

## A Field Study of Factors that Affect Acid-Volatile Sulfide Concentrations

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Received 18 May 2014; revised 30 August 2014; accepted 15 September 2014; published online 30 September 2014

**ABSTRACT.** The spatial variability of acid-volatile sulfide (AVS) and its influential factors were studied through regression analysis to explain the spatial distribution of AVS and to predict the variability of metal availability under changing conditions simply and effectively. The AVS equation is used to derive oxidation-reduction potential (Eh), sulfate-reducing bacteria (SRB), organic carbon (OC), and total sulfur (TS). The relationships of these variables with AVS were then analyzed. Moreover, their effect on AVS was quantified through linear regression (LR) and principal component regression (PCR). These two regression equations were analyzed using a histogram of residual values and by comparing mean relative error (MRE) and root-mean-square error (RMSE) values. LR (Model 1) and PCR (Model 2) models were established as well. The MRE and RMSE values in the PCR model were 21.9 and 25.9%, respectively. In terms of these values, the PCR model is more accurate than the LR model. Furthermore, its predictive results were more reasonable. In conclusion, the PCR model can be used to predict the AVS concentrations based on the OC, Eh, SRB, and TS values. This model simplifies and facilitates the evaluation of metal toxicity under field conditions and can thus be used to manage sediments contaminated with metals.

**Keywords:** acid-volatile sulfide, spatial variability, influencing factors, principal component regression, linear regression

### 1. Introduction

Acid-volatile sulfide (AVS) was introduced by Di Toro et al. (1990) as a measure of Cd bioavailability. It is operationally defined as the amount of sulfide that can be volatilized during the extraction of cold 1N HCl. AVS-bound metals are extracted simultaneously; these metals are therefore known as simultaneously extracted metals (SEM) (Rickard et al., 2005). Heavy metal pollution has recently attracted much attention mainly because it cannot be biologically or chemically degraded and it strongly threatens the environment and human health (Kim et al., 2006; Forsythe et al., 2010). In response, the ecological risks associated with heavy metals are being evaluated (Lee et al., 2005; Lei et al., 2013). Di Toro formulated the [SEM-AVS] model that predicts the binding of metals to sulfide. It also suggests that sediment pore water is nontoxic when AVS > SEM (on a molar basis). Conversely, the metals are released into the sediment pore water and can be toxic to aquatic life when AVS < SEM (Di Toro et al., 1990, 2005). Many experiments indicate that this model is a useful predictor of both acute and chronic toxic effects on both freshwater

and marine environments (Casas et al., 1994; Hare et al., 1994; Ankley, 1996; Berry et al., 1996; Leonard et al., 1996). Consequently, many researchers believe that AVS is an important indicator of bioavailability in anaerobic sediments (USEPA, 2005; Prica et al., 2008; Brix et al., 2010; Nguyen et al., 2011).

The concentration of AVS in aquatic sediments is a function of both the rate at which S (-II) is produced and the rate at which it is lost by either oxidation or diffusion. As a result, AVS concentrations vary with the factors that affect the supply of organic matter, the rate of sulfate reduction, and the redox status of the sediments (Oehm et al., 1997; Van Griethuysena et al., 2005). That is, AVS concentrations are expected to vary both temporally with the seasons and spatially with sediment quality (Van Den Berg et al., 1998; Burton et al., 2007). Thus, the temporal variation and spatial heterogeneity of AVS generates very different AVS distribution patterns across various field locations and seasons. Consequently, the variations in metal availability are difficult to interpret.

The behavior of the metals in contaminated sediments is induced by the complex combination of physical, chemical, and biological processes (Van Griethuysena et al., 2005; Hong et al., 2014). Thus, the biogeochemical reactions associated with various factors must be understood to quantify the toxicity of the metals in sediments. The lack of a reasonable explanation for this phenomenon may limit the applicability of AVS in natural systems in that the availability of trace metals can

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be regarded as highly variable given their spatial variability under field conditions (Mackey et al., 1996; Van Den Hoop et al., 1997). Metal-associated risks may vary across different sites even at near-constant metal or SEM concentrations because of the spatial variation in environmental conditions, including oxidation-reduction potential ( $Eh$ ) and AVS, by extension (Van Griethuysen et al., 2006). The temporal variation and spatial heterogeneity of AVS are mainly caused by its susceptibility to various factors, including the physical and chemical properties of sediments (Leonard et al., 1993). Specifically, AVS can be affected by redox state, organic matter, particle size composition, sulfate content (Morse et al., 1999; Van Griethuysen et al., 2004), overlying water characteristics, biological factors, and hydrological conditions (Van Griethuysena et al., 2006; de Lange et al., 2008). Therefore, a model is developed and applied to clarify the underlying biogeochemical processes and the release behavior of the trace metals in sediments.

Researchers have used various models to explain the effect of biogeochemical processes on the availability of metals in sediments (Di Toro et al., 1996; Oehm et al., 1997; Fang et al., 2002; Van Griethuysena et al., 2005; Canavan et al., 2007; Adeline et al., 2011; Wadhawan et al., 2013; Dale et al., 2013; Murphy et al., 2014; Hong et al., 2014). Most of these models are diagenetic and are based on complicated thermodynamic equilibrium calculations that require many parameters (Di Toro et al., 1996; Fang et al., 2002; Van Griethuysena et al., 2005; Canavan et al., 2007; Adeline et al., 2011; Dale et al., 2013; Murphy et al., 2014; Hong et al., 2014). Given the complexity of this calculation, a related software was developed (Van Griethuysena et al., 2005; Canavan et al., 2007; Adeline et al., 2011). The results predicted by this software are good for some physicochemical indices but are poor for other variable ones. Some researchers also conducted simulation tests to determine the required parameters (Wadhawan et al., 2013; Dale et al., 2013; Murphy et al., 2014; Hong et al., 2014). Nonetheless, the experimental work needed was heavy. Furthermore, the selected parameters are inconclusive if the field conditions are not well-simulated.

