**TRACE METALS DISTRIBUTION IN SURFACE WATER FROM MADA RIVER, NASARAWA STATE, NIGERIA**

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Accepted: October 19, 2011

**Abstract**

*Surface water samples were collected from Mada River during dry and rainy seasons for the determination of suspended particulates, dissolved and mobile forms ofCd, Cr Cu, Fe, Ni, Mn, and Zn concentrations. Trace metal levels were quantitatively determined using Atomic absorption spectrometry (AAS). Concentrations of the metal forms showed spatial and temporal variations. Fe concentration predominated in all the forms. Trace metal concentrations increased downstream. Suspended trace metal concentrations were higher compared to the dissolved form during dry season. Trace metal levels generally decreased during rainy season. Suspended trace metal concentrations were below the world average standard values. The log $K_d$valuesfor suspended/dissolved solids trace metal concentrations were greater than 1 during rainy season. Correlations far trace metal concentrations in the suspended phase was strong for Cr and Pb (0.9628) and Zn with Cu (0.9207), while Mn correlated significantly with Zn (0.8970) and Ni (0.8135)during the rainy season.*

***Key words: Trace metals, dissolved, suspended, mobile, surface water***

## INTRODUCTION

The pollution of the aquatic environment with trace metals is a common, important, and growing problem around the world as trace metals are non-biodegradable, persistent, ubiquitous and toxic (Kucuskzegin *et al.,* 2008; Krissanakriangkrai *et al.,* 2009; Ozturk *et al,* 2009; Tukura *et al,* 2011a). Metals that are deposited in the aquatic environment may accumulate in the food chain and cause ecological damage and posing a risk to human health, such as cancer, mutations and miscarriage in humans, and also affect growth and metabolism of plants (Buszewski *et al,* 2000; Okafor and Opuene, 2006, Solaiefa/.,2Q10).

Trace metals in natural waters are induced from various sources. Natural geological weathering of rocks and soils, directly exposed to surface waters, is usually the largest source. Another source is anthropogenic input from mining, domestic and industrial activities (Al-Weher, 2008; Abdul *et al,* 2009; Tukura *etal,* 2012).

Ecotoxicity, mobility and bioavailability of trace metals depend strongly on their chemical forms and the nature of binding and not total metal concentration (Prendez and Adriana, 2003). In the hydrosphere, trace metals exist as dissolved or filterable, suspended particulates, mobile, and sediments (Prendez and Adriana, 2003; Tukura *et al,* 2009). Once metals are introduced into the aquatic system, they undergo interactive reactions with water bodies through series of processes including dissolution/precipitation and sedimentation or re-suspension during migration and then finally settled down as bed sediment (Zoumis *et al,* 2001; Abdul *et al,* 2009). Within the aqueous environment, trace metals can associate with ligands to form complexes. Complexation by ligands controls metal availability, by regulating its dissolved free ion concentration (Dzombak and Morel, 1990).

Organic complexation may increase or decrease adsorption of trace metals affecting transport and fatