



Research papers

Relationship between heavy metal contents and clay mineral properties in surface sediments: Implications for metal pollution assessment



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ABSTRACT

Clay minerals in surface sediments can affect the adsorption of heavy metals. However, few historical studies have focused on the influence of fine clay mineral characteristics on metal sorption. Since the reactions between heavy metals and fine clay minerals in sediments remain obscure, this study investigates the influence of fine clay mineral characteristics on metal sorption in a typical urbanizing small watershed. Clay minerals, including nanoparticles with various size fractions ranging from 1000 to 2000 (clay), 450–1000 (fine clay), and 220–450 (very fine clay) nm were used to demonstrate their transformation from well crystalline to poorly crystalline. The nanoparticles were collected and evaluated by determination of their surface area, X-ray diffraction, scanning electron microscopy (SEM) and chemical analyses. The relationship between metal content and properties of the surface sediments was also revealed by canonical correlation analysis. With smaller particle sizes, nanoparticles (very fine clay) were observed to be poorly crystalline, possibly indicating few repetitions of unit cells as a result of preferential structural disruption of other crystal planes caused by pressure-induced phase transition in the fine-size fractions. The first canonical matrix (M) variables of metal contents can be predicted by both surface area and pore volume, followed by kaolinite and illite contents. On the other hand, the category of metal, i.e., Cu, Cr, Zn, or Pb, was significantly correlated with the first 'M' canonical variables. The data obtained in the present study are of fundamental significance in advancing our understanding of the reactions between heavy metals and fine clay minerals in the terrestrial ecosystem.

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1. Introduction

It has been widely accepted that surface sediments play a crucial role in the accumulation of heavy metals, acting as both sinks for and sources of pollutants (Santschi et al., 1997). The adsorption of heavy metals to sediment constituents is one of the most important processes that determines the mobility and bioavailability of heavy metals in aquatic environments. Earlier studies have identified two of the most important geochemical components affecting metal bioavailability in aquatic systems: metal oxides and organic materials (Perret et al., 2000; Wang and Li, 2011). These factors are crucial for binding and adsorption of heavy metals onto surface sediments, as indicated by various analytical and evaluation methods, such as correlation analyses, sequential extraction, specific or selective extraction, a combination of chemical extraction and adsorption techniques, and

selective extraction–adsorption–statistical analyses (Dong et al., 2002, 2003; Turner, 2004; Li et al., 2006, 2009).

This last procedure has been applied to accurately estimate the relative roles of Fe oxides, Mn oxides and organic materials in natural surface coatings on the adsorption of heavy metal and provides significant insight into the mechanisms of heavy metal associations with the adsorptive components of heterogeneous aquatic sediments (Wang and Li, 2011). Clay minerals in surface sediments also affect the adsorption of heavy metals, and may do so in combination with Fe, Mn amorphous oxides, and organic materials, some of which may cover clay surfaces (Li et al., 2009).

Several studies have explored the relationship between heavy metals and clay minerals, including pure clays, such as illite, smectite, kaolinite, vermiculite, rectorite, and clay minerals in soil and sediment (Zhang et al., 2004; Vega et al., 2004; Grafe et al., 2007; Kim et al., 2007; Malferrari et al., 2007). For example, the clay minerals in some lacustrine sediments in Mexico were predominantly composed of a Si-rich allophane and smectite, with a lower concentration of halloysite (Kim et al., 2007). Given the range of possible clay mineral compositions, the reactions between heavy metals and clay minerals in the sediments are

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expected to be complex. Although critical information regarding the role of mineralogy in sediment adsorption is not available, a better understanding of these processes may be important in determining the manner in which heavy metals are transferred from a liquid mobile phase to a solid phase. Few historical studies have focused on the influence of clay mineral characteristics on metal sorption.

It is clear that as environmental problems become more severe, there will be a greater need to understand the nature and physicochemical properties of environmental nanoparticles in natural systems (Dreher, 2004; Biswas and Wu, 2005). There has been a great deal of evidence indicating that inorganic and organic colloids (1–1000 nm) in natural systems such as soils, earthquake-generating faults, groundwater, streams, rivers, lakes and oceans, as well as in the atmosphere play an important role in the circulation of nutrients and pollutants (Lin et al., 2005; Hochella et al., 2008; Navrotsky et al., 2008). In particular, nanominerals and mineral nanoparticles in the environment have been present throughout the evolutionary development of hominids, and our exposure to these substances through inhalation, ingestion, and dermal pathways are important foci of nanotoxicology (Hochella et al., 2008). For example, environmental nanoparticles were found to have a high sorption capacity for Zn, As, and Pb, and Al-, Fe-, and Mn-oxides, and sulfides (Hochella et al., 2005; Isaure et al., 2005). Mayo et al. (2007) reported that 12-nm magnetite particles were roughly 200 times more effective in removing As (III) and As(V) from water than 20 and 300 nm particles, indicating size-dependent effects.