Moreover, few studies have focused on the AVS model. Thus far, a model has not been established to predict its distribution. A model based on the one-dimensional, advective-dispersive mass balance equation was presented to detect the temporal and vertical variations in AVS, simultaneously extracted cadmium ( $SEM_{Cd}$ ), and the cadmium concentration of the pore water in sediments (Di Toro et al., 1996). It reproduced the major features of the experimental data but did not successfully reproduce the cadmium concentrations in pore water. A similar model was established to describe the vertical distribution of AVS and to examine the observed AVS concentrations in the sediments of Donghu Lake (Fang et al., 2002). The predicted values and the monitored ones are biased partly because the key parameters are not calibrated based on the simulation tests. The equation for stepwise multiple regression has been used to predict the spatial distribution of AVS concentrations in the sediments of Canadohta Lake, PA, as well as the variability of AVS concentrations with influential

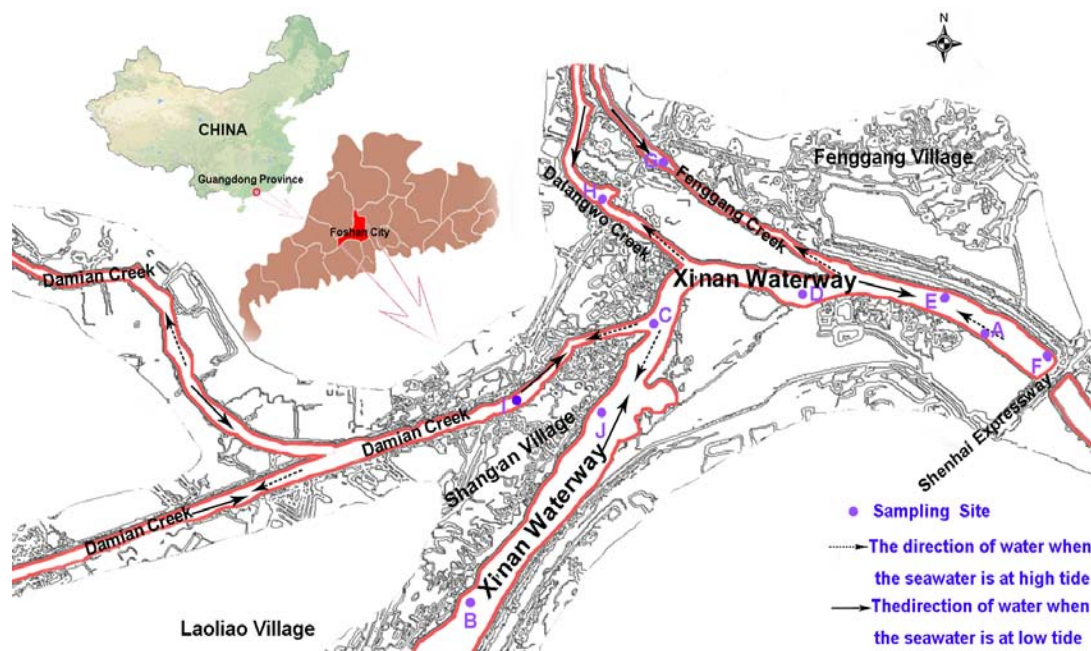
factors. These factors include water depth, organic carbon (O-C), water contents, and Fe concentrations (Oehm et al., 1997). The resultant model is highly significant ( $p < 0.001$ ), but its predictive power is only modest (Oehm et al., 1997). Although this equation is unsuccessful in this case, regression analysis is a simple and feasible method to address the AVS prediction problem. The regression model may also quantify the effect of various factors. Regression analysis has been used in many fields. It reflects a variable (the dependent variable) to another or to a group of variables (variables) (Rajab et al., 2013; Kumar et al., 2013). Linear regression (LR) is the most commonly used regression method for prediction partly because it is relatively simple, practical, and convenient (Shi et al., 2013; Font-i-Furnols et al., 2013). Principal component regression (PCR) is another regression equation that has also been applied effectively in many fields to analyze data (Keithley et al., 2009; Antanasijević et al., 2013). However, few studies have employed it to predict the factors in sediments.

This paper mainly discusses the dominant factors that influence the spatial distribution of AVS to quantify the effect of these factors on AVS after LR and PCR analyses and to determine the model that most effectively describes the variability of AVS concentrations. Furthermore, this study aims to predict the variability of metal availability in aquatic sediments under changing conditions.

## 2. Materials and Methods

### 2.1. Study Area

The Pearl River Delta (PRD) is composed of the three main branches (the North River, West River, and East River) of the Pearl River, which is the second largest river in China after the Yangtze River in terms of annual average flow. This delta is also the most economically developed region in this country and is among the most important international manufacturing bases. Hence, it is known as “the World’s Factory”. The Xi’nan Waterway is 41.6 km long and connects the major cities of Guangzhou and Foshan. It is upstream of the Guangzhou section of the Pearl River. This waterway flows from Xi’nan Gate (located in Sanshui District in Foshan City), through Guangyao Town in the Nanhai District of Foshan, and to Lishui Town and Heshun Town. Finally, it enters the Guangzhou section of the Pearl River (shown in Figure 1). Much industrial and domestic wastewater is discharged into the Xi’nan Waterway with the rapid economic growth and the significant increase in population. As a result, the water quality declines. This pollution attracts much attention because water quality strongly affects Foshan City and Guangzhou City, which are two important cities in southern China. The Fenggang section of the Xi’nan Waterway was thus selected as the main study area for its representative characteristics. Three branches (namely, Damian Creek, Dalangwo Creek, and Fenggang Creek) flow into the main channel of this section (Figure 1). Nonetheless, its water quality is deteriorating because of the varied and heavy pollutant loads. The hydrological hydrodynamic conditions are also complex in this section, and it is strongly influenced by semidiurnal tides, which cause the con-



**Figure 1.** The study area and the sampling stations in the Xi'nan Waterway.

stantly changing conditions. In addition, zones of both good and poor water quality intersect in this area.

## 2.2. Sample Collection

Ten sampling stations (Figure 1) represented the sediments of the Xi'nan Waterway sediments on the basis of a previous study (Li et al., 2008). The reference factors include the geometric characteristics of the riverway, hydrology, distribution of pollution sources, and locations of wastewater outlets (Table 1). Sediment samples were collected in triplicate within an area of approximately 1 m<sup>2</sup> in January 2011 using a columnar core sampler (Eijkelpamp Beeker-04.23.SB, made in the Netherlands). The sediments were separated into upper and lower layers mainly in accordance with their characteristics and natural interface. In addition, stations B and D displayed a clear sub-interface; therefore, the sediments in these stations were divided into three layers (upper, middle, and lower). The sediment samples were sliced in an anaerobic environment and placed in plastic bags immediately after sampling. The bags were filled with N<sub>2</sub>, sealed, and then transferred into a box filled with ice. The samples were stored in the laboratory at -4 °C for future analysis. Water was sampled as follows: The surface layer of the sediments and the overlying water were collected together using the core sampler. The water overlying the sediments at 5 - 10 cm was removed with a siphon after the samples settled for 30 min.

