Simultaneously extracted metals /acid volatile sulfide in surface sediments from Damietta Port and the offshore area

Mohamed A. Okbah, Ehsan M. Abo El-Khair *, Hesham M. Moustafa

Department of Marine Chemistry, National Institute of Oceanography and Fisheries, Egypt *Department of Oceanography, Faculty of Science, Alexandria University, Egypt Corresponding author: E mail: m okbah@yahoo.com

Received 15th October 2009, Accepted 15th September 2010

Abstract

The relationships between zinc, copper, nickel, lead, cadmium and amorphous iron sulfides were performed to predict the bioavailability and toxicity of metals in Damietta Port and offshore sediments. Sulfides were measured as acid volatile sulfide (AVS). The results of grain size analysis and organic matter of the investigated area showed that the sediments of the offshore area were characterized by sand fraction (2.84-83.04 %) and low levels of organic matter (0.55 to 0.98 %), these values of organic matter increased twice inside the port. The average values of simultaneously extracted metals (SEM) in Damietta Port sediments were, 12.11 ± 1.95 , 5.16 ± 1.18 , 0.23 ± 0.08 , 6.56 ± 0.92 and 0.65 ± 0.29 µmole g⁻¹, dry weight, for Zn, Cu, Ni, Pb and Cd, respectively, while the results were 1.30 ± 0.58 , 0.71 ± 0.17 , 0.11 ± 0.04 , 1.23 ± 0.71 and 0.18 ± 0.09 µmole g⁻¹, dry weight, respectively for the offshore samples. Generally, the concentrations of trace metals in both areas were in the order of Zn > Pb > Cu > Cd > Ni. The difference value between AVS and ΣSEM is an important tool of trace metals bioavailability and ecological risk. The range and average values of Σ EM concentration ranged from 1.96 to 29.94 (14.70 \pm 8.16) μmole g⁻¹, the results revealed significantly difference between the two regions of the study area. The levels of AVS concentrations showed spatial variations, the range and average values of AVS were between 7.74 and 40.57 (24.12±9.53) μmole g⁻¹. The ratio of ΣSEM/AVS was recorded to be less er than 1 at all the offshore sediments except at two stations as well as at five stations located inside the port($\Sigma SEM/AVS > 1$), which suggests that the metals have toxicity potential found in these sediments.

Key words: Acid Volatile Sulfide, simultaneously extracted metals, sediments, Damietta Port, off shore area

1. Introduction

ISSN: 1687-4285

Damietta Port is considered as semi enclosed water body mainly affected from loading/unloading operations, municipal and agricultural wastes resulting from Damietta Governorate. The Port is connected with Damietta Branch of the River Nile through a connecting navigational channel of 4.5 Km length, 90 m width and with an average 5 m depth. Untreated domestic wastewater with agricultural and industrial wastes still released through a number of drainages and outfalls along the coastal area of study. In sediments, sulfides are produced through the digenesis (breakdown) of organic matter. Under anoxic condition, sulphate (SO₄²⁻), which is abundant in marine waters (2700 mg/L), (Di Toro et al., 1990), is used as the electron donor to oxidize organic matter. The reduction of SO_4^{2-} to H_2S produces HCO_3^{2-} as a by-product, thereby creating a net alkalization that can buffer the effects of acid generation. The production of AVS may play an important role in the binding and precipitation of trace metal cations as insoluble sulfides (Lee et al.,

2000). Trace metal sorption onto AVS has been shown to affect the mobility and toxicity of trace metals in aquatic environments (Mikac et al., 2000). Sulfides can play an important role in controlling the speciation and the environmental risks of trace metals in aquatic sediments. When sediments are reduced, trace metals present in the interstitial water can either adsorb to, (co)precipitate with or replace Fe and Mn in FeS or MnS minerals (Morse and Cornwell, 1987; Di Toro et al., 1991). They are considered to be less mobile and less bio-available to benthic organisms, leading to a reduction of the environmental risk. Depending on the amount of sulfide present in the system, the mobility could even be very low, if all trace metals are removed from the pore water phase and immobilized as solid sulfide minerals. For this reason, the sulfide chemistry of sediments has received much attention in the past decade (Allen et al., 1993; Leonard et al., 1996; Ankley et al., 1996; HuertaDiaz et al., 1998; Van den Berg et al., 1998). In general, the bioavailability and toxicity of metals in sediments is related to the geochemical speciation and chemical activity of the metals in the interstitial water of the sediment. Di Toro et al. (1992)

