after reclamation, the sediment was covered by fill materials. The reclamation area was initially saturated by seawater and then by terrestrial fresh groundwater, as can be seen

from Fig. 1. The water environment of the sediment changes markedly because seawater is saline and alkaline but groundwater is slightly acidic and has high dissolved oxygen. As shown in Table 2 the mean pH of the seawater in winter and summer is 7.9 and 7.7, respectively. The mean pH of the groundwater in reclamation areas in winter and summer is 7.0 and 7.2, respectively. The lower pH of groundwater may be partly due to the gradual displacement of seawater by terrestrial groundwater, and partly resulted from oxidation of the  $\text{FeS}_2$  and  $\text{FeS}$  to  $\text{H}_2\text{SO}_4$  during the air-dried period of the marine sediment (Meyer et al., 1994). The studies carried out by Preda and Cox (2000) showed that coastal sediment provided the required conditions for iron sulfide accumulation. The iron sulfides formed were stable under undisturbed anoxic conditions; however, when land reclamation progressed, the sediment with iron sulfide was exposed to oxidizing conditions and the following chains of chemical reactions that produce sulfuric acid were triggered (Nordstrom, 1982; Bierens De Haan, 1991):



The oxygen from air or water was the initial driving force for pyrite decomposition. As the pH dropped due to the release of  $\text{H}^+$ , the concentration of ferric iron increased as in Eq. (2), and this phase then became the most important oxidizing agent. The sequence continued with major production of acid in Eq. (3). Therefore, iron sulfide oxidation during reclamation may contribute much to groundwater pH drop.

The salinity of the seawater ( $>25\%$ ) is much greater than that of the groundwater sampled inside the reclaimed land

Table 3  
Recovery of metal concentration in the Certified Reference Materials (unit:  $\text{mg kg}^{-1}$ )

Reference materials		V	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
GBW07313	Certified <sup>a</sup>	112 $\pm$ 5	58.4 $\pm$ 1.3	334 $\pm$ 56	76.7 $\pm$ 1.2	150 $\pm$ 4	424 $\pm$ 8	160 $\pm$ 3	0.25 $\pm$ 0.06	29.3 $\pm$ 1.1
	Found <sup>b</sup>	110.84	58.84	312.56	75.34	148.73	412.78	155.39	0.21	28.63
GBW07302	Certified <sup>a</sup>	16.5 $\pm$ 2.8	12 $\pm$ 4	240 $\pm$ 30	2.6 $\pm$ 1.0	5.5 $\pm$ 2.1	4.9 $\pm$ 0.7	44 $\pm$ 7	0.07 $\pm$ 0.02	32 $\pm$ 8
	Found <sup>b</sup>	15.64	11.14	223.21	2.23	5.13	5.52	42.16	0.05	39.88

<sup>a</sup> Certified Standard Reference Material (marine sediment, China).

<sup>b</sup> Mean of three replicates of each analysis.

Table 4

Metal concentrations in marine sediment from three reclamation sites (all results are shown in mg kg<sup>-1</sup> dry weight)

		V	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
Site A (n = 22)	Mean	113.68	75.96	624.58	21.68	33.12	34.63	119.25	0.40	49.45
	Range	86.4–144.22	56.86–96.38	512.62–698.74	12.90–38.70	21.63–52.96	21.37–74.21	77.36–192.39	0.28–0.68	34.46–67.77
Site B (n = 6)	Mean	87.86	49.20	490.72	22.12	22.00	25.41	102.31	0.44	56.70
	Range	65.70–104.39	25.14–64.94	431.58–542.13	18.91–27.60	11.87–29.83	12.43–41.59	73.08–128.36	0.39–0.53	52.05–62.20
Site C (n = 6)	Mean	67.42	40.91	343.82	42.61	19.96	16.06	76.79	0.38	40.20
	Range	55.67–78.36	34.20–47.81	287.54–375.68	34.21–62.22	15.33–25.57	14.57–17.51	62.63–93.01	0.30–0.45	33.18–48.83

(<5‰) (Table 2). The decreased water salinity after reclamation indicated that the seawater was replaced gradually by terrestrial groundwater. Laboratory studies conducted by Lau and Chu (1999) on sediments collected from a coastal wetland demonstrated that when the salinity shifted from 15‰ to 5‰, it resulted in marked changes in levels of contaminants in sediment extracts at 25 °C. Nelson et al. (1981) suggested that the equilibrium distribution of metals between solids and solutes was mediated primarily by physico-chemical factors. It is expected then that the changes in physico-chemical parameters such as pH and salinity of the water around the sediment may induce some metal exchange between the sediment and pore water.