## 2.3. Sample Analysis

Prior to water and sediment sampling, surface water transparency, water depth, and water temperature were measured. The geographical coordinates were determined by a mobile

global positioning system at each sampling station (Trimble JUNO SB). The dissolved oxygen (DO) was measured *in situ* with a portable device (YSI550A-12). COD<sub>Cr</sub> was evaluated using the potassium dichromate method (GB11914-89) shortly after the water samples were taken back to the laboratory.

The AVS concentrations were determined by the purge-and-trap method (Allen et al., 1993). The amount of sulfate-reducing bacteria (SRB) in the sediments was measured by the most probable number method, and the results were expressed in CFU·g<sup>-1</sup> units (Castillo et al., 2012). *Eh* was measured *in situ* with a portable redox device (Orion portable ORP). Upon ignition, OC content was expected to decrease by 0.58 times (loss on ignition after heating for 3.5 h at 550 °C) (Van Griethuysen et al., 2006). The freeze-dried sediment samples were ground and then digested by the HNO<sub>3</sub>-HCl-H<sub>2</sub>O<sub>2</sub> method (USEPA Method 3050B). Finally, total sulfur (TS) was measured by inductively coupled plasma atomic emission spectroscopy (Van Den Hoop et al., 1997).

## 2.4. Data Analysis

LR and PCR were used to analyze the measured values of AVS concentrations, OC, *Eh*, SRB, and TS in the upper sediments of 26 core sediment samples. During this process, the upper sediments from the core sediment sample were excluded in stations B, F, and I. These data were used to verify the models based on the calculated mean relative error (MRE) and root-mean-square error (RMSE):

$$MRE = \frac{1}{n} \sum_{i=1}^n \left| \frac{Z_1 - Z_2}{Z_1} \right| \quad (1)$$

**Table 1.** Sediment Sampling Sites at the Xi'nan Waterway and the Environmental Conditions

Stations	Water Depth (cm)	*Transparency (cm)	*Temperature (°C)	*DO (mg·L <sup>-1</sup> )	*pH	*COD <sub>Cr</sub> (mg·L <sup>-1</sup> )	Specific locations	Sampling strategy
A	87	62	12.2	3.7	6.9	22.6	Downstream of Xi'nan Waterway in Fenggang section.	Influenced by sewage from Fenggang Creek.
B	28	28	12.9	5.3	7.2	20.3	Upstream of Xi'nan Waterway.	Located at the upstream of the Xi'nan Waterway. The water quality was in a good condition. It could be a referee site.
C	51	44	12.7	3.2	7.0	21.7	Intersection between Damian Creek and Xi'nan Waterway.	This station was influenced by the sewage from Damian Creek, which can reflect the polluted degree of Xi'nan Waterway after merge the polluted water from Damian Creek.
D	20	20	13.1	4.3	6.6	29.1	After the intersection between Dalangwo Creek and Xi'nan Waterway.	Influenced by the bad water quality from Dalangwo Creek. The river widens here with slow flow speed and facilitated the deposition of pollutants.
E	31	31	12.1	2.7	6.8	51.2	After the intersection between Dalangwo Creek and Xi'nan Waterway.	Influenced by the sewage from Fenggang Village and Fenggang Creek.
F	54	42	11.9	2.5	7.1	31.2	Downstream of Xi'nan Waterway in Fenggang section, near Xi'nan Bridge.	Influenced by the sewage from Fenggang village.
G	61	36	11.7	0	5.8	80.3	Mid-downstream of Fenggang Creek.	Influenced by the sewage from Fenggang Village and the water quality were in a bad condition.
H	24	24	12.7	2.3	6.7	39.7	Downstream of Dalangwo Creek.	Dalangwo Creek was influenced by sewage from coastal village and the water quality was in a bad conditions.
I	57	31	13.1	2.9	7.2	25.6	Midstream of Damian Creek.	Influenced by lager number of sewage and industrial wastewater discharged into the two tributary of Damian Creek.
J**	48	46	12.7	4.3	7.0	32.3	Midstream of Xi'nan Waterway, near a large alluvial beach.	Influenced by the sewage from Shang'an Village. The river widens here with slow flow speed and facilitated the deposition of pollutants.

\* The indicator of the overlying water.

\*\* Due to the broken-down sampler, in Station J only two samples were collected (the values in the station are arithmetic averages of two figures). The other stations had respectively three samples (the values in the table are arithmetic averages of three figures).

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (Z_1 - Z_2)^2} \quad (2)$$

where  $Z_1$  is the measured AVS concentration;  $Z_2$  is the value predicted by the model; and  $n$  is the number of correction sites. All data analyses were conducted with SPSS 10.0.

The data sets of OC,  $Eh$ , SRB, and TS conform to normal distributions (according to the Kolmogorov-Wilk Test in SPSS) with significance values of 0.583, 0.368, 0.930, and 0.398, respectively.

### 3. Results

#### 3.1. Spatial Distribution of AVS

Table 1 shows the environmental conditions at the 10 sampling stations. The upstream water samples were of higher quality than the downstream water ones. Furthermore, the water quality at the mainstream was better than that of the branches. Water quality was lowest at stations G (located in Fenggang Creek) and E (near Fenggang Village), which confirmed that Fenggang Creek is among the largest pollution sources. In fact, this section of the river is considered a water quality interface of the Xi'nan Waterway because of the discharge of sewage from the branch creeks.