Since the reactions between heavy metals and fine clay minerals in sediments remain obscure, the present study investigates the influence of fine clay mineral characteristics on metal sorption in a typical urbanizing small watershed.

2. Material and methods

2.1. Study area

The Bantou watershed covers approximately 205 km² in northwest Xiamen, Fujian Province, China (Fig. 1) (Yu et al., 2014). The local climate is subtropical monsoon with a warm season (average atmospheric temperature > 20 °C) from April to October and a wet and cold season (with typhoons, average temperature < 20 °C) from November to March. The watershed is composed of five subwatersheds delineated from a digital elevation map (DEM) in 2010: forested headwater subwatershed (I), forest–farm land–urban land mixed subwatershed (II), forest and agriculture dominated watershed (III), residential subwatershed (IV), and developing estuarine subwatershed (V).

2.2. Surface sediment sampling

Surface sediment samples (20-cm depth) were collected at six monitoring sites in March 2014 using a grab bucket sampler. Samples were collected into polyethylene bags and stored in a cooler during transport back to the laboratory, where they were stored in a refrigerator at 4 °C. The sediment samples were sieved through a 2-mm sieve to remove stones and debris and then mixed.

2.3. Separation of surface sediment

The sample was milled into powder using an agate mortar and pestle. The ground surface sediment sample was suspended in double deionized water (DDW) (500 mL) and dispersed by ultrasonication at 170 W and 60 kHz for 1 min using a NEY 300

Ultrasonic instrument (NEY, Barkmeyer Division, Yucaipa, CA). The suspension was then passed through a 300-mesh sieve (50 µm) to remove the sand fraction from the suspension of dispersed mineral particles by wet sieving. The < 2000-nm-sized fraction was then collected by sedimentation in accordance with Stokes' Law (Jackson, 2005). The time required to separate surface sediments 450–1000 nm and 220–450 nm in size was calculated using the modified Stokes equation (Laidlaw and Steinmetz, 2005). To collect the size fraction of 450–1000 nm, the suspension (< 1000 nm size fraction) was centrifuged at 980 × g (3370 rpm) for 6 min at 4 °C, using a Hitachi CR21 refrigerated centrifuge, which had a R12A3 rotor with polycarbonate tubes and settling sample height of 10 cm. The settled particles were resuspended in DDW and sonicated at 170 W and 60 kHz for 1 min. The dispersed suspension was then repeatedly centrifuged and washed seven times using similar centrifugation and dispersion methods to obtain the size fraction of 450–1000 nm. The suspension (< 450-nm-sized fraction) collected from the aforementioned centrifugation (980 × g for 6 min) was centrifuged at 6840 × g (9000 rpm) for 15 min by the same ultracentrifugal sedimentation method to obtain the < 220-nm-sized fraction in the suspension. The settled particles were resuspended in DDW, then repeatedly centrifuged and washed seven times as described above to collect the size fraction of 220–450 nm.

2.4. Basic property analysis

The pH and electrical conductivity (EC) of samples were measured in distilled water (sediment: solution = 1:2.5). Cation exchange capacity (CEC) of the sediments was determined using the conventional ammonium–sodium exchange method with ammonium–acetate buffered solution at pH 7.0 (Wang et al., 1996). Exchangeable cations in the sediments were extracted using 1 M NH₄Cl solutions and centrifuged at 17,400 × g for 20 min. Concentrations of K, Na, Ca, and Mg in supernatants were measured using a Perkin Elmer Optima 7000 DV ICP-OES spectrometer. The total heavy metal content was measured using an inductively coupled plasma–mass spectrometer (ICP-MS, 7500 CX, Agilent, USA), after acid digestion (concentrated HNO₃–HClO₄) (Lee et al., 2006). A standard reference material of the sediment (SRM 2704, National Institute of Standards and Technology [NIST]) was used to check method accuracies and the results were within ± 5% of the certified values.

2.5. Characterization techniques

Samples of the surface sediments were characterized using specific surface area, X-ray diffraction analysis (XRD), Fourier-transform infrared absorption spectrometry (FT-IR), and scanning electron microscopy (SEM).

Specific surface area: Specific surface area was determined on precipitates (100 mg) using the Brunauer–Emmett–Teller (BET) equation with a Nova 2000 analyzer (Quanta Chrome).

XRD analysis: The precipitates were examined by XRD using CuKα radiation on a Rigaku Geigerflex X-ray diffractometer equipped with a graphite monochromator, operating at 35 kV and 15 mA at a step-scan of 0.02°/s. The X-ray patterns were recorded in the range of 3–50°2θ.

SEM analysis: One drop of suspension was dried on a carbon-coated film on copper grids (3.05 mm in diameter), and examined under a JEOL SEM (JEM 100 CXII) operated at 100 kV for selected area electron diffraction (SAED).

