Partitioning Characteristics of Heavy Metals in a Non-Tidal Freshwater Ecosystem

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ABSTRACT: Trace metals in the aquatic environment have to date come essentially from naturally occurring geochemical resources. However, this has been enhanced by anthropogenic activities resulting in pollution. Consequently, correlations and partitioning of trace metals in the dissolved phase, suspended particulate matter (SPM) and sediments were investigated in five selected sites along the Taylor Creek, southern Nigeria. The degree of correlations between the various metals was different in each of the investigated matrices. In the matrices studied, not many significant correlations ($P<0.05$) were recognized. Only Ni-Cd (r=0.95), Mn-Cd (r=0.63), Mn-Ni (r=0.64) are correlated in the sediments and in SPM, Fe-Cr (r=0.54) and Zn-Ni (r=0.72), which suggests that the sources are not common for both matrices. In the dissolved phase, no strong correlations ($P<0.05$) between the trace metals are obvious. The best correlations are observed for Ni-Zn (r=0.72) and Cd-Pb (r=0.65). Partitioning coefficients (K_d) of trace metals between dissolved phase and SPM are generally low, which is typical for fresh water ecosystems and fairly stable over the creek all through the seasons. Thus, the state of the aquatic ecosystem indicates that the trace metals, which are bio-accumulatable, could contribute to inferior biodiversity and shifts in community composition from sensitive to tolerant taxa.

Key words: Correlations, Partitioning, Dissolved phase, Sediments, Suspended particulate matter, Trace metals, Taylor creek

INTRODUCTION

Municipal and industrial discharges, urban storm-water runoff, and agricultural drainage can result in trace metals, nutrients, pesticides, and organic wastes being transported into aquatic ecosystems. In aquatic ecosystems, contaminants are often rapidly removed from the water column via sorption processes. Given that trace metals are not subject to degradation processes, they tend to accumulate in benthic sediments (Bryan and Langston, 1992). However, trace metals are not necessarily fixed permanently to sediments; rather they may be remobilized via chemical, physical, and biological processes (Salomons, *et al.*, 1987). The pollution of aquatic ecosystems by trace metals is a significant problem (Rayms-Keller *et. al.*,

1998), as trace metals constitute some of the most hazardous substances that can bio-accumulate (Tarifeno-Silva *et al.*, 1982; Zweig *et al.*, 1999). Metals that are deposited in the aquatic environment may accumulate in the food chain and cause ecological damage while also posing a risk to human health (Grimanis *et al.*, 1978; Adams *et al.*, 1992). Taylor creek, a non-tidal freshwater environmental unit, is situated in Gbarain clan in the Yenagoa Local Government Area of Bayelsa State in the Niger Delta, southern Nigeria. The Creek is 16km North-northeast (NNE) from the state capital of Bayelsa State and enjoys the humid tropical climate characterized by the hot and wet conditions associated with the movement of the Inter-Tropical Convergence Zone (ITCZ) north

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and south of the equator. As a result, the study environment has two major seasons, the dry season and the wet season and experiences consistently high temperatures (about 32 ^{O}C) all year round. Since temperature varies only slightly, rainfall distribution, over space and time, becomes a single most important factor (Okafor and Opuene, 2007).

In addition, the only perceptible activity in the area is oil industry activities. The Etelebou Flow Station, which is located on second order distributaries, discharges liquid effluents (either discharged untreated or with only primary treatment) into Etelebou creek, a tributary of Taylor creek. Thus, Taylor creek is a receptor of a highly polluted creek (Okafor and Opuene, 2007). To date, information regarding the correlations and partitioning of trace metals in the dissolved phase, suspended particulate matter (SPM) and sediments of the creek and its effects is very limited. However, the correlations and partitioning of trace metals between environmental matrices of other aquatic ecosystems have been studied by different researchers (Nguyen *et al.*, 2005; Jain and Sharma, 2001; Munksgaard and Parry, 2001; Baeyens *et al.*, 1998; Hung *et al.*, 2001; Liu *et al.*, 2001). Following the above, the objective of this study was to provide inter-metal correlations in the dissolved phase, SPM and sediments, which could present information on the probable sources of the trace metals in Taylor creek as well as their partitioning in the water column.