Table 2 shows the monitoring results for AVS and SEM in the surface and deep-level sediments, respectively. The AVS concentrations averaged  $6.987 \mu\text{mol}\cdot\text{g}^{-1}$  and ranged from  $0.734 \mu\text{mol}\cdot\text{g}^{-1}$  to  $30.519 \mu\text{mol}\cdot\text{g}^{-1}$ . The coefficient of variation was 93.62%, and AVS variability was strong in the surface sediment. Among the five heavy metals examined, the concentration of  $\text{SEM}_{\text{Zn}}$  was highest with a maximum of  $14.099 \mu\text{mol}\cdot\text{g}^{-1}$ . That of  $\text{SEM}_{\text{Cd}}$  was lowest with a maximum of  $0.005 \mu\text{mol}\cdot\text{g}^{-1}$ . The AVS in the lower sediment layers averaged  $6.433 \mu\text{mol}\cdot\text{g}^{-1}$  and ranged from  $0.207 \mu\text{mol}\cdot\text{g}^{-1}$  to  $41.453 \mu\text{mol}\cdot\text{g}^{-1}$  (Table 2). The maximum coefficient of variation was 153.09%. The AVS concentrations were generally higher in the surface sediments than in the lower layers, whereas the variability of the lower layers was greater than that of the surface (Figure 2). Both the maximum and minimum AVS values are obtained in the lower sediment layers. Table 3 compares the AVS concentrations from the Xi'nan Waterway with those in other rivers and suggests that AVS concentrations are relatively high in this area. This AVS concentration is similar to that in the Vaal River (Van Griethuysen et al., 2003). It is also higher than that in the Mississippi River (Lawra et al., 2001) and in the Douro River (Ana et al., 2005), but lower than that in the Foshan Waterway (Li et al., 2008).

#### 3.2. Toxicity Analysis Based on the SEM-AVS Model

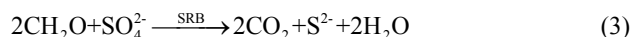
Table 4 depicts the values of  $\Sigma\text{SEM}_5$ ,  $\Sigma\text{SEM}_5\text{-AVS}$ , and  $(\Sigma\text{SEM}_5\text{-AVS})/f_{\text{OC}}$  from the 10 sampling stations in the Xi'nan Waterway. The SEM values indicate that station J has the highest concentration of heavy metals ( $23.210 \mu\text{mol}\cdot\text{g}^{-1}$ ), followed by station H. However, these two stations are not the most contaminated area when AVS and OC are taken into ac-

count. Specifically, the  $\Sigma\text{SEM}_5$  values of six sampling stations exceed that of AVS, most notably at station G ( $3.759 \mu\text{mol}\cdot\text{g}^{-1}$ ). If SEM-AVS exceeds  $2 \mu\text{mol}\cdot\text{g}^{-1}$  or if  $(\text{SEM-AVS})/f_{\text{OC}}$  exceeds  $150 \mu\text{mol}\cdot\text{g}^{-1}$ , then the probability of toxic affection is significant ( $> 90\%$ ) (Di Toro et al., 2005; USEPA, 2005). Moreover, the heavy metals in stations G and A are likely to be either acutely or chronically toxic to benthic organisms, according to the SEM-AVS criterion. However, these organisms are safe when OC is considered given  $(\text{SEM-AVS})/f_{\text{OC}}$  values lower than  $150 \mu\text{mol}\cdot\text{g}^{-1}$ . The analysis above generally reveals that the potential ecological risks are low despite the numerous heavy metals in the sediments because the river is rich in organic matter and active sulfides, which constrain the toxicity of these metals.

### 4. Discussion

#### 4.1. Influential Factors of AVS

The main component of AVS is S (-II), which is usually formed in anaerobic sediment during reduction of  $\text{SO}_4^{2-}$  by OC in combination with SRB (Di Toro et al., 1990; De Lange et al., 2008). The redox sequence begins with aerobic bacteria using oxygen as an electron acceptor. Once all of the oxygen is consumed, nitrate is then applied, followed by manganese and iron. The redox potential declines gradually. The reaction process is expressed by the following equation:



According to Equation (3), AVS can form when the sulfur supply is sufficiently high and when the conditions in the sediment favor sulfate reduction, such as in moderately to strongly reducing environments with SRB (Van Griethuysen et al., 2006). Therefore,  $Eh$ , OC, SRB, and TS were identified as the main factors in this discussion. Table 4 shows the monitoring results of these factors in surface sediments, and Table 5 depicts the analysis results of the correlations among  $Eh$ , SRB, OC, TS, and AVS.

$Eh$  is an important factor because AVS is only detected under reducing conditions. Along with water content, this factor is significantly correlated with AVS and sediments (Mackey et al., 1996); sediments with high AVS concentrations tend to have low  $Eh$  and high water content. Figure 3-A depicts the negative correlation between  $Eh$  and AVS in this study; nonetheless, this inverse relationship is insignificant ( $r = -0.202$ ,  $p = 0.294$ ). Therefore, the strongly reducing condition (low  $Eh$ ) is necessary but may not always generate a high AVS concentration although AVS is a product of anaerobic and strongly reducing conditions. For example,  $Eh$  was low at station F ( $-113 \text{ mV}$ ), but AVS was low as well ( $1.457 \mu\text{mol}\cdot\text{g}^{-1}$ ).

Equation (3) suggests that OC affects AVS considerably because S (-II) (the major component of AVS) is usually produced through the reduction of sulfate by organic carbon. Table 6 displays the OC contents of surface sediments from the sampling stations, and the statistics reveal that OC con-

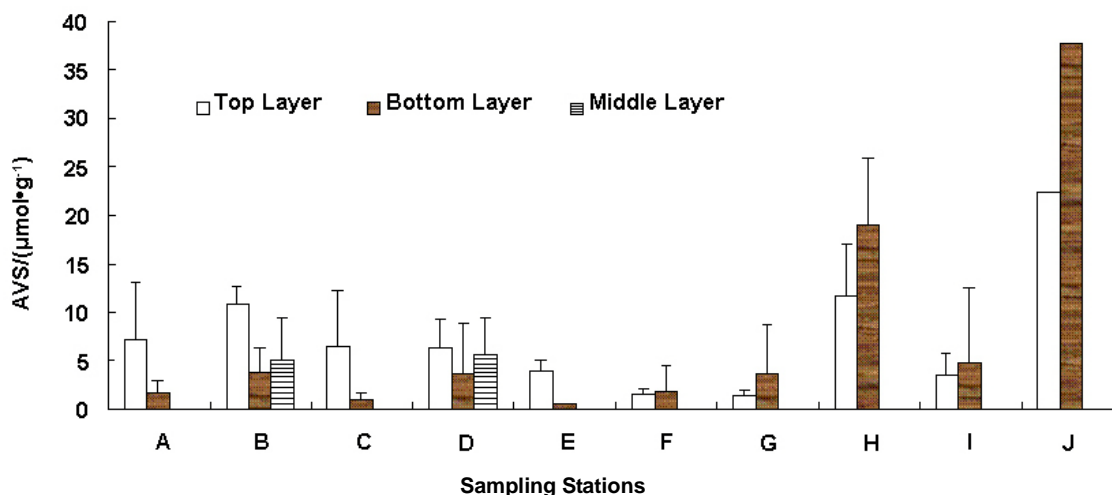


Figure 2. Spatial distribution of AVS in the Xi'nan Waterway.