2.6. Statistical analysis

A canonical correlation analysis (CCA, Proc Cancorr) was conducted on metal content and the properties of surface sediment

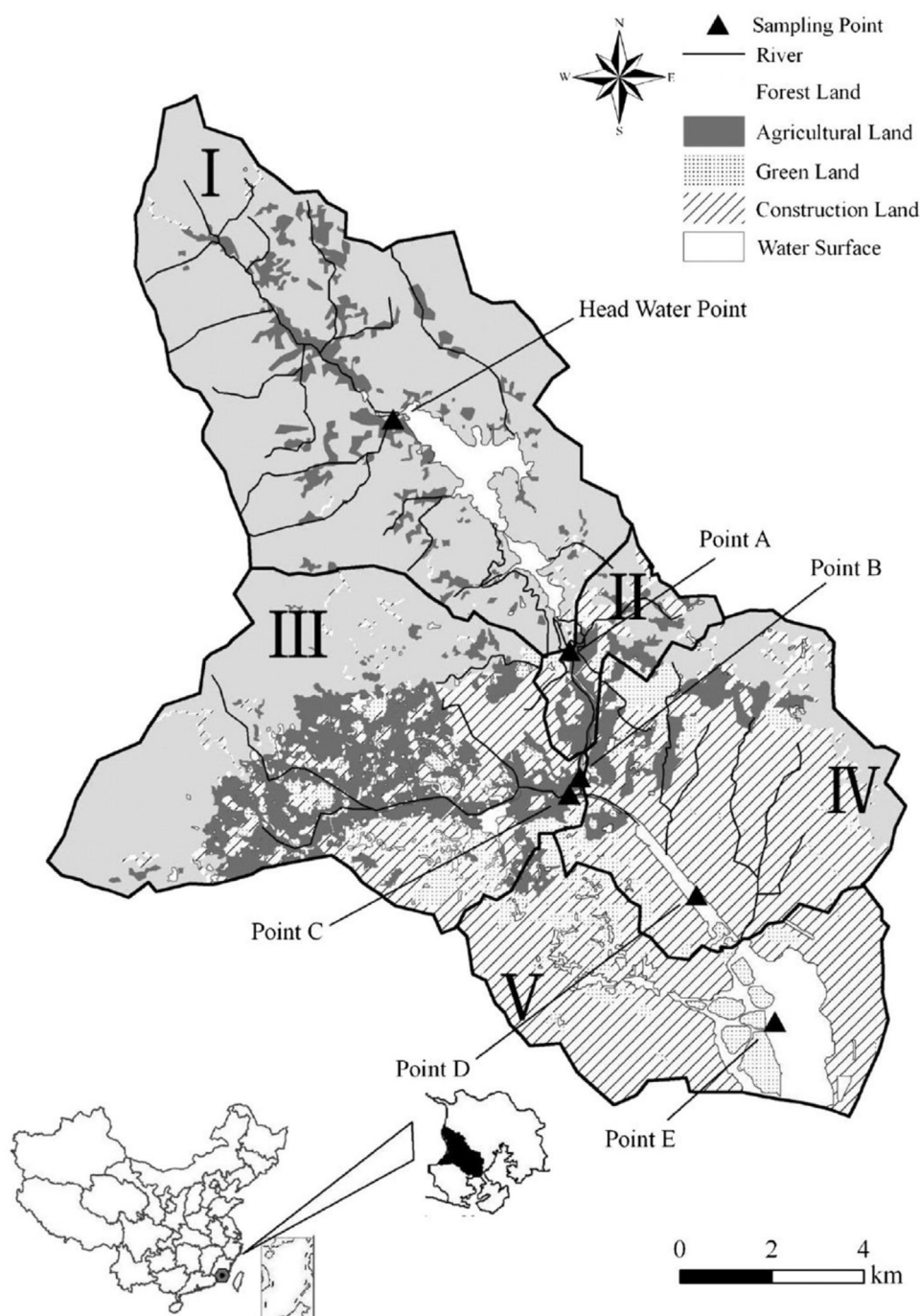


Fig. 1. Map of the Bantou watershed in Jimei County, Xiamen, China. Five subwatersheds are identified based on DEM data and named as forested headwater subwatershed (I), mixed subwatershed (II), agricultural dominated watershed (III), old residential subwatershed (IV), and estuarine subwatershed (V). (Yu et al., 2014).

datasets to identify predominant factors from one dataset to another, that is, the interactive relationships between metal contents and the properties of surface sediments. The statistical software SAS[®] 9.1 for Windows[®] (SAS Institute Inc., Cary, NC, USA) was used for all analyses.