Egyptian Journal of Aquatic Research, 2011, 37(1), 31-40

conducted laboratory tests with marine and freshwater organisms to determine which factors controlled the toxicity of metals in sediments. Their results showed that the mortality of the animals was related to both the quantity of toxic heavy metals and the acid volatile sulfide (AVS) released from acidified sediments. The AVS-bound metals (Zn, Cu, Cd, Ni and Pb) extracted at the same time are simultaneously called extracted metals (SEM). The ratio and the difference between both AVS and SEM give an indication of sediment potential toxicity (Di Toro et al., 1990). The previous studieds of Di Toro et al. (1990), Carlson et al. (1991) and Ankley et al. (1993) showed that acid-volatile sulfide (AVS) is an important in regulating the acute toxicity of cadmium both in marine and freshwater sediments.

The aim of this work is to evaluate the degree of trace metals (Zn, Cu, Ni, Cd and Pb) contamination using the acid volatile sulfide (AVS) and simultaneously extracted metals (SEM) in Damietta Port and the offshore area sediments.

2. Materials and methods

2.1. Study area and sediment sampling

Damietta Port is situated 10.5 km. west of Damietta Nile Branch westward Ras El-Bar, and 70 km. away from Port Said. The port installation extends on an area of 11.8 Km². It is bordered by an imaginary line connecting the eastern and western external breakwaters. Surficial sediment samples (0-20cm depth) were collected from nineteen locations (Figure 1) at Damietta Port (stations 1-10) and the offshore area (stations I - IX). The sediments were rapidly placed and stored in acid-wash plastic vials with no airspace above the sediments. Samples were immediately, sealed and transported on ice to the laboratory. They were then frozen for later use. Additional sub-samples of sediments were collected for the analysis of grain size, water content and total organic matter content.

2.2. Analytical methods

Grain size was determined by the sieving technique, the sediments largely revealed dominated by the silt-clay. The percentage of water content was calculated by the difference between wet and dry weight of sediment sample. The total organic matter content was determined as the difference between dry weight (105°C, 24 h to a constant mass) of the sediment and weight of the residue after combustion for 2 h at 550 °C to determine the ignition loss (Parker, 1983).

Acid volatile sulfide (AVS) is operationally defined as the amount of sulfide that can be volatilized during a cold acid extraction. The most widely applied method for the determination of AVS

and SEM is the purge and trap method, developed by Morse and Cornwell (1987) and Allen et al. (1993) and used by Van den Hoop et al. (1997) and Van den Berg et al. (1998). The procedure of the method consisted of a round-bottom reaction flask connected to a trapping vessel containing 50 mL of 0.5N NaOH solution. After sparging for 10 mins with N₂ gas, the wet sediment sample (about 1 g) was added and sparged for another 10 mins with N2 gas. The sediment suspension was acidified with 20 mL of 1 N HCl and stirred for 15 mins at room temperature (cold extraction) to form H₂S, which subsequently collected in a NaOH solution with a continuous N2 flow. According to the method described by Allen et al. (1993), dissolved sulfide concentration in the NaOH solution was measured spectrophotometrically (using a Shimadzu double beam spectrophotometer UV-150-02). The acidified sediment suspension in the reaction flask was filtered through a Whattman 0.45-mm membrane, and the concentrations of trace metals (SEM) determined with Atomic Absorption spectrophotometer (AAS).

2.3. Quality control

All glass and plasticware were cleaned by soaking in 10% HNO₃ (v/v) for 12 hs, followed by soaking and rinsing with deionized water (Milli-Q). All of the chemicals used in the present study were analyticalreagent grade. The analysis of calibration curves, blanks, spikes, and standard recoveries were performed. 10 μ mol g⁻¹ of sulfide and metals were added to wet sediment. The mean recovery for AVS was 93% and metal (SEM) recoveries were 95%. All results are expressed with respect to sediment dry weight. The concentrations of AVS were employed in duplicate measurements; the analytical precision was approximately 10%. Method validation and quality control samples were done using a reference material (HISS-1, National Research of Council of Canada). Table1 illustrates the concentrations for different metals in the reference materials. The variation coefficients were; 4.2% for Cu; 7.4% for Zn; 6.5% for Pb and 8.7% for Cd.