Table 2. Concentrations of AVS and SEM in the Sediments ( $\mu\text{mol}\cdot\text{g}^{-1}$ )

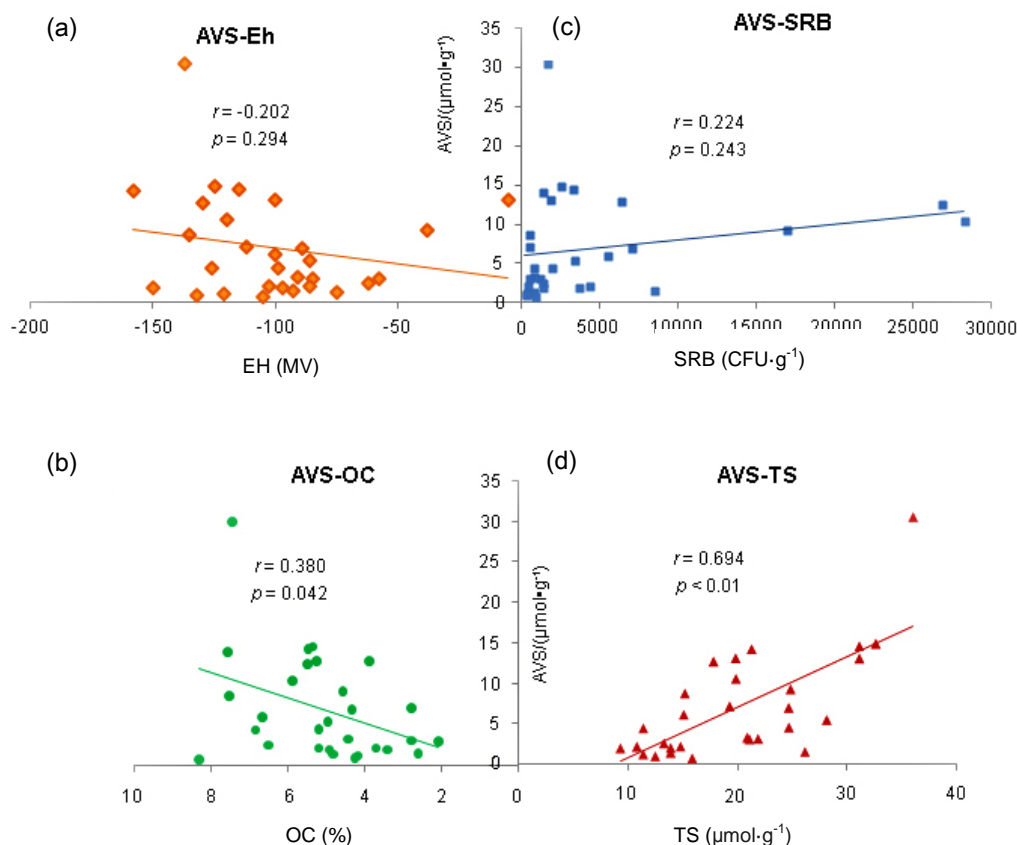
Stations	Layer	AVS	SEM <sub>Cu</sub>	SEM <sub>Pb</sub>	SEM <sub>Zn</sub>	SEM <sub>Ni</sub>	SEM <sub>Cd</sub>
A	top	7.188 ±5.770	0.475±0.346	0.092±0.023	9.141±12.976	0.357±0.281	0.005±0.003
	bottom	1.625±1.302	0.335±0.155	0.228±0.088	2.138±2.079	0.144±0.171	0.007±0.004
B	top	10.835±1.720	0.697±0.127	0.216±0.021	1.235±0.259	0.306±0.121	0.005±0.001
	middle	4.924±4.490	0.462±0.013	0.162±0.006	1.341±0.713	0.115±0.016	0.007±0.005
	bottom	3.703±2.703	0.546±0.223	0.232±0.051	1.457±1.149	0.274±0.308	0.006±0.003
C	top	6.518 ±5.705	1.062±1.336	0.319±0.253	5.435±5.004	0.970±1.074	0.064±0.066
	bottom	0.931±0.773	0.173±0.036	0.102±0.034	0.410±0.031	0.238±0.144	0.003±0.001
D	top	6.320±2.919	1.493±1.749	0.222±0.207	4.349±3.926	0.538±0.500	0.028±0.028
	middle	5.484±3.877	0.517±0.237	0.117±0.016	1.675±0.946	0.475±0.247	0.013±0.008
	bottom	3.544±5.355	1.617±2.398	0.190±0.088	2.972±4.072	0.660±0.784	0.019±0.026
E	top	3.847±1.106	0.401±0.306	0.217±0.011	1.429±0.858	0.118±0.119	0.005±0.002
	bottom	0.538±0.078	0.534±0.270	0.215±0.035	1.211±0.447	0.299±0.216	0.005±0.003
F	top	1.457±0.623	0.310±0.306	0.104±0.042	0.882±0.747	0.103±0.110	0.006±0.007
	bottom	1.862±2.547	1.067±0.908	0.296±0.136	4.972±3.958	1.990±1.732	0.075±0.097
G	top	1.380±0.621	0.964±0.697	0.323±0.167	3.504±3.089	0.323±0.281	0.025±0.025
	bottom	3.654±5.024	0.617±0.485	0.308±0.166	2.437±2.267	0.436±0.360	0.021±0.026
H	top	11.643±5.351	1.160±0.676	0.201±0.024	9.621±6.542	0.661±0.426	0.021±0.012
	bottom	18.917±6.930	1.350±0.130	0.217±0.051	7.457±3.983	0.732±0.190	0.021±0.011
I	top	3.438±2.316	0.358±0.274	0.111±0.050	0.912±0.551	0.140±0.102	0.010±0.010
	bottom	4.719±7.771	0.228±0.126	0.128±0.094	0.574±0.296	0.385±0.488	0.003±0.002
J	top	22.377	6.502	0.629	14.099	1.854	0.126
	bottom	37.730	5.289	0.62	11.52	2.864	0.118