3. Results and discussion

3.1. Selected physical and chemical properties of surface sediments

The basic properties of surface sediments are presented in Table 1. The pH of surface sediments at the six monitoring points

ranged from 6.13 to 8.27. Electrical conductivity (EC) of the sediment refers to its ability to conduct an electric current and is an indicator of the total dissolved inorganic salts and other solids. EC values in the study area ranged between 121.3 and 1063.9 $\mu\text{S cm}^{-1}$ and increased from headwater to site E. The content of dissolved inorganic salts and other solids in the sediment also increased from headwater to site E. The surface sediments at point E had significantly higher pH and EC values than those of other points. This could be attributed to urban discharge or seawater intrusion. The concentrations of exchangeable cations in the sediment increased from headwater to site E, which may explain the trend of the EC in Table 1. The CEC and exchangeable cations of surface sediments at the headwater was significantly lower than at other

Table 1
Properties and characteristics of sediments.

Sample	pH	EC ($\mu\text{S cm}^{-1}$)	CEC (cmol kg^{-1} sediment)	Exchangeable (cmol kg^{-1} sediment)					Particle distribution (%)			Texture
				K ⁺	Na ⁺	Ca ²⁺	Mg ²⁺	Sum	Sand	Silt	Clay	
Head water	6.34	121.3	5.2	0.21	0.63	1.90	0.31	3.05	98.3	1.5	0.2	Sand
Point A	6.13	322.6	9.6	0.11	0.49	3.19	0.33	4.12	51.7	33.2	15.2	Sandy Loam
Point B	8.02	408.7	13.5	0.33	0.75	8.17	1.23	10.48	5.7	64.5	29.8	Silty Clay Loam
Point C	7.30	616.3	10.6	0.19	0.73	6.70	0.61	8.24	63.5	28.5	8.0	Sandy Loam
Point D	7.42	912.7	13.2	2.07	1.63	2.72	2.72	9.15	2.8	59.4	37.8	Silty Clay Loam
Point E	8.27	1063.9	12.4	3.32	1.57	4.01	2.87	11.76	78.3	15.2	6.5	Sandy Loam

points. Exchangeable cations of surface sediments showed a similar pattern to that of EC. Grain size of sediments can indicate spatial inhomogeneity. Thus, a wide range of heavy metal concentrations can be detected. Some investigations have shown that if grain size varies greatly and is not accounted for, the comparison of metal concentrations in different sampling locations can be inaccurate (Jernstrom, 2010). The average percentage composition of the sediment is 50.1% sand, 33.7% silt, and 16.2% clay. Thus, the surface sediment of the Bantou watershed is predominantly sand and silt (with greater sand contents than silt) and a small quantity of clay. The surface sediments at points B and D generally had significantly higher clay contents than those at other points.

3.2. Surface area and pore volume of surface sediments

Analyses by N₂ adsorption/desorption revealed that BET surface areas were 27.66–39.68, 40.51–46.34, and 59.87–68.34 m² g⁻¹ for clay, fine clay, and very fine clay, respectively (Table 2). Generally, very fine clay of surface sediments had significantly higher BET surface areas than clay and fine clay. The sequence of the total pore volume was very fine clay (0.1527–0.1739 cm³ g⁻¹) > fine clay (0.1231–0.1461 cm³ g⁻¹) > clay (0.1123–0.1235 cm³ g⁻¹). Micropore and macropore volumes of surface sediments showed a similar pattern to that of total pore volume. The accumulation of heavy metals in sediments is regulated by the granular composition of sediments. Grain size affects the surface area, micropore

and macropore volume of surface sediments, and the degree of chemical partitioning into sediments. Therefore, metals are generally found to be largely associated with the fine-grain fraction that has been traditionally used to study heavy metal pollution in sediments.

3.3. The clay mineral composition of surface sediments

Mineralogical studies of surface sediments have clearly demonstrated that they are not only sensitive indicators of their environment, but also provide valuable insight into regional hydrodynamics, including patterns of sediment transport and deposition (Preda and Cox, 2005). Several authors have investigated the mineral character of marine sediment, in particular the speciation and distribution of clay minerals, which can help to determine the sources and depositional conditions (Rajkumar et al., 2012). Clay mineral compositions of surface sediments evaluated in the present study are summarized in Table 3. The clay fraction was dominated by illite (36–46%), chlorite (27–40%), and kaolinite (18–25%), with small amounts of smectite (3–7%). The composition of the fine clay fraction was similar to that of the clay fraction; however, the very fine clay fraction was dominated by kaolinite (36–41%), illite (26–35%), and chlorite (25–38%). The main factor controlling marine distribution of clay minerals is the nature of the dominant particle sources. With decreased particle size, XRD revealed poorly crystalline nanoparticles, indicating that repetitions

Table 2
Surface area and pore volume of surface sediments.