#### 4.2. Concentrations of metals in marine sediment

Table 4 shows the concentrations of the nine metals (V, Cr, Mn, Co, Ni, Cu, Zn, Cd and Pb) in marine sediment samples from the three reclaimed sites. The total concentrations of these metals especially Cr, Mn, Ni, Cu, Zn and Pb in the sediment are relatively high and the sediment can be classified as moderately polluted based on the standard set by the United States Environmental Protection Agency (2000). This raises concern regarding the biological and environmental impacts of metals if they are released from the sediment after the water environment (pH and salinity) is changed. Comparison of the concentrations of V, Cr, Mn, Ni, Cu and Zn in sediment from the three sites reclaimed at different times shows that the most recent buried sediment has a relatively higher concentration than that buried earlier (Fig. 3). For an example the sediment in Site A was buried 5 years later than that in Site B, all the

metals, except Co, Cd and Pb, in the sediment from Site A have higher concentrations than Site B. Studies carried out by some previous researchers (Salomons et al., 1987; Gambrell et al., 1991) showed that the drop of pH in the overlying water prevented a transfer of trace metals to the sediment in the estuarine environment and also caused a desorption from the sediment. Therefore, it may be expected that lower pH and salinity may enhance the desorption and dissolution ability of the sediment and contribute to lowered V, Cr, Mn, Ni, Cu and Zn in sediment. It is believed that these processes are time-dependent and more metals may be released from the sediment if it is buried earlier. This may explain why concentrations of most of the metals in the sediment decrease from Sites A–C.

#### 4.3. Metal concentrations in groundwater in wet and dry seasons

Fig. 4 presents the nine metals in groundwater samples collected from the reclaimed area and the original coastal land in wet and dry seasons in 2004. The chemistry of groundwater in the original coastal land was studied by Chen et al. (2007). All the nine metals in the groundwater samples collected from the original coastal area had lower concentrations in November 2004 than in July 2004 (Table 5). However, all the metals except Zn in groundwater samples within the reclamation areas had higher concentrations in November than in July. It is not surprising that the concentrations of metals in groundwater in the original coastal land in July are higher. In Shenzhen, July is the rainy season and leaching is more significant than the dry season including

Table 5

Metal concentrations in groundwater within and peripheral to reclamation site (unit: µg L<sup>-1</sup>)

	Sampling		V	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
In reclamation Site A (n = 22)	July 2004	Mean	17.71	2.04	1155.32	3.35	3.57	1.32	12.52	0.55	1.83
		Range	5.29–50.24	0.68–4.71	8.93–8749.57	1.24–15.12	1.45–10.53	0.24–3.66	2.20–81.29	0.02–3.40	0.09–16.62
	November 2004	Mean	20.29	2.06	1391.90	5.98	10.78	1.76	7.93	0.6	1.98
		Range	7.32–66.66	0.72–4.84	18.87–10210.45	1.32–20.51	3.14–19.18	0.53–3.69	1.16–45.64	0.05–5.28	0.21–30.78
In original coastal land (n = 16)	July 2004	Mean	3.45	1.17	634.16	1.86	2.76	1.07	32.47	0.06	9.71
		Range	0.50–21.85	0.24–4.06	19.39–7479.68	0.21–9.64	0.45–8.37	0.11–4.06	1.23–577.60	0.02–0.15	0.15–62.84
	November 2004	Mean	1.74	1.02	429.93	1.12	1.63	0.83	30.11	–	8.87
		Range	0.59–8.77	0.08–3.58	22.08–6027.12	0.26–7.19	0.23–5.94	0.33–2.18	0.74–585.21	–	0.09–50.90
Analytical precision (%)		2.6	2.6	0.3	0.7	0.3	1.4	2.3	1.7	2.1	

–, Below detection limit.