Table 3. The Comparison of the AVS Concentration of Xi'nan Waterway with Other Rivers ( $\mu\text{mol}\cdot\text{g}^{-1}$ )

Study area	High AVS	Low AVS	Average	Reference
Mississippi, America	1.2±0.4	0.002±0.001	—	(Lawra et al. 2001)
Foshan Waterway, the Pearl River Delta, China	69.579	0.339	20.283	(Li et al. 2008)
Vaal River, Netherlands	40.35	0.44	6.66	(van Griethuysen et al. 2003)
Five rivers in Finlan, Europe	—	—	1.422	(Burton et al. 2007)
Douro River Mouth, Portugal	2.8 ± 1.3	0.004 ± 0.003	—	(Ana et al. 2005)
Brisbane River, Australia	22.61	0.33	—	(Mackey et al. 1996)
The Xinan Creek, the Pearl River Delta, China	41.453	0.207	6.684	*This study

\* A total of 64 samples from the surface, middle, and bottom layers were measured.

“—”: Unavailable.



**Figure 3.** The relationship among AVS and Eh, SRB, OC TS.

**Table 4.** Concentrations of SRB, OC, TS, Eh, and the Difference between SEM and AVS in Surface Sediment of the Xi’nan Waterway ( $\mu\text{mol}\cdot\text{g}^{-1}$ )

Stations	SRB ( $\text{CFU}\cdot\text{g}^{-1}$ )	OC (%)	TS ( $\mu\text{mol}\cdot\text{g}^{-1}$ )	Eh (mv)	$\sum\text{SEM}_5$	$\sum\text{SEM}_5\text{-AVS}$	$(\sum\text{SEM}_5\text{-AVS})/f_{\text{OC}}$
A	7175±1091	3.62±0.89	27.292±3.373	-62±50	10.070	2.882	79.613
B	23989±6196	5.32±0.68	20.818±3.615	-96±50	2.459	-8.376	-157.444
C	1147±506	4.16±1.26	20.847±1.023	-83±22	7.850	1.332	32.019
D	409±32	4.13±2.97	18.507±3.013	-111±25	6.630	0.310	7.506
E	1256±559	6.18±0.87	16.446±7.178	-96±32	2.170	-1.677	-27.136
F	211±78	4.55±0.57	11.562±0.847	-113±24	1.405	-0.052	-1.143
G	897±296	6.03±1.99	13.019±3.352	-110±38	5.139	3.759	62.338
H	2979±471	5.27±0.27	30.596±2.275	-109±20	11.664	0.021	0.398
I	4422±938	4.60±1.81	14.593±0.621	-100±3	1.531	-1.907	-41.457
J*	1397	7.51	28.631	-148	23.210	0.833	11.092

\*The values in the station are arithmetic averages of two figures.

centrations average 5.05% and ranges from 2.08% to 8.32%. These values are relatively high compared with those of other rivers (Van Den Berg et al., 1998; Li et al., 2008). Abnormally high concentrations of organic matter are also generated by the large amount of domestic, industrial, and agricultural wastewater discharged previously. Figure 3-B exhibits the positive and significant correlation between OC and AVS ( $r = 0.380$ ,  $p < 0.05$ ). The Eh value of the overlying is either below zero or the surface sediments are all under strongly reducing

conditions although the DO of the overlying water reaches a certain range ( $2.3$  to  $5.3 \text{ mg}\cdot\text{L}^{-1}$ ) at most stations. This phenomenon may mainly be attributed to the fact that the high OC content has exhausted the DO at the interface of the water overlying the sediment. Although DO concentration is  $4.3 \text{ mg}\cdot\text{L}^{-1}$  (the highest in all 10 stations) in station J, this sample is the most reduced (with an Eh value of  $-148 \text{ mV}$ , which is the lowest among the 10 stations). Moreover, the maximum OC content is 7% (also the highest among all of the stations).



The correlative analysis results also support this inference in that OC was significantly associated with *Eh* ( $r = -0.384, p < 0.05$ ).

Most of the S (-II) in the sediments is produced by SRB (Rickard et al., 2005). Thus, AVS concentration is expected to be closely related to SRB. The current study demonstrates this relationship in Figure 3-C, which shows the close and positive correlation between SRB and AVS ( $r = 0.312, p = 0.089$ ). SRB are sensitive to the living environment, and they are generally active when the conditions are anaerobic and when the sediment is rich in organic matter because this matter provides the sources of carbon and nitrogen (Gramp et al., 2010) necessary for AVS formation. For instance, the highest AVS values were observed at station B, which is under an anaerobic and strongly reducing condition (the average *Eh* is -96 mV) and has sufficient OC (the average OC is 5.32%). The largest number of SRB was also detected at this station. However, this study indicates that SRB activity is significantly inhibited by the toxic pollutants in the river. Although OC is high at station G (the average is 6.03%) and *Eh* is low (the average is -110 mV), the amount of SRB is low as well (the average is 897 CFU·g<sup>-1</sup>). This result is related to the numerous toxic substances that are discharged as pollutants and that handicap the growth rate and biological activity of SRB.

**Table 5.** The Correlation Coefficient between SRB, OC, TS, *Eh* and AVS

	OC	<i>Eh</i>	SRB	TS	AVS
OC	1				
<i>Eh</i>	-0.384*	1			
SRB	0.022	0.230	1		
TS	-0.055	0.160	0.366	1	
AVS	0.380*	-0.202	0.321	0.694**	1

\*Correlation is significant at the 0.05 level (2-tailed).

\*\*Correlation is significant at the 0.01 level (2-tailed).