Sample	BET Surface area (m ² g ⁻¹)			Pore Volume (cm ³ g ⁻¹)		
	Micropore	External	Total	Micropore	Macropore	Total
Clay (1–2 μm)						
Head water	1.52	26.14	27.66	0.0002	0.1221	0.1223
Point A	1.35	38.33	39.68	0.0003	0.1232	0.1235
Point B	1.33	34.86	36.19	0.0003	0.1222	0.1225
Point C	0.79	33.44	34.23	0.0001	0.1154	0.1155
Point D	1.63	35.49	37.12	0.0002	0.1121	0.1123
Point E	0.74	34.44	35.18	0.0001	0.1151	0.1152
Fine clay (0.45–1 μm)						
Head water	–	–	–	–	–	–
Point A	1.51	44.83	46.34	0.0006	0.1445	0.1451
Point B	2.26	41.45	43.71	0.0004	0.1441	0.1445
Point C	1.24	40.14	41.38	0.0003	0.1228	0.1231
Point D	2.35	43.14	45.49	0.0003	0.1458	0.1461
Point E	2.12	38.39	40.51	0.0003	0.1317	0.1320
Very fine clay (0.22–0.45 μm)						
Head water	–	–	–	–	–	–
Point A	3.51	64.83	68.34	0.0007	0.1732	0.1739
Point B	3.86	63.45	67.31	0.0004	0.1639	0.1643
Point C	2.73	57.14	59.87	0.0004	0.1523	0.1527
Point D	4.01	66.59	70.60	0.0006	0.1735	0.1741
Point E	3.43	58.22	61.65	0.0004	0.1549	0.1553

–: Not available.

Table 3
Clay mineral composition of surface sediments.

Sample	Major Clay Minerals (%)			
	Kaolinite	Illite	Chlorite	Smectite
Clay (1–2 μm)				
Head water	23	38	40	0
Point A	25	36	39	0
Point B	21	46	33	0
Point C	21	39	36	4
Point D	18	42	27	3
Point E	19	45	29	7
Fine clay (0.45–1 μm)				
Head water	–	–	–	–
Point A	29	33	38	0
Point B	25	43	32	0
Point C	26	36	36	2
Point D	23	37	27	3
Point E	22	43	30	5
Very fine clay (0.22–0.45 μm)				
Head water	–	–	–	–
Point A	36	26	38	0
Point B	38	35	27	0
Point C	41	34	25	0
Point D	40	32	28	0
Point E	39	34	27	0

–: Not available.