3. Results and discussion

3.1 Acid volatile sulfide (AVS) and simultaneously extracted metals (SEM)

The concentrations of reactive sulfide in anoxic sediments play a major role in the bioavailability and toxicity of specific cationic metals of environmental concern (e.g. Cu, Cd, Pb, Ni, and Zn). Because these metals are capable of forming relatively insoluble sulfide minerals, the reaction between soluble metal species with sulfide serves to partition metals from porewater into the solid phase (Edenborn, 2005).

Hansen *et al.* (1996) showed that the reactive sulfide or the acid-volatile sulfide (AVS) in sediments is defined operationally as the amount of sulfide volatilized by the addition of 1 N HCl. Leonard *et al.* (1999) suggested that the AVS in uncontaminated sediments often consists of iron monosulfide minerals, such as amorphous FeS, mackinawite and greigite. The iron and manganese sulfides solubility's are much greater than other common heavy metal sulfides (Simpson *et al.*, 1998)

The concentration of acid volatile metals considerably showed difference between the sediment samples. The concentration of AVS and SEM (μmol g ⁻¹, dry weight) in the sediments at the different stations is shown in Figure 2. The levels of AVS and SEM were relatively high inside the port (from Station 1 to Station 10) than those reported in the other sites in the open coastal areas (offshore stations from I to IX).

The contents of Acid volatile sulfide (AVS) ranged from 31.80 $\mu mol~g^{-1}$ at station 9 to 40.57 $\mu mol~g^{-1}$ at station 3 with an average value (36.50 \pm 3.42 $\mu mol~g^{-1}$) inside Damietta Port, while in the offshore area, it ranged between 7.74 $\mu mol~\bar{g}^{1}$ at station IX and 13.28 $\mu mol~g^{-1}$ at station II with an average (10.32 \pm 1.98) $\mu mol~g^{-1}$.

The range and the average concentrations (dry weight) of simultaneously extracted metals (SEM) in Damietta Port sediments were, 10.06-15.25 (12.11 \pm 1.95) $\mu\text{mol g}^{-1}$ for Zn, 3.55-6.82 (5.16 \pm 1.18) $\mu\text{mol g}^{-1}$ for Cu , 0.09-0.32 (0.23 \pm 0.08) $\mu\text{mol g}^{-1}$ for Ri, 5.42 - 8.07 (6.56 \pm 0.92) $\mu\text{mol g}^{-1}$ for Pb and 0.21 - 0.95 (0.65 \pm 0.29) $\mu\text{mol g}^{-1}$ for Cd, while the results for the offshore sediment samples were 0.75 - 2.36 (1.30 \pm 0.58) $\mu\text{mol g}^{-1}$ for Zn , 0.52 - 0.99 (0.71 \pm 0.17) $\mu\text{mol g}^{-1}$ for Cu, 0.07- 0.17 (0.11 \pm 0.04) $\mu\text{mol g}^{-1}$ for Ni, 0.42 - 2.14 (1.23 \pm 0.71) $\mu\text{mol g}^{-1}$ for Pb and 0.08- 0.31 (0.18 \pm 0.09) $\mu\text{mole g}^{-1}$ for Cd (Table 3). Generally, the concentrations of the trace metals were in the order of Zn > Pb > Cu > Cd > Ni.

Comparison of the metals concentration between the two regions, the results can be arranged from relatively high concentration (AVS and SEM) in the port area and to low level recorded at the offshore stations. This may be related to the different content of organic matter and grain size analysis. Zheng *et al.* (2004) showed that the production of AVS in aquatic systems is mediated by sulfate –reducing bacteria, which reduces inorganic sulfate to sulfide. The other factor, which plays an important role in the high levels of AVS is the low redox condition (< -100mv), this condition is necessary for sulfate – reducing bacteria to have an optimal growth (Howard and Evans, 1993).