AVS is the most active component in all of the sedimentary sulfides (which are collectively known as “the sulfur pool”) (Van Griethuysen et al., 2006). Morse et al. (2004) stated that AVS constitutes a major and persistent fraction of the total reduced sulfide in sediments. Leonard et al. (1993) demonstrated that sulfate limitation is more important in freshwater than in marine sediments. Our data (Table 6) also suggest that the amount of sulfide is adequate to generate AVS, which indicates that a large portion of the sulfide must be derived from the sewage deposits within the sediments. Moreover, our research reports a significant correlation between TS and AVS ( $r = 0.694, p < 0.01$ ), as shown in Figure 3d.

**4.2. Linear Regression (LR) Analysis of Influential Factors**

The four factors of interest (*Eh*, OC, SRB, and TS) were analyzed with the LR module in SPSS (Liu et al., 2003; Wu et al., 2009). Table 6 depicts the variance analysis of the regression equation (Model 1) and indicates that  $F = 11.008 > 2.78$  (at 5% significance level). Furthermore, the regression equa-

tion is highly significant ( $p < 0.01$ ). In this sense, the correlations of the four variables are significant at a 95% certainty (Torrecilla et al., 2009).

The residual diagnostic Durbin-Watson statistic ( $DW = 1.680$ ) suggests that the residual values are independent of one another because  $DW$  is close to 2. The coefficient of determination ( $R^2 = 0.677$ ) demonstrates that the application model can explain 67.7% of the changes in the dependent variable and that an LR relationship exists between the multiple independent variables and the dependent variables.

Table 6 presents the coefficients of variables and the test of significance results. The OC and TS variables display  $t > 2.064$  (at a 5% significance level). However, the *Eh* and SRB variables do not generate similar results.

Therefore the independent variables *Eh* and SRB are related to the dependent variable AVS in the regression model (Model 1) but at a confidence level of  $< 95\%$ . Thus, a PCR analysis is conducted subsequently. According to Table 6, the regression equation (Model 1) is expressed as follows:

$$\Gamma = -20.924 + 1.434 \times OC - 0.040 \times Eh + 0.460 \times SRB + 0.657 \times TS \tag{4}$$

Table 6 also shows the sequence of the four factors:  $TS > OC > Eh > SRB$ . The absolute value of their standard partial regression coefficients are 0.717, 0.351, 0.204, and 0.087, respectively.

The measured OC, TS, *Eh*, and SRB from the upper-core sediment samples in stations B, F, and I were inputted into the two regression equation models. Table 7 exhibits the calculated results, which are the predictive values of the model. Moreover, the MRE and RMSE values were calculated to compare the measured and predicted AVS concentrations of the model. In the LR analysis model, MRE and RMSE were 61.9% and 77.3%, respectively. These high values may be ascribed to the multicollinearity in this model, which complicates the accurate estimation of parameters (Rajab et al., 2013; Antanasijević et al., 2013). Therefore, the influential factors were analyzed further through the PCR model.

**4.3. Principal Component Regression (PCR) of Influential Factors**

**4.3.1. Principal component analysis (PCA)**

Prior to PCA, sample adequacy was measured by Kaiser-Meyer-Olkin (KMO) and Bartlett’s test of sphericity was conducted (Marhaba et al., 2009; Hao et al., 2013). The KMO inspection coefficient was 0.513, and the Bartlett ball degree inspection displayed a probability of  $p = 0.134 > 0.01$ . These results refute the hypothesis that the four variables are independent of one another. They also demonstrate that the data are suitable for PCA (Mevik et al., 2007; Pumure et al., 2011). The PCA findings indicate that all of the information (100%) can be explained by the four principal components and that only two of these components are suitable for further analysis



**Table 6.** Analysis of Variance to the Linear Regression Equation and Regression Parameter (Model 1)\*

Variance	Sum of squares	df	Mean square	F	Sig.
Regression	761.838	4	190.459	11.008	0.000*
Residual	363.351	21	17.302	—	—
Total	1125.189	25	207.761	—	—
	Unstandardized B	Coefficients Std. Error	Standardized Coefficients Beta	t	Sig.
Constant	-20.924	6.449		-3.244	0.004
OC	1.434	0.558	0.351	2.568	0.018
Eh	-0.04	0.027	-0.204	-1.443	0.164
SRB	0.460	0.731	0.087	0.628	0.536
TS	0.657	0.124	0.717	5.311	0.000

\*Dependent Variable: AVS

with respect to eigenvalue (eigenvalue > 1). These two components explain most of the information (70.124%) shown in Table 8; thus, they were extracted for the PCR analysis.

#### 4.3.2. PCR

The two principal components derived from PCA were employed as independent variables for the PCR analysis. AVS acted as the dependent variable (Antanasijević et al., 2013). The analysis results reported a correlation coefficient of R = 0.786, determination coefficient of R<sup>2</sup> = 0.618 (that is, the application model can explain 61.8% of the total variation), and adjusted R<sup>2</sup> = 0.618. The residual diagnostic DW = 1.943 was closer to 2 in this model (DW = 1.680) than that in Model 1, thereby indicating that its residual value is more independent than that of Model 1 (Abdul-Wahab et al., 2005). The relationship between the dependent AVS variable and the two independent variables is increasingly significant, as demonstrated in Table 9: F = 18.576 > 3.37 (at a 5% significance level), which was greater than that in Model 1 (F = 11.008). Table 9 lists the coefficients of Model 2. The constant and the variables C1 and C2 display abs (t) > 2.056 (at a 5% significance level); thus, the independent variables C1 and C2 are related to the dependent variable AVS at a 95% confidence level in the regression model. This finding signifies the completion of the PCR; according to Table 9, the equation (Model 2) is written as follows:

$$\gamma = -19.198 + 0.341 \times OC - 0.064 \times Eh + 0.672 \times SRB + 0.647 \times TS \quad (5)$$

Figure 4 shows the histogram of the residual values for Models 1 and 2. Although these residual values typically follow a normal distribution (thereby confirming that these two models are accurate in different ways), the histogram of Model 2 adheres to this distribution more strictly than that of Model 1, thus indicating that the PCR analysis was more useful than the LR one in this case. Moreover, the MRE and RMSE values were calculated to compare the measured and predicted AVS concentrations of the model, as depicted in Table 7. In the PCR model, these values were 21.9% and

25.9%, respectively. Therefore, the PCR model is more accurate than the LR model in terms of MRE and RMSE, and the predictive results of the PCR model were more reasonable than those of the LR model.