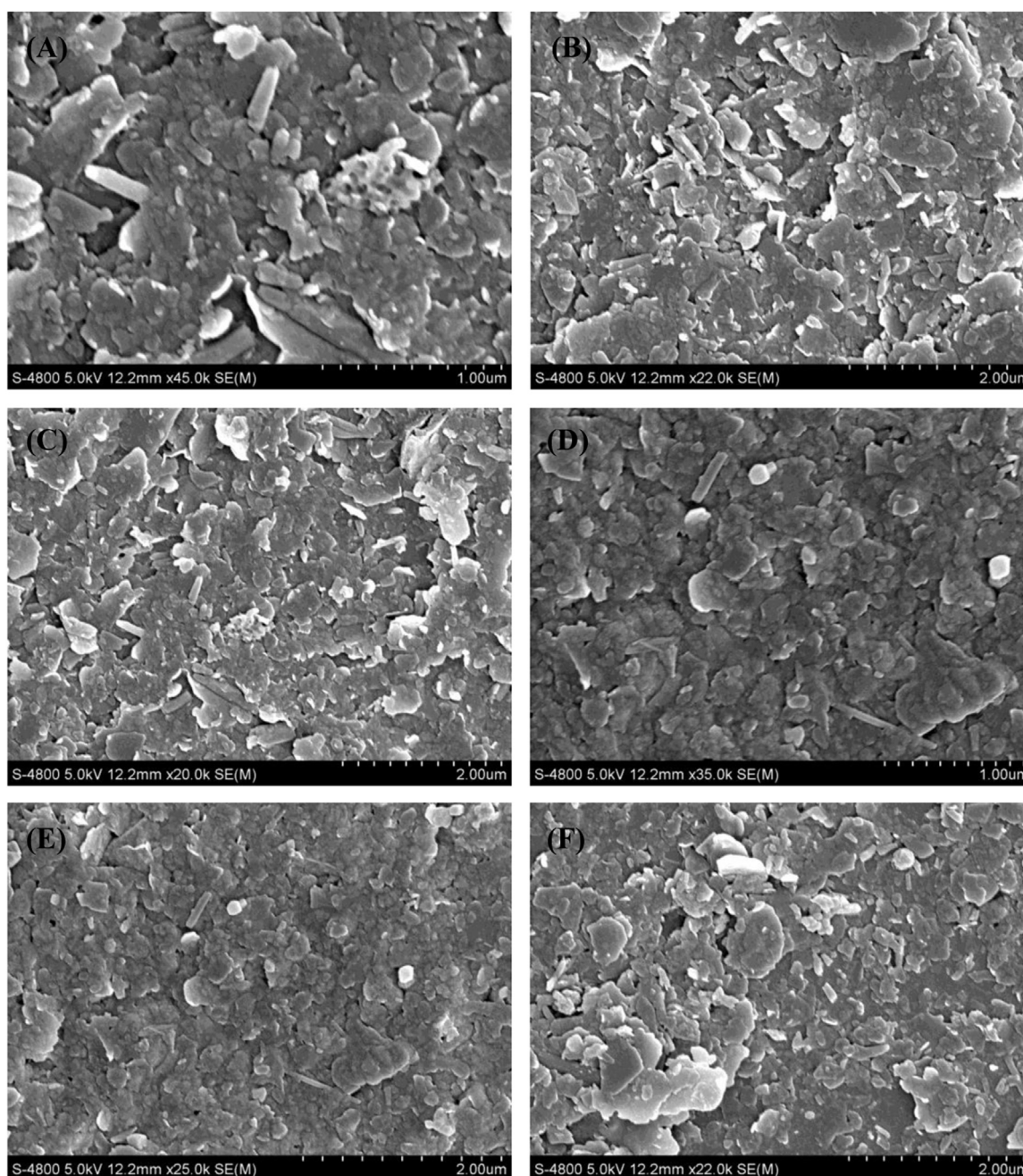


Fig. 2. Scanning electron microscopic (SEM) images of sediment particles: (A) clay of point C (B) fine clay of point C (C) very fine clay of point C (D) clay of point D (E) fine clay of point D (F) very fine clay of point D.

of unit cells were apparently few because of preferential structural disruption of other crystal planes, caused by pressure-induced phase transition in the fine size fractions. Fine-grained marine sediments derived from fluvial processes are deposited in near-shore and continental margins, and only a small amount is transported to the deep sea. The fine-grained sediments are composed of clay minerals and amorphous materials. The composition and relative abundance of clay minerals are controlled by their source rocks and weathering conditions. Their distribution on the continental shelf and slope is controlled by depositional processes, particularly current circulation patterns and the settling of clay minerals in response to energy conditions (Boldt et al., 2012). Knowledge of these processes can help to predict the transport pathways of pollutants, which are preferentially controlled in fine-grained sediments.

3.4. Electron microscopy

SEM images of sediment particles are presented in Fig. 2. Illite was the most common particle observed by electron microscopy, with slab-like shapes. Smectite assumed scale-like or flower-like shapes and appeared to be comparatively smaller, but was present only in minimal quantities. Chlorite was translucent and comparatively larger and kaolinite had a relatively good crystal shape. Generally, fine clay and very fine clay are shapeless, hollow colloids that are deformed and aggregated.

3.5. Heavy metal concentrations in surface sediments

It is difficult to make an overall assessment of the degree of heavy metal contamination of sediments because of variations in

heavy metal concentrations with location and contents of various particle sizes, and other organic materials in the sediments (Rubio et al., 2000). In the present study, we compared our measurements of heavy metal concentrations in the sediment with published values for surface sediments to assess contamination levels of the Bantou watershed. Furthermore, particle size distribution is one of the most important factors affecting the capacity of sediments to accumulate heavy metals. Heavy metal concentrations in surface sediments generally increased with decreasing grain size, because of the affinity of metals to bind with finer particles (O'Reilly Wiese et al., 1995). The concentrations of individual heavy metals are discussed as follows.

Copper is an essential element in humans; however, at high levels, it accumulates in the blood, liver, and kidneys and causes anemia, renal and intestinal irritations, coma, death, and Wilson's disease (Gratten et al., 2003). The concentrations of Cu were 8.26–28.91 mg kg⁻¹, 39.32–68.32 mg kg⁻¹, and 57.21–89.24 mg kg⁻¹ sediment for clay, fine clay, and very fine clay, respectively (Fig. 3). The highest Cu content was in the very fine clay fraction and the lowest, in the clay fraction. In polluted areas, Cu concentrations between 20.0 and 343.0 mg kg⁻¹ have been reported (Spencer and MacLeod, 2002; Sullivan and Taylor, 2003; Santamaria-Fernandez et al., 2005). Unpolluted areas are characterized by Cu levels between 1.0 and 13.0 mg kg⁻¹ (Spencer and MacLeod, 2002; Sullivan and Taylor, 2003; Santamaria-Fernandez et al., 2005). In comparison to these previous reports, the concentrations of Cu in the samples used for the present study were in the middle range (8.26–89.24 mg kg⁻¹). Therefore, the samples under investigation were deemed to be moderately polluted by Cu.

Zn is a common metal in the human environment. Little is known about its toxic effects in humans (Homady et al., 2002). High levels of Zn can cause pancreatitis, anemia, muscle pain, acute renal failure, and death (Pais and Jones, 1997). The range of Zn concentrations in the sediments under investigation was from 4.62 to 270.72 mg kg⁻¹ (Fig. 3). The highest Zn content was detected in the very fine clay fraction and the lowest in the clay fraction. Previous studies have shown that Zn concentrations in polluted sediments can be as high as 4,000 mg kg⁻¹ (Aloupi and Angelidis, 2002; Alomary and Soraya, 2007; Leivuori, 1998; Spencer and MacLeod, 2002). When compared to the values reported in previous studies, values obtained in the present study indicated no pollution of the samples by Zn.