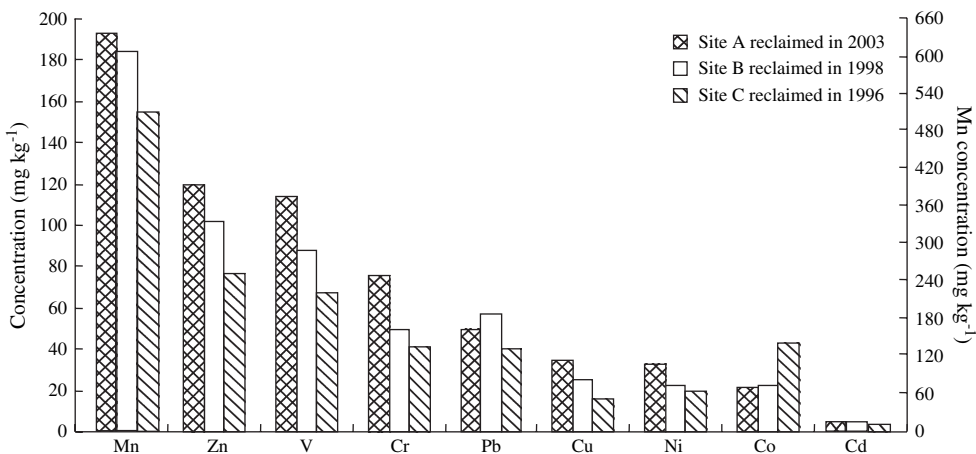


Fig. 3. Comparison of metal concentrations in marine sediment below the three reclamation sites.

November. Studies in Brazil showed that leaching enhanced dissolution of residual minerals at the ground surface and induced relatively high metal concentrations in groundwater in rainy season (Sondag et al., 1997). Similar seasonal changes in groundwater chemistry were also observed in Hong Kong (Leung et al., 2005). On this basis, the concentrations of metals in groundwater in the rainy season should be higher than those in the dry season. But in the recently reclaimed Site A, all the studied metals except Zn in groundwater display higher concentrations in November than in July (Fig. 4). Therefore, it is likely that there exists a more enriched metal source contributing to the groundwater in the recently reclaimed areas.

A comparison of metal concentrations in groundwater samples collected from the original coastal land with those within Site A shows that all the metals except Zn and Pb in groundwater within Site A display higher concentrations than those in the original coastal area, no matter in dry or wet seasons (Fig. 5). The original coastal areas have busy highways but Site A was not yet developed at the time of the study. Contamination by high traffic volume may cause high concentrations of Zn and Pb in soil (Wong et al., 1996; Li et al., 2004). It is believed that the elevated concentrations of Zn and Pb in groundwater from the original coastal land may be associated

with soil contaminated by Zn and Pb due to busy traffic. However, marked increases in concentrations of V, Cr, Mn, Co, Ni, Cu and Cd within groundwater of Site A may result from release of these metals from the sediment to the water due to changes in the water environment. Fill materials in the reclaimed land inevitably compressed the marine sediment, which could lead to the release of metals, especially those bound to relatively large particles, to the surrounding water from the contaminated sediment (Gambrell, 1994). The relatively high concentrations of V, Cr, Mn, Ni and Cu in groundwater in reclamation areas also agree well with the gradually decreased concentrations of these metals in the buried marine sediment.

It may be argued that the fill materials may contribute to the metals in the groundwater. Chemical analysis shows that the metal composition of the fill materials is much lower than that of the sediment (Table 6). It is reasonable to assume that the metal contribution of the fill materials to groundwater is negligible compared to the marine sediment. Therefore, it can be concluded that the elevated metal concentrations of groundwater in the reclamation areas are most likely associated with metal release from the sediment.

In the present study, the gradual decrease of V, Cr, Mn, Ni and Cu in marine sediment in Sites A, B and C and the relative

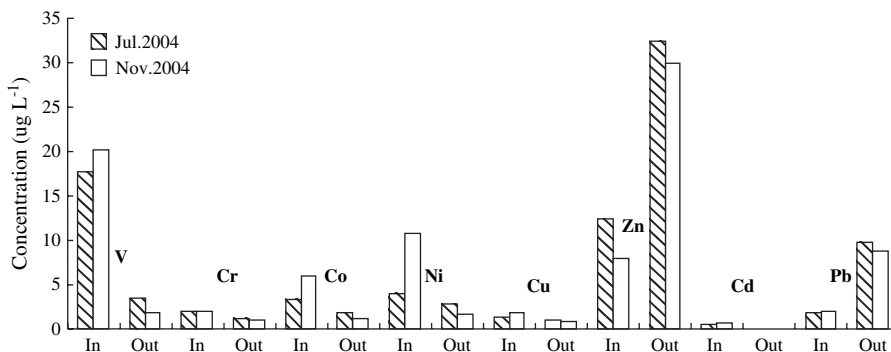


Fig. 4. Metal concentrations in groundwater samples collected in reclaimed area and outside the reclaimed area (the original coastal area) in wet and dry seasons in 2004.