**Table 7.** The MRE and RMSE Based on the Difference between Measured Values and Predicted Values

Station	Measured values (μmol·g <sup>-1</sup> )	Predicted values (Model 1) (μmol·g <sup>-1</sup> )	Predicted values (Model 2) (μmol·g <sup>-1</sup> )
B	10.556	10.071286	10.2671594
F	1.224	-0.219645	0.87737232
I	2.009	0.741435	2.70748084
MRE		61.9%	21.9%
RMSE		77.3%	25.9%

**Table 8.** The Results of Principal Component Analysis (PCA)

	Component 1	Component 2
Eigenvalues	1.683	1.122
% of Variance	42.077	28.047
Cumulative %	42.077	70.124
OC	-0.567	0.659
Eh	0.729	-0.396
SRB	0.666	0.520
TS	0.622	0.509

The PCR model provided a simple and effective prediction method for AVS concentrations based on OC, Eh, SRB, and TS data. The monitoring of AVS is highly demanding and requires much skill; for instance, the samples cannot be exposed to air, which can strongly affect the AVS content. Thus, various measures have been implemented in this regard. Furthermore, the entire measurement process must be completed under anaerobic conditions. The established PCR model simplifies and facilitates the evaluation of metal toxicity given that these environmental indicators are easier to obtain than AVS. It also enables PCR application and the prediction of environmental variables that are relatively difficult to measure. In addition, the model can effectively explain the various distribu-

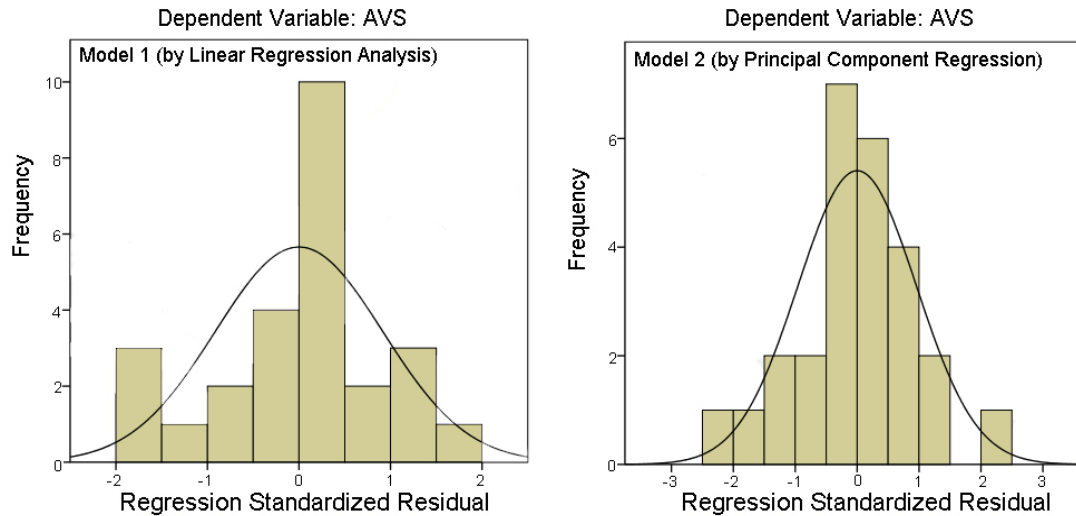


Figure 4. The histogram comparison of residuals between Model 1 and Model 2.

Table 9. Analysis of Variance to the Principal Component Regression (PCR) Equation and Regression Parameter (Model 2)

Variance	Sum of squares	df	Mean square	F	Sig.
Regression	694.951	2	347.475	18.576	0.000
Residual	430.238	23	18.706		
Total	1125.189	25			
	Unstandardized B	Coefficients Std. Error	Standardized Coefficients Beta	t	Sig.
Constant	-19.198	4.632		-4.144	0.000
C1	0.362	0.071	1.447	5.080	0.000
C2	0.829	0.137	1.725	6.054	0.000

tion patterns of AVS in aquatic sediments because the effects of the main influencing factors have been quantified.

### 5. Conclusions

Regression analysis was used to study the spatial variability of AVS and its influential factors in aquatic sediments under changing conditions. The monitoring results showed that AVS concentrations are highly variable and range from 0.734  $\mu\text{mol}\cdot\text{g}^{-1}$  to 30.519  $\mu\text{mol}\cdot\text{g}^{-1}$ . The coefficient of variation is 93.62% in surface sediments and 153.09% in the lower sediment layers.

The analysis focused on *Eh*, SRB, OC, and TS based on the AVS equation. *Eh* is negatively correlated with AVS ( $r = -0.202, p = 0.294$ ), and OC is positively and significantly correlated with AVS ( $r = 0.380, p < 0.05$ ). Furthermore, SRB is closely and positively correlated with AVS ( $r = 0.312, p = 0.089$ ), and TS is significantly correlated with AVS ( $r = 0.694, p < 0.01$ ). The qualitative analytical results also reveal that TS and OC are the most important impact factors, with the sequence  $\text{TS} > \text{OC} > \text{Eh} > \text{SRB}$ .

LR (Model 1) and PCR (Model 2) models were established as well. In the PCR model, the MRE and RMSE values were 21.9% and 25.9%, respectively. Therefore, the PCR mo-

del is more accurate than the LR model as per these values. This finding is partly attributed to the fact that a PCR analysis may rectify the multicollinearity introduced by LR. In addition, Model 2 is more reasonable than Model 1 in terms of their histograms of residual values.

In conclusion, the PCR equation is a simple and effective way to predict AVS concentrations using the data of the main factors OC, *Eh*, SRB, and TS. This model also facilitates the interpretation of the spatial heterogeneity of AVS and the evaluation of metal toxicity under field conditions. Thus, it can be applied in the management of metal-contaminated sediments.

**Acknowledgments.** Thank Dong Han-ying, Gan Hua-yang, Fang Zhan-qiang, and Zhang Zai-wang for the sampling and all the technical support. This work was partly funded by National Natural Science Foundation of China (Grant No.41001341), Open Research Fund Program of the State Key Laboratory of Subtropical Building Science (Grant No. 2011KB12), Special Project on the Integration of Industry, Education and Research of Guangdong Province, China (Grant No. 2012B091100143), Science and Technology Program of Guangdong Province, China (No. 2011B030800006), and the Fundamental Research Funds for the Central Universities (Grant No. 2014ZZ0012).

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