After As, Pb is second on the top-20 list of the most poisonous heavy metals. Its target organs are the bones, brain, blood, kidneys, reproductive and cardiovascular systems, and the thyroid gland (Homady et al., 2002; Massadeh et al., 2004). The concentrations of Pb in the samples of the present study were between 14.92 and 93.21 mg kg⁻¹. The highest Pb content was detected in the very fine clay fraction and the lowest in the clay fraction. Several studies of Pb in sediments have been conducted in various regions. High levels of Pb (26–630 mg kg⁻¹), have been reported in polluted areas (Aloupi and Angelidis, 2002; Alomary and Soraya, 2007; Leivuori, 1998) and low levels (0.5–60 mg kg⁻¹) have been detected in unpolluted regions (Aloupi and Angelidis, 2001; Feldstein et al., 2003; Leivuori, 1998). In comparison to these previous reports, the values obtained in the present study indicate no pollution of the samples by Pb.

Metallic nickel and nickel compounds are used in numerous industrial and commercial applications, such as stainless steel and other nickel alloys, electroplating, foundries, catalysts, batteries, electronics, ceramics, pigments, and coinage (Huggins et al., 2011). Nickel bioavailability and related biochemical processes are strongly dependent on the chemical and physical form of the element (Schaumloffel, 2012). In the present study, concentrations of Ni were between 15.17 and 37.49 mg kg⁻¹. However, there was no significant variation in Ni contents between fractions. The results for total Ni levels in the sediment were higher than the threshold effects level (22.7 mg kg⁻¹), but lower than the probable effects level (48.6 mg kg⁻¹), according to the Interim sediment quality assessment values (1994) and the United States Environmental Protection Agency (1998).

Cr contamination of soil and groundwater is a significant problem worldwide. Cr (VI) in waters is highly toxic, corrosive, carcinogenic, and has a very high solubility (Zhang et al., 2014). Concentrations of Cr in the samples of the present study were between 11.37 and 127.84 mg kg⁻¹. The highest Cr content was in the very fine clay fraction and the lowest, in the clay fraction. The results for total Cr levels in the sediment were higher than the threshold effects level (43.4 mg kg⁻¹), but lower than the probable effects level (111.0 mg kg⁻¹), according to the Interim sediment quality assessment values (1994) and the United States Environmental Protection Agency (1998).

As is a toxic element that is classified as a human carcinogen (WHO, 2000). Low levels of As exposure can cause gastrointestinal

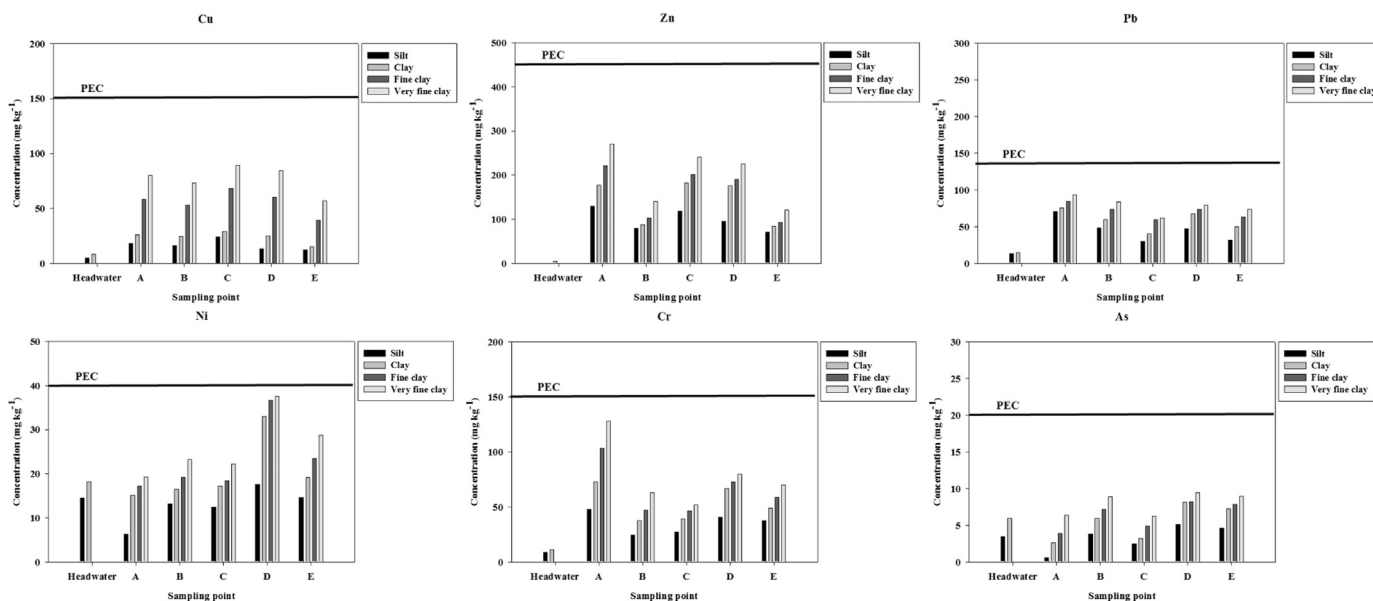


Fig. 3. Heavy metal content (Cu, Zn, Pb, Ni, Cr, and As) in sediment.