MATERIALS & METHODS

The study area stretched from Agbia/Nedugo to Polaku along Taylor Creek, which comprised of five sampling sites. The entire stretch from Agbia/Nedugo to Polaku is about 16km and lies between longitude 006°17^{I} to 006°21^{I} E and latitude 05°01^{I} to 05°05^{I} N respectively. Samplings of surface waters were carried out monthly for the period January 2006 to December 2006 from the sampling sites. Surface water samples were collected with nitric acid pre-rinsed 1L plastic containers. After collection, the samples were placed in cooler boxes with ice bags whilst being transported to the laboratory and kept at about 4°C before analysis. Surficial sediments were collected monthly from each of the five sampling sites adjacent to where the surface waters were

sampled in the period January to December 2006 by the grab method using an Ekman grab sampler on 3 to 4 locations, representing approximately 2-3cm of surficial bottom sediments, within each sampling site, and wrapped with aluminium foil to avoid contamination, frozen and taken to the laboratory. Individual site (sediment) sample was thawed and air-dried at ambient temperature and pulverized to < 50mm using a shatter-box grinding mill. The water samples, after filtration with 45 mm Whatman filter paper, were acidified and pre-concentrated. The filtrates were digested with a mixture of 10ml of conc. nitric acid and 2ml of conc. perchloric acid respectively.

Two grams (2g) of air-dried sediment samples were also weighed using a high precision microscale for each case, moistened with water and put into a 50ml conical flask. To each weighed sample, 10ml of conc. nitric acid and 2 mL of conc. perchloric acid were added and heated with a water bath to near dryness. The mild acid treatment was optimal to digest organic matter with associated metals so as to extract metals linked by adsorption to the sediments, which together represent bio-available or leachable metals of the surficial sediments. Each solution was allowed to cool and subsequently filtered into a 50 mL volumetric flask. Following acid digestion, all samples were analysed for 7 elements: Cd, Cr, Pb, Ni, Mn, Zn and Fe by flame atomic absorption Spectrophotometry using Buck Scientific Model 200A Spectrophotometer, equipped with a high sensitivity nebulizer. Calibration of Buck Scientific Model 200A Spectrophotometer was performed before every run by successive dilution of a 100mg/L Multi-Element Instrument Calibration Standard solution (Fisher Scientific) that was in a range covering the concentration levels in the analysed samples. For each batch of elemental analyses, intra-run quality insurance standard (1 mg/L, Multi-Element Standard Solution, Fisher Scientific) was checked for reading variation and precision of every 10 samples. Internal blanks were used to assess any background contamination originating from sample manipulation and preparation. Blanks were processed exactly as respective regular samples as well (Okafor and Opuene, 2007).

The accuracy of sample manipulation for the heavy metals was checked using samples of CASS-

4 (seawater) and PACS-2 (sediment) Matrix Certified Reference Materials (Tables 1 and 2) with known concentration for certain metals and were found to be ≥87% for Cd, Pb, Ni, and Zn (Cantillo and Calder, 1990).The relationship between inter-metal correlations in the matrices of the creek was tested using Pearson Product Moment Correlation Coefficient. Relationships between the dissolved phase, SPM and sediments are discussed via the corresponding partition coefficients. All statistical analyses were done using Analysis Toolpak and SPSS soft- wares, with significance based on an α of 0.05 (Zar, 1990).

RESULTS & DISCUSSION

The assessment of trace metals and their correlations in Taylor creek reflected the degree of pollution, which is considered by many regulatory agencies to be one of the principal risks to the aquatic ecosystem (Table 3). The mean levels of Cd, Cr, Pb, Mn, Ni and Zn in the dissolved phase were higher than the interim standards for aquatic life and domestic use (FEPA, 1991; WHO, 1989). Based on the guidelines, direct use of water from the creek without treatment may aggravate poor health of sensitive groups. For example, the criterion for Pb in water for domestic use is 0 to 1.70 μg/L (FEPA, 1991). At levels > 100 μg/L,

possible neurological damage in fetuses and young children may occur (Fatoki et al., 2002). For some of the metals studied in the surface sediments, except for Cd, the levels were higher than the metal levels in the sediments of Montevideo Harbor, Uruguay (Muniz et al., 2004). Although, it is apparent that the concentration levels of the metals may be due, partly, to catchments in-washings (Ibok et al., 1989), oil industry activities are also implicated (Nwadinigwe and Nwaorgu, 1999). Besides, the study sites are located in the lower reaches of Taylor creek suggesting that inputs from Etelebou creek, a tributary of Taylor creek, may be an influencing factor. In spite of the levels of trace metals in the sediments, we can deduce that the sediments presented concentrations that were at the Persaud et al. (1992) Severe Effect Level and may cause adverse biological effects except for Cr, Ni and Zn respectively. Absolute values of K_d in Taylor creek, as presented in Table 4, is defined as the ratio of the particulate metal concentration (mg/kg) over the dissolved metal concentration (mg/L):

$$K_d = \frac{[\text{particulate metal concentration] (mg/kg)}}{[\text{Dissolved metal concentration] (μg/L)}}$$

The concentration of Cd, Cr, Pb, Ni, Fe, Mn and Zn is presented in Table 3.