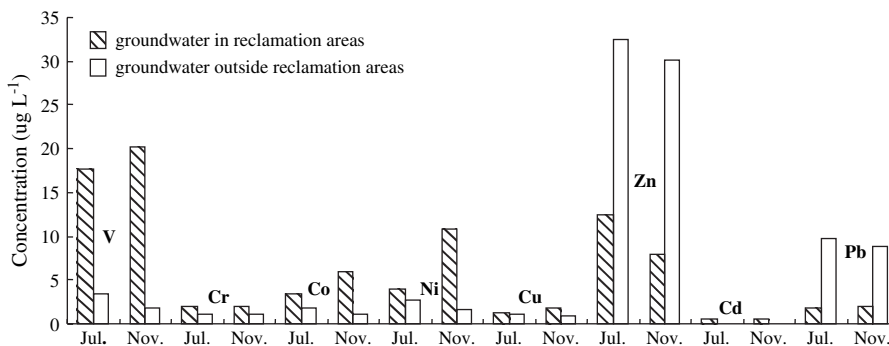


Fig. 5. Comparison of metal concentrations in groundwater samples within and outside reclamation areas.

high concentrations of the five metals in groundwater within Site A have shown that these metals are mobilized from the sediment phase to the solution phase. Metal release from marine sediment is affected by pH and salinity and the lower pH and salinity may be helpful for metal release from marine sediment (Gambrell et al., 1991; Lau and Chu, 1999). Therefore, the mobilization of these metals from sediment phase to the solution phase may be due to the coupling effect of pH and salinity changes in the water environment before and after land reclamation.

However, the present study cannot explain the behavior of all the metals. Among the nine metals in this study, V, Cr, Mn, Ni, Cu and Cd seem to behave similarly and are believed to be released easily from the sediment to the groundwater after land reclamation, while Zn and Pb show different behavior. Co seems to behave very differently from the other eight metals studied. This indicates the degree of the complexity of the underlying mechanisms controlling the mobility of the metals in the sediment–water system of the reclaimed areas.

## 5. Conclusion

Field soil and water sampling and laboratory analyses were carried out to understand the changes of metals in the subsurface system in the reclaimed land in Shenzhen, China. Three facts were observed from the chemical analyses: (1) the sediment buried for a longer period has lower metal concentrations; (2) groundwater in the reclaimed area has higher metal concentrations than in the original coastal land; and (3) groundwater in the reclamation area has higher concentrations in the dry season than in the wet season while the

groundwater in the original land shows typically the opposite trend. An attempt was made to explain these facts. In the reclamation area, the marine sediment which was submerged by seawater before reclamation was saturated gradually with terrestrial groundwater after reclamation. This has led to the changes in physico-chemical parameters such as reduction in pH and salinity. It is believed that these physico-chemical changes enhance the mobility of metals accumulated in the sediment. The metals such as V, Cr, Mn, Ni, Cu and Cd were then released from the sediment to groundwater. Therefore, the metal concentrations in the sediment decrease as burial time increases. The release of the metals from the sediment to the pore water can also explain why the metals in groundwater in November 2004 displayed higher concentrations than in July 2004 in the reclamation area and why the metal concentrations in the groundwater in the reclaimed land were higher than in the original coastal land in both the dry and wet seasons of 2004. The metals in the groundwater in the reclamation site will eventually flow to the sea and may have adverse effects on the coastal environment. It is suggested that these possible negative impacts on the coastal environment should be evaluated before a large-scale land reclamation project is carried out.

In the preliminary study, the spatial difference of chemistry of marine sediment in Sites A, B and C before reclamation is assumed to be negligible because the marine sediment in the three reclaimed sites was derived from a similar source. For a better understanding of the underlying mechanism affecting the mobility of metals in the reclamation land, more detailed field sampling and rigorous laboratory research under controlled conditions should be carried out. These will be topics of further study.

Table 6

Comparison of metal concentrations in fill materials and marine sediment in reclamation Site A (unit: mg kg<sup>-1</sup>)

	V	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb
Fill materials	Mean 17.04	8.08	178.12	42.46	1.89	8.30	32.32	0.20	39.61
(n = 11) <sup>a</sup>	Range 7.21–36.42	2.01–24.27	29.68–237.51	1.21–151.54	0.21–4.88	2.82–27.73	20.27–44.85	0.12–0.25	11.61–68.81
Marine mud	Mean 113.68	75.96	624.58	21.68	33.12	34.63	119.25	0.40	49.45
(n = 22)	Range 86.40–144.22	56.86–96.38	512.62–698.74	12.90–38.70	21.63–52.96	21.37–74.21	77.36–192.39	0.28–0.68	34.46–67.77

<sup>a</sup> Data of fill materials are unpublished.