Table 4

Canonical redundancy analysis of correlations between metal contents and properties of surface sediments.

Standardized variance of the metal content explained by						Standardized variance of the properties explained by					
Canonical	Their own		Canonical R ²	The properties		Canonical	Their own		Canonical R ²	The metal content	
Variable number	Canonical variables			Canonical variables		variable number	canonical variables			Canonical variables	
	Proportion	Cumulative proportion		Proportion	Cumulative proportion		Proportion	Cumulative proportion		Proportion	Cumulative proportion
1	0.1027	0.1027	0.9894	0.1016	0.1016	1	0.2202	0.2202	0.9894	0.2179	0.2179
2	0.4319	0.5346	0.9855	0.4256	0.5273	2	0.4709	0.6911	0.9855	0.4641	0.6819
3	0.0562	0.5909	0.9417	0.053	0.5803	3	0.0731	0.7642	0.9417	0.0689	0.7508
Squared multiple correlations between the metals content and the first M canonical variables of the properties						Squared multiple correlations between the properties and the first M canonical variables of the properties					
M			1	2	3	M			1	2	3
Metal	Cu		0.0555	0.7448	0.7492	Minerals	Kaolinite		0.1562	0.6438	0.6606
	Zn		0.0244	0.7266	0.7377		Illite		0.0677	0.6254	0.7428
	Pb		0.0266	0.7251	0.7535		Chlorite		0.0114	0.0763	0.4442
	Ni		0.0648	0.1492	0.2357	Smectite		0.2805	0.3409	0.341	
	Cr		0.0091	0.7412	0.8023	Surface area	t-Plot micropore area		0.4118	0.8109	0.8641
	As		0.0694	0.0983	0.2674		t-Plot external surface area		0.1908	0.8894	0.9241
							BET surface area		0.2076	0.8884	0.9249
						Pore volume	t-Plot micropore volume		0.1849	0.7749	0.8368
					t-Plot macropore volume			0.3343	0.8842	0.8843	
					Total pore volume			0.3337	0.8852	0.8853	

irritation, decreased production of red and white blood cells, abnormal heart rhythm, blood vessel damage, and “pins and needles” sensations in the hands and feet (Abernathy et al., 2003). Concentrations of As observed in the present study were between 2.67 and 9.49 mg kg⁻¹. However, there was no significant variation in As levels between fractions. The mean value for total As in the sediment was between 11.3 and 55.8 mg kg⁻¹ (Mandal and Suzuki, 2002; Pandey et al., 2004). These results are higher than the threshold effects level (7.2 mg kg⁻¹), but lower than the probable-effects level (42.0 mg kg⁻¹), according to the Interim sediment quality assessment values (1994) and the United States Environmental Protection Agency (1998).

3.6. The relationship between metal contents and properties of surface sediments

The relationship between metal content and the properties of surface sediments were revealed by CCA (Table 4). The canonical variables of metal content were related to the second canonical variable at 43.19% (59.09% in total by the next three canonical variables) and the second canonical variable of the properties at 42.56% (58.03% in total by the next three canonical variables). The canonical variables of the properties were related to the second canonical variable at 47.09% (59.09% in total by the next three canonical variables) and the second canonical variable of metal content at 42.56% (58.03% in total by the next three canonical variables). The first ‘M’ canonical variables of the metal contents can be predicted by both surface area and pore volume, followed by kaolinite and illite levels. On the other hand, the type of metal, that is, Cu, Cr, Zn, and Pb, was significantly correlated with the first ‘M’ canonical variables of the properties.

4. Conclusions

The present study focused on the influence of fine clay mineral characteristics on metal sorption. The nanoparticles had highly specific surface areas, and were fine, shapeless, and hollow colloids that were aggregated. XRD and SEM analyses revealed that the nanoparticles (very fine clay) were poorly crystalline. The results indicated that there were apparently few repetitions of unit cells because of preferential structural disruption of other crystal planes caused by pressure-induced phase transitions in fine size fractions. The highest metal content was generally in the very fine clay fraction and the lowest, in the clay fraction. Based on the results of CCA, metal contents were significantly correlated with surface area and pore volume, followed by kaolinite and illite levels. The findings of the present study are of fundamental significance to advancing deeper understanding of the reactions between heavy metals and fine clay minerals in the terrestrial ecosystem.

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