Table 1. Measurement Accuracy of Standard Material (CASS-4)

Value type	Cd	Fe	Pb	Ni	Zn
Certified Value, mg/L	0.026	0.713	0.0098	0.314	0.381
Measured Value, mg/L	0.024 (0.006)	0.653 (0.06)	0.0088 (0.002)	0.304 (0.01)	0.361 (0.02)
Recovery	92.31%	91.59%	89.80%	96.82%	94.75%

*The values in parentheses are standard deviations

Table 2. Measurement Accuracy of Standard Material (PACS-2)

Value type	Cd	Cr	Pb	Ni	Zn
Certified Value, μg/g	1.000	90.7	183	39.5	364
Measured Value, μg/g	0.770 (0.13)	86.3 (4.40)	174 (9.00)	37.4 (2.1)	340 (24)
Recovery	87%	94.38%	95.08%	94.68%	93.41%

*The values in parentheses are standard deviations

Table 3. Mean levels of trace metals in SPM, dissolved phase and sediments

Source	Parameter (Mean ± SD)						
	Cd	Cr	Pb	Ni	Fe	Mn	Zn
SPM, μg/g dry dry weight	0.0059 ± 0.0076	0.0062 ± 0.0053	0.019± 0.02	0.067 ± 0.023	1.15 ± 2.54	0.09 ± 0.303	0.083 ± 0.181
Dissolved phase, μg/mL	0.0023 ±0.007	0.0024 ± 0.0093	0.0079 ± 0.03	0.026 ± 0.03	0.49 ± 2.63	0.035 ± 0.354	0.032 ± 0.223
Sediments, μg/g dry weight	2.870± 2.599	3.233± 4.467	115.16± 251.3	10.18± 8.732	5148.0 ± 49.90	266.92± 287.22	107.73± 98.61

The calculated results show that the log (K_d) values for Cd, Cr, Pb, Fe, Ni, Mn and Zn were comparatively constant and low unlike the log (K_d) values of the Scheldt Estuary and Lake Balaton (Baeyens, *et al.*, 1998; Nguyen, *et al.*, 2005). And also, K_d values in Lake Balaton ranged from 4.3 to 6.0 in June 2000 and from 3.3 to 6.4 in September 2001 due to the influence of stormy weather conditions (Nguyen, *et al.*, 2005), which shows variations between the seasons. Conversely, the seasonal and spatial distributions of K_d in Taylor creek were rather stable for the metals studied. The stable K_d values of the metals may be due to the nature of the dissolved metals in the creek. For the levels of Cd, Cr, Fe, Pb, Ni, Mn and Zn, inter-metal correlations appear to be different in the environmental matrices (Tables 5-7). While, inter-metal relationships exist between Cd-Ni (r=0.95) and considerable correlation between Cd-Mn (*r*=0.63) and Ni-Mn (*r*=0.64) for the sediments, which were comparable to correlation coefficients reported elsewhere (Hung, *et al.*, 2001; Liu, *et al.*, 2001), there were no strong correlations between the trace metals in SPM. The correlation matrix for SPM shows significant inter-metal relationships (*P*<0.05) between Ni-Zn (*r*=0.72). Considerable correlations between Cd-Pb (*r*=0.50) and Cr-Fe (*r*=0.52) were also observed in SPM. According to Nguyen *et al.* (2005), a considerable number of significant correlations in SPM of Lake Balaton were observed between Cr and other metals. However, Jain and Sharma (2001) found very strong correlations on similar metals from the Hindon River in India. In addition, it was observed that all particulate trace metals are negatively correlated with the amount of SPM that was similar to the trend in Hindon River (Jain and Sharma, 2001), which may be due to a dilution process of permanently suspended matter, loaded in trace metals coupled with the temporary re-suspension of bottom sediments less contaminated by metals (Nguyen, *et al.*, 2005).

Table 4. Absolute values of log (K_d)

Trace metal	log (*K*d)
Cd	0.41
Cr	0.41
Fe	0.41
Pb	0.33
Mn	0.41
Zn	0.41
Ni	0.41

Strong correlations between Ni and Zn in the SPM and dissolved phases suggest similar partitioning mechanism in the creek. The significant correlations between Ni-Zn in the two phases confirm the impact of the surrounding soil on the environmental matrices. In the dissolved phase, no strong correlations between the trace metals were obvious. The best correlations, significant at *P*<0.05, were observed for Ni-Zn (*r*=0.72) and Cd-Pb (*r*=0.65). This implies that the cycling of the correlated metals may be associated. Also significant but relatively weak correlations (r≥0.50) were observed between Cr-Fe and Pb-Ni respectively. Furthermore, only few correlations between dissolved trace metals have been reported (Munksgaard and Parry, 2001).