3. 2. Sediment Toxicity Evaluation

The particle size distribution and total organic matter of the study area are given in Table 2. The

relative percentage of sand, silt and clay in the sediments of Damietta Port were in the range (3.48-45.09 %) for sand, (16.06-39.12 %) for silt and (28.67-71.43 %) for clay. The sand fraction is dominated in the sediments of the offshore area (2.84-83.04 %). Organic matter in the sediments ranged from 0.55 to 0.98 % for the offshore area, these values increased twice inside Damietta Port (ranged from 1.28 to 1.89 %)

To test the toxicity of the sediments, the ratio of ΣSEM/AVS was calculated. We compared the sum of SEM-Zn, SEM-Cu, SEM-Ni, SEM-Pb and SEM-Cd with the AVS concentration. The results as shown in Table 4 revealed the bioavailability and toxicity of trace metals (Zn, Cu, Ni, Pb and Cd) in the sediment samples. The values of AVS, Σ SEM, SEM -Fe, ΣSEM / AVS ratio and NAVS / SEM-Fe are recorded which took as a tool to determine the extent of toxicity risk. If the ratio of SEM / AVS is higher than 1, the concentration of metals in the sediment is toxic; and the ratio is lower than 1, the concentration in the sediment is below toxic levels regardless of the total metal concentration, proposed that when the ratio of SEM / AVS is lesser than 1, the toxic metals were precipitated as insoluble metal sulfides and hence not biologically available (Di Toro et al., 1992)

In the present study, the ratio of SEM / AVS was lower than 1 in the two regions (Damietta Port and the offshore sediments), the ratio of SEM / AVS ranged from 0.61 to 0.77 (average; 0.67 \pm 0.06 for Damietta Port and from 0.21 to 0.46 (average; 0.33 \pm 0.09) for the offshore area. These data allowed us to recognize the sediments as low risk and nontoxic. All the sediment samples of Damietta Port have an AVS level ranged between 30 to 40 $\mu mol \ g^{-1}$ while it is appeared lesser than 13 $\mu mol \ g^{-1}$ in the offshore.

According to USEPA (2004), the assessment of metal toxicity is based on the difference between the corresponding SEM and AVS molar concentrations. The SEM / AVS molar ratios are an indicator of the amount of metals present in the sediment pore water. In this approach, each sample falls into one of three categories: associated adverse effects on aquatic life are probable; associated adverse effects on aquatic life are possible; or no indication of associated adverse effects.

According to this approach of USEPA evaluation, when Σ SEM - AVS is more than 5, the sediment sample is classified as associated adverse effects on aquatic life are probable. When the difference between Σ SEM and AVS is ranged from zero to 5, the sampling site is classified as associated adverse effects on aquatic life are possible. On the other hand, when the variance is lesser than zero, the sediment is classified as no indication of associated adverse effects. From this point and the ratio of Σ SEM / AVS, the present sediment samples are classified as no indication of associated adverse effects.

The results of trace metals revealed that Zn, Pb and Cu were the dominating elements, accounting for about 95 % of SEM in Damietta Port and ranged from 87 to 95% of SEM. The SEM-Zn concentration is predominated over other metals, which is evident in all sediment samples. It represents about 50% of

the total amount of SEM in Damietta Port and from 28 to 45 % of total SEM in the offshore area., whereas the contribution of the more toxic Pb and Cd to the SEM is ranged from 18 to 45 % for Pb and from 1 to 6 % for Cd.

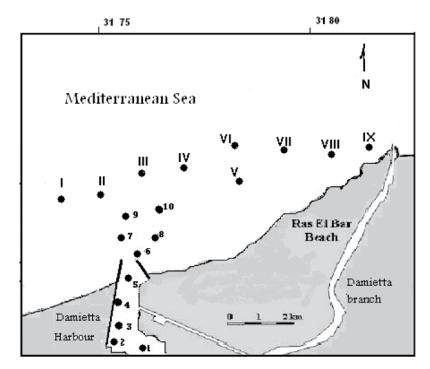


Figure 1. Sampling location.