## Acknowledgement

The study was partially supported by the “Two Bases” Project of National Natural Science Foundation of China, the Research Grants Council of the Hong Kong Special Administrative Region (HKU 7105/02P), and Committee on Research and Conference Grants (CRCG) at the University of Hong Kong. Field assistance in collecting data at the Shekou site from local geotechnical companies including Shenzhen Research and Design Institute, China Academy of Railway Sciences, Shenzhen Gongkan Geotechnical Engineering Co. Ltd, and Shenzhen Geotechnical Engineering Company are highly appreciated. We thank Ms Jianmin Huang, Mr. Guoping Ding, Haipeng Guo and Chiman Leung for their contributions to this research.

## References

- Angelidis, M.O., Aloupi, M., 1997. Assessment of metal contamination in shallow coastal sediments around Mytilene, Greece. *International Journal of Environmental Analytical Chemistry* 68 (2), 281–293.
- Bierens De Haan, S., 1991. A review of the rate of pyrite oxidation in aqueous systems at low temperature. *Earth-Science Reviews* 31, 1–10.
- Chen, K.P., Jiao, J.J., Huang, J.M., Huang, R.Q., 2007. Multivariate statistical evaluation of trace elements in groundwater in a coastal area in Shenzhen, China. *Environmental Pollution* 47, 771–780.
- Chen, Z., Kostaschuk, R., Yang, M., 2001. Heavy metals on tidal flats in Yangtze Estuary, China. *Environmental Geology* 40 (6), 742–749.
- Daskalakis, K.D., O'Connor, T.P., 1995. Normalization and elemental sediment contamination in the coastal United States. *Environmental Science and Technology* 29 (2), 470–477.
- De Carlo, E.H., Anthony, S.S., 2002. Spatial and temporal variability of trace element concentrations in an urban subtropical watershed, Honolulu, Hawaii. *Applied Geochemistry* 17, 475–492.
- Gambrell, R.P., 1994. Trace and toxic metals in wetlands – a review. *Journal of Environmental Quality* 23, 883–891.
- Gambrell, R.P., Wiesepape, J.B., Patrick, W.H., Duff, M.C., 1991. The effects of pH, redox and salinity on metal release from a contaminated sediment. *Water, Air and Soil Pollution* 57, 359–367.
- Hall, L.A., 1989. The effects of dredging and reclamation on metal levels in water and sediments from an estuarine environment off Trinidad, West Indies. *Environmental Pollution* 56, 189–207.
- Jiao, J.J., 2002. Preliminary conceptual study on impact of land reclamation on groundwater flow and contaminant migration in Penny's Bay. *Hong Kong Geologist* 8, 14–20.
- Jiao, J.J., Leung, C.M., Chen, K.P., Huang, J.M., Huang, R.Q., 2005. Physical and chemical processes in the subsurface system in the land reclaimed from the sea. In: *Collections of Coastal Geo-Environment and Urban Development*. China Dadi Publishing House, Beijing, China, pp. 399–407.
- Jiao, J.J., Nandy, S., Li, H.L., 2001. Analytical studies on the impact of reclamation on groundwater flow. *Ground Water* 39 (6), 912–920.
- Lau, S.S.S., Chu, L.M., 1999. Contaminant release from sediments in a coastal wetland. *Water Research* 33 (4), 909–918.
- Leung, C.M., Jiao, J.J., Malpas, J., Chan, W.T., Wang, Y.X., 2005. Factors affecting the groundwater chemistry in a highly-urbanized coastal area in Hong Kong: an example from the Mid-Levels area. *Environmental Geology* 48 (4–5), 480–495.
- Li, X.D., Lee, S.L., Wong, S.C., Shi, W.Z., Thornton, I., 2004. The study of metal contamination in urban soils of Hong Kong using a GIS-based approach. *Environmental Pollution* 129, 113–124.
- Markiewicz-Patkowska, J., Hursthouse, A., Przybyla-Kij, H., 2005. The interaction of heavy metals with urban soils: sorption behaviour of Cd, Cu, Cr, Pb and Zn with a typical mixed brownfield deposit. *Environmental International* 31, 513–521.