In view of total metal concentrations in the water column as the sum of dissolved and particulate metal concentrations, correlations between these metals are much better than those in the individual phases (Table 8). Again Ni-Zn correlation is recognized as one of the strongest with a correlation coefficient *r*= 0.72. Despite insignificant correlations of Mn with other metals in the dissolved or SPM phase, total Mn correlates well with Ni (*r*= 0.77). One other significant correlation is between Mn-Zn (*r*= 0.64). The fact that total Pb was correlated with SPM levels (*r*=0.97) implies a strong dependence of Pb on SPM content in the water column, which was also observed in Bynoe river (Munksgaard and Parry, 2001). The strong dependence of total Pb on the amount of SPM reflects the importance of the particulate phase. This therefore indicates that the more the SPM in the water column, the higher the volumetric particulate metal level. In Taylor creek, the low mean depth and the preponderance of silt in the sediments indicates that the bottom and surficial sediments are easily disturbed in the flood time of the year and resuspended, thus increasing the quantity of SPM. Owing to such situation, Fe, Pb, Mn and Zn metals were observed to be remobilized that impacted the dissolved phase (Table 9), which was confirmed by the correlation coefficients for the metals: Fe in sediments was appreciably correlated to Fe in the dissolved phase (*r*=0.84), Pb in sediments was significantly correlated to Pb in the dissolved phase (*r*=0.998), Mn in sediments was extensively correlated to Mn in the dissolved phase (*r*=0.90)

Table 5. Pearson product moment correlation coefficients between particulate metal levels

	Cd	Cr	Pb	Ni	Fe	Mn	Zn
Cd	1						
Cr	-0.61524	1					
Pb	0.47496	-0.1349	1				
Ni	0.275733	-0.48737	-0.46188	1			
Fe	-0.24305	0.521066	0.008761	-0.60681	1		
Mn	0.247107	0.105773	0.204431	0.12518	-0.00806	1	
Zn	-0.13885	-0.27765	-0.86775	0.720149	-0.26383	-0.11465	1

Table 6. Pearson product moment correlation coefficients between dissolved metal levels

	Cd	Cr	Pb	Ni	Fe	Mn	Zn
Cd	1						
Cr	-0.61492	1					
Pb	0.65117	-0.78497	1				
Ni	0.274452	-0.48817	0.499155	1			
Fe	-0.24298	0.520656	-0.47952	-0.60607	1		
Mn	0.246703	0.105567	0.281182	0.12561	-0.00807	1	
Zn	-0.14088	-0.27894	0.249695	0.719814	-0.2638	-0.11465	1

Table 7. Pearson product moment correlation coefficients between metal levels in sediments

	Cd	Cr	Pb	Ni	Fe	Mn	Zn
Cd	1						
Cr	0.102928	1					
Pb	-0.04827	-0.24783	1				
Ni	0.949162	0.267419	-0.18831	1			
Fe	-4.8E-17	3.73E-16	-2E-17	7.23E-17	1		
Mn	0.63202	0.175812	0.40707	0.642074	3.88E-16	1	
Zn	0.246692	0.06336	0.120621	0.305322	1.55E-16	0.393387	1

Table 8. Pearson product moment correlation coefficients between total metal levels in the water column

	Cd	Cr	Pb	Ni	Fe	Mn	Zn
Cd	1						
Cr	-0.63835	1					
Pb	-0.79782	0.7631	1				
Ni	0.38147	-0.89251	-0.42762	1			
Fe	0.303247	0.506326	0.102509	-0.56348	1		
Mn	0.337201	-0.50756	-0.09499	0.769786	-0.02124	1	
Zn	0.062601	-0.57229	-0.34928	0.720839	-0.43109	0.640942	1

Table 9. Pearson product moment correlation coefficients between similar metals in sediments and dissolved phase

METAL	Pb in sediments	Fe in sediments	Mn in sediments	Zn in sediments
Pb in dissolved phase	0.551998085	-	-	-
Ni in dissolved phase	-	-	-	-
Fe in dissolved phase	-	0.835076741	-	-
Mn in dissolved phase	-	-	0.90304601	-
Zn in dissolved phase	-	-	-	0.771223728

and Zn in sediments was considerably correlated to Zn in the dissolved phase (r=0.71) respectively.

CONCLUSION

Inter-metal correlations are dissimilar in the dissolved phase, SPM and sediments of Taylor creek. The amount of strong and significant correlations was better in the sediments than in dissolved phase and SPM respectively. Strong correlations between Ni and Zn in the dissolved phase and SPM suggest analogous partitioning mechanisms in Taylor creek. Significant

correlations between the metals in the phases point to the fact that the sources of the trace metals are not common. Correlations of total metal levels were also noted to be better than the individual phases. Besides, total Pb was correlated with SPM levels, which shows a strong dependence of Pb on SPM content in the water column. Furthermore, Fe, Pb, Mn and Zn metals were observed to be remobilized that impacted the dissolved phase Thus, the physical state of the aquatic ecosystem points to the fact that the trace metals, which are bio-accumulatable, could contribute to lower biodiversity and shifts in community composition from sensitive to tolerant taxa.

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