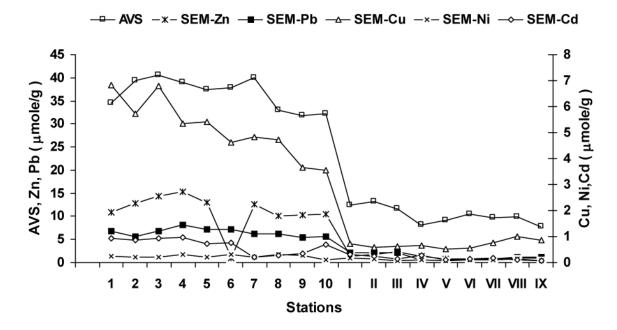


Figure 2. Concentration of Acid Volatile Sulfide.AVS (μmole/g dry weight) and Simultaneously Extracted Metals (SEM) in Surficial Sediments of Damietta Port (Stations 1 – 10) and Offshore Area (Stations – IX) during 2007

Table 1. The concentrations for different metals (mg kg−1) in the reference materials (HIS9, National research of Council of Canada).

Metal	Found	Certified	
Zn	4.74 ± 0.79	4.60 ± 1.21	
Cu	2.19 ± 0.37	2.08 ± 0.08	
Pb	3.03 ± 0.40	2.83 ± 0.74	
Cd	0.024 ± 0.09	0.022 ± 0.028	

Table 2. Grain Size Analysis, Type of Sediment and Total Organic Matter (TOM) in Surficial sediments, Damietta Port and Offshore Area, during 2007.

Stations	Sand %	Silt %	Clay %	Type Sediment	TO M %	
Damietta Port						
1	43.36	20.79	31.37	Sandy Mud 1.35		
2	16.51	20.79	62.70	Sandy Clay	1.58	
3	3.48	26.17	70.34	Clay	1.28	
4	23.22	16.06	60.72	Sandy Clay 1.4		
5	19.58	21.43	59.00	Sandy Clay	1.89	
6	4.00	25.94	69.75	Clay	1.78	
7	6.85	21.71	71.43	Clay	1.38	
8	6.96	36.12	56.91	Clay	1.54	
9	13.93	39.12	46.92	Mud	1.29	
10	45.09	26.29	28.67	Sandy Mud 1.5:		
Min.	3.48	16.06	28.67	1.29		
Max.	45.09	39.12	71.43	1.8		
Offshore Area						
I	15.76	39.00	45.24	Sandy Mud 0.5		
П	83.04	14.19	2.76	Silty Sand 0.		
III	54.99	38.62	6.40	Silty Sand	0.89	
IV	28.70	39.40	31.89	Sandy Mud	0.71	
V	70.26	11.00	18.80	Clayey Sand 0.6		
VI	17.79	56.20	26.10	Sandy Silt 0.85		
VII	2.84	48.87	48.30	Mud 0.98		
VIII	23.32	50.34	24.30	Sandy Silt 0.67		
IX	35.09	23.30	41.60	Sandy Silt 0.77		
Min.	2.84	11.00	2.76	0.55		
Max.	83.04	56.20	48.30	0.98		

Okbah, M. A. et al.

Table 3. Minimum and maximum and the average \pm SD concentration of acid volatile sulfide (μ mole/g dry weight) and simultaneously extracted metals (SEM) in surficial sediments of Damietta Port and offshore area During 2007.

Stations	AVS	S EM-zn	SEM _{Cu}	S EM _{Ni}	S EM _{Pb}	SEM _{Cd}
	Damietta Port					
Min.	31.80	10.06	3.55	0.09	5.42	0.21
Max.	40.57	15.25	6.82	0.32	8.07	0.95
Ave rage	36.50	12.11	5.16	0.23	6.56	0.65
SD	3.42	1.95	1.18	0.08	0.92	0.29
	Offshore Area					
Min.	7.74	0.75	0.52	0.07	0.42	0.08
Max.	13.28	2.36	0.99	0.17	2.14	0.31
Ave rage	10.32	1.30	0.71	0.11	1.23	0.18
SD	1.98	0.58	0.17	0.04	0.71	0.09

Table 4. Concentration of ∑SEM, SEM - Fe, ∑SEM / AVS and NAVS/Fe in surficial sediments of Damietta Port and offshore area.