- Meyer, J.S., Davidson, W., Sundby, B., Oris, J.T., Laurén, D.J., Förstner, U., Hong, J., Crosby, D.G.S., 1994. The effects of variable redox potentials, pH, and light on bioavailability in dynamic water–sediment environments. In: Landrum, P.F., Bergman, H.L., Benson, W.H. (Eds.), *Bioavailability – Physical, Chemical, and Biological Interactions*. Lewis Publ., Boca Raton, pp. 155–170.
- Morillo, J., Usero, J., Gracia, I., 2004. Heavy metal distribution in marine sediments from Southwest coast of Spain. *Chemosphere* 55, 431–442.
- Nelson, P.O., Chung, A.K., Hudson, M.C., 1981. Factors affecting the fate of metals in the activated sludge process. *Journal of the Water Pollution Control Federation* 53, 1323–1333.
- Nordstrom, D.K., 1982. Aqueous pyrite oxidation and the consequent formation of secondary iron materials. In: Kittrick, J.A., Fanning, D.S., Hossner, L.R. (Eds.), *Acid Sulfate Weathering*. Soil Science Society of America, Madison, pp. 37–56.
- Owen, R.B., Sandhu, N., 2000. Metal accumulation and anthropogenic impacts on Tolo Harbour, Hong Kong. *Marine Pollution Bulletin* 40 (2), 174–180.
- Pagliai, A., Varriale, A., Crema, R., Galletti, M., Zunarelli, R., 1985. Environmental impact of extensive dredging in a coastal marine area. *Marine Pollution Bulletin* 16, 483–488.
- Power, M., Attrill, M.J., Thomas, R.M., 1999. Heavy metal concentration trends in the Thames estuary. *Water Research* 33 (7), 1672–1680.
- Preda, M., Cox, M.E., 2000. Sediment–water interaction, acidity and other water quality parameters in a subtropical setting, Pimpama River, Southeast Queensland. *Environmental Geology* 39 (3–4), 319–329.
- Salomons, W., de Rooij, N.M., Kerdijk, H., Bril, J., 1987. Sediments as a source for contaminants? *Hydrobiologia* 149, 13–30.
- Schneider, P.M., Davey, S.B., 1995. Sediment contamination off the coast of Sydney, Australia: a model for their distribution. *Marine Pollution Bulletin* 31 (4–12), 262–272.
- Schubel, J.R., Kennedy, V.S., 1984. The estuary as a filter: an introduction. In: Kennedy, V.S. (Ed.), *The Estuary as a Filter*. Academic, Orlando, FL, USA, pp. 1–11.
- Simpson, S.L., Maher, E.J., Jolley, D.F., 2004. Processes controlling metal transport and retention as metal-contaminated groundwaters efflux through estuarine sediments. *Chemosphere* 56, 821–831.
- Smith, J.A., Millward, G.E., Babbedge, N.H., 1995. Monitoring and management of water and sediment quality changes caused by a harbour impoundment scheme. *Environment International* 21 (2), 197–204.
- Sondag, F., Soubies, F., Fortune, J.P., Dupré, B., Magat, P., Melfi, A., 1997. Hydrogeochemistry on soils and sediments in the area of the Lagoa Campestre lake (Salitre, MG, Brazil): chemical balances of major and trace elements and dynamics of rare earth elements. *Applied Geochemistry* 12, 155–162.
- Tam, N.F.Y., Wong, Y.S., 2000. Spatial variation of metals in surface sediments of Hong Kong mangrove swamps. *Environmental Pollution* 110, 195–205.
- Tam, N.F.Y., Yao, M.W.Y., 1999. Three digestion methods to determine concentrations of Cu, Zn, Cd, Ni, Pb, Cr, Mn and Fe in mangrove sediments from Sai Keng, Chek Keng, and Sha Tau KOK, Hong Kong. *Bulletin of Environmental Contamination and Toxicology* 62, 708–716.
- USEPA (United States Environmental Protection Agency), 2000. Prediction of Sediment Toxicity Using Consensus-based Freshwater Sediment Quality Guidelines. EPA 905/R-00/007. Great Lakes National Program Office, Chicago, Illinois.
- Wong, M.H., Chen, T.B., Wong, J.W.C., 1996. Trace metal contaminants of the Hong Kong soil environment: a review. In: *Contaminants and Soil Environment in the Australia-Pacific Region*. Kluwer Academic Publisher, Dordrecht, pp. 501–511.
- 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 wetlands. *Environmental Toxicology and Chemistry* 19 (30), 535–542.