	Damietta Port				
Stations	ΣSEM	SEM-Fe	ΣSEM / AVS	NAVS/Fe	ΣSEM -AVS
1	25.63	54.00	0.74	16.37	-8.84
2	25.22	78.23	0.64	18.07	-14.14
3	29.24	62.47	0.72	18.14	-11.33
4	29.94	48.69	0.77	18.69	-9.10
5	26.50	72.11	0.71	15.12	-10.90
6	23.29	58.36	0.62	24.93	-14.55
7	24.12	42.65	0.61	36.91	-15.74
8	21.50	44.12	0.65	26.16	-11.54
9	20.08	45.78	0.63	25.60	-11.72
10	20.35	39.21	0.63	30.32	-11.89
Min.	20.08	39.21	0.61	15.12	-8.84
Max.	29.94	78.23	0.77	36.91	-15.74
Ave rage	24.66	55.26	0.67	23.53	-11.78
SD	3.58	13.95	0.06	7.60	1.00
			Offshore Area		
I	4.59	34.21	0.37	22.89	-7.83
II	4.86	38.25	0.37	22.01	-8.42
III	5.31	29.85	0.46	21.17	-6.32
IV	3.01	28.39	0.37	18.42	-5.23
V	1.96	40.41	0.21	17.87	-7.22
VI	2.15	37.28	0.21	22.32	-8.32
VII	2.63	27.65	0.27	25.35	-7.01
VIII	3.20	32.15	0.32	20.81	-6.69
IX	3.28	28.24	0.42	15.79	-4.46
Min.	1.96	27.65	0.21	15.79	-4.46
Max.	5.31	40.41	0.46	25.35	-8.42
Ave rage	3.48	33.14	0.33	20.71	-6.79
SD	1.25	4.94	0.09	3.22	-0.40

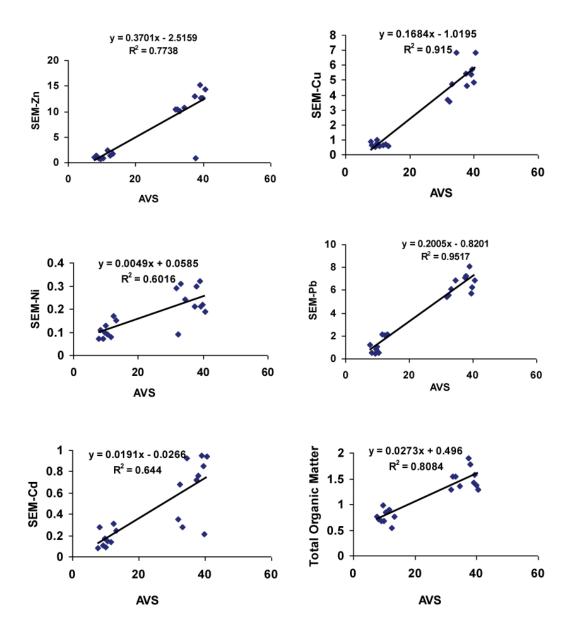


Figure 3. Relationships between pairs of variables; AVS and simultaneously extracted metals (Zn, Cu, Ni, Pb and Cd in μ mole/g) and total organic matter (%).

Fang et al. (2005) showed that trace metals are associated with AVS may be released within sediments through storms, dredging activities, oxidation, etc., and may have adverse environmental impacts because the dredging process will certainly increase concentration of bioavailability trace metals and disturb the sedimentation dynamics. Also, they revealed that the sequential extraction procedure must be used as an additional tool for assessing the bioavailability and toxicity of metals in sediment. Although the role of AVS is to transform the metals from biologically available chemical species into insoluble sulfides, the sedimentary sulfide system is of highly dynamic nature.

3.3. NAVS / SEM-Fe

Hydrogen sulfide reacts with ferrous iron to form the amorphous FeS; it represents the majority of AVS. Leonard et al. (1993) showed that the content of AVS reflects a balance between sulfide productions, iron availability and oxidation. Based on the previous studies, the extraction of Fe by 1M HCl (SEM-Fe) is an important factor in relationship between AVS and SEM; it has been called reactive Fe (Feng et al., 2008). As shown in Table 4, the results showed that 11 sampling stations revealed reactive Fe bounded to AVS is more than 20% and 8 sites have low percentage of reactive Fe, the percentage lower than 20%, which represents low stability with respect metal-sulfide system in the study area. Cooper (1999) showed that the abundance and enough sulfides to trap trace metals when Fe is bounded to AVS and more than 20% of NAVS/SEM -Fe and AVS variations do not necessarily result in temporal variations in diagenetically available metals within anoxic sediments.

3.4. Statistical Analysis

The relationships among AVS and reactive trace metals; Cd, Cu, Ni, Pb, and Zn were demonstrated in Figure3. There was significant positive correlation between the amount of Cd, Cu, Ni, Pb, and Zn in the sediments and the amount of AVS (r = 0.80, 0.96, 0.78, 0.98 and 0.99 respectively at n=19, p<0.05), suggesting that the system was dominated by copper, lead and zinc sulfides. The relationship between the organic matter content and AVS was also positively correlated (r=0.90 n=19 at p>0.05), suggesting a similarity in its sources and/or binding processes to the sediments. However, the results revealed the important role of organic matter and reactive sulfides in the accumulation of trace metals within sediments under anoxic conditions of marine environment.

Conclusions

To predict the bioavailability and toxicity of trace metals in aquatic sediments, it is important to study the metal-specific sulfide interactions. In the present study, the results indicate that the processes between iron and sulfur interactions produced sufficient of AVS to trap the reactive concentrations of trace metals (Cd, Cu, Ni, Pb, and Zn) in the surface sediment of Damietta Port. The geochemical controls on trace metal retention in sediments of the study area appear to be affected by the importance of AVS as a tool to evaluate the suitability of anaerobic sediments to trap metals (Cd, Cu, Ni, Pb, and Zn) in the form of metal sulfides.

References

- Allen, H.E.; Fu, G. and Deng, B.: 1993, Analysis of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments. *Environmental Toxicology and Chemistry*, 12: 1441-1453.
- Ankley, G.; Mattson, V.R.; Leonard, E.N.; West, C. W. and Bennett j.: 1993, Predicting the Acute Toxicity of Copper in Freshwater Sediments: Evaluation of the Role of Acid-Volatile Sulfide, *Environmental Toxicology and Chem* istry, 12: 315-320.
- Ankley, G.T.; Di Toro, D.M.; Hansen, D.J. and Berry, W.J.: 1996, Assessing the ecological risks of metals in sediments. *Environmental Toxicology and Chem*istry, 15: 2053-2055.
- Carlson, A.R.; Phipps, G.L.; Mattson, V.R.; Koslan, P.A. and Cotter, A.M.: 1991, The role of acid volatile sulfide in determining cadmium bioavailability and toxicity in freshwater sediments. *Environmental Toxicology and Chem*istry, 10: 1309-1319.
- Cooper, D.C.: 1999, Selective Extraction Chemistry of Toxic Metal Sulfides from Sediments. *Aquatic Geochemistry*, 5: 87-97.
- Di Toro, D.M.; Mabony, L.D.; Hansen, D.J.; Scott, K.J.; Hicks, M.B.; Mays, S.M. and Redmond, M.S.: 1990, Toxicity of cadmium in sediments: The role of acid volatile sulfide. *Environmental Toxicology* and Chemistry, 9:1489-1504.
- Di Toro, D.M.; Hansen, D.J.; Berry, W.S.; Swartz, R.C.; Cowen, C.E.; Pavlou, S.P.; Allen, H.E.; Thomas, N.A. and Paquin, P.R.: 1991, Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environmental Science and Technology*, 10: 1541-1583.
- Di Toro, D.M.; Mahony, J.D.; Hansen, D.J.; Scoff, K.J.; Carbon, A.R. and Ankley, G.T.: 1992, Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments. *Environmental Science and Technology*, 26: 96-101.
- Edenborn, H. M.: 2005, Rapid detection of bioavailable heavy metals in sediment pore waters using acid-volatile sulfide gel probes. *Environmental Geology*, 47: 660-669.
- Fang, T.; Li, X. and Zhang, G.: 2005, Acid volatile

- sulfide and simultaneously extracted metals in the sediment cores of the Pearl River Estuary, South China. *Ecotoxicology and Environmental Safety*, 61: 420–31.
- Feng, L.; Wen, Y.M.; and Zhu, P.T.: 2008, Bioavailability and toxicity of heavy metals in a heavily polluted river, in PRD, China. Bulletin of Environmental Contamination and Toxicology, 81: 90-94.
- Hansen, D.J.; Berry, W.J.; Mahony, J.D.; Boothman,
 W.S.; Di Toro, D.M.; Robson, D.L.; Ankley, G.T.;
 Ma, D.; Yan, Q. and Pesch, C.E.:1996, Predicting the toxicity of metal-contaminated field sediments using interstitial concentration of metals and acid-volatile sulfide normalizations. *Environmental Toxicology and Chemistry*, 15: 2080-2094.
- Howard, D.E. and Evans, R.D.: 1993, Acid volatile sulfide (AVS) in a seasonally anoxic mesotrophic lake: seasonal and spatial changes in sediment AVS. Environmental Toxicology and Chemistry, 12:1051-1057.
- HuertaDiaz, M.A.; Tessier, A. and Carignan, R.: 1998, Geochemistry of trace metals associated with reduced sulphur in freshwater sediments. Applied Geochemistry 13: 213-233.
- Lee, J.S.; Lee, B.G.; Choi, H.J.; Luoma, S.N.; Koh, C.H.and Brown, C.L.: 2000, Influence of acid volatile sulfides and metal concentrations on metal partitioning in contaminated sediments. *Environmental Science and Technology*, 34: 4511-4516.
- Leonard, E.N.; Mattson, V.R.; Benoit, D.A. Hoke, R.A. and Ankley, G.T.: 1993, Seasonal variation of acid volatile sulfide in sediment cores from three northeastern Minnesota lakes. *Hydrobiologia*, 271: 87-95.
- Leonard, E.N.; Cotter, A.M. and Ankley, G.T.: 1996, Modified diffusion method for analysis of acid volatile sulfides and simultaneously extracted metals in freshwater sediment. *Environmental Toxicology and Chemistry*, 15:1479-1481.
- Leonard, E.N.; Mount, D.R. and Ankley, G.T.: 1999, Modification of metal partitioning by

- supplementing acid volatile sulfide in freshwater sediments. *Environmental Toxicology and Chemistry*, 18: 858-864.
- Mikac, N.; Niessen, S.; Ouddane, B. and Fisher, J. C.: 2000, Effects of acid volatile sulfides on the use of hydrochloric acid for determining solid-phase associations of mercury in sediments. *Environmental Science and Technol* ogy, 34, 1871-1876.
- Morse, J.W. and Cornwell, J.C.: 1987, Analysis and distribution of iron sulfide minerals in recent anoxic marine sediments. *Marine Chemistry*, 22: 55-69.
- Parker, J.C.: 1983, A comparison of methods used for measurement of organic matter in sediments. *Chemistry and Ecology*, 1: 201-210.
- Simpson, S.L.; Apte, S.C.; Batley, G.E.: 1998, Effect of short-term resuspension events on trace metal speciation in polluted anoxic sediments. *Environmental Science and Technology*, 32: 620-625
- USEPA: 2004, The incidence and severity of sediment contamination in surface waters of the United States (National Sediment Quality Survey). EPA 823-R-04-007, Second EditionWashington, DC: U.S. Environmental Protection Agency, Office of Water.
- Van den Hoop, M.A.G.T.; Den Hollander, H.A.; Kerdijk, H.N.: 1997, Spatial and seasonal variations of acid volatile sulphide (AVS) and simultaneously extracted metals (SEM) in Dutch marine and freshwater sediments. Chemosphere 35: 2307-2316.
- Van den Berg, G.A.; Loch, J.P.G.; Van der Heijdt, L.M.; Zwolsman, J.J.G.: 1998, Vertical distribution of acid-volatile sulfide and simultaneously extracted metals in a recent sedimentation area of the river Meuse in the Netherlands. *Environmental Toxicology and Chem*istry, 17: 758-763.
- Zheng, L.; Xu, X.Q. and Xie, P.: 2004, Seasonal and vertical distribution of Acid volatile sulfide and metal bioavailability in a shallow subtropical lake in China. *Bulletin of Environmental Contamination and Toxicology*, 72: 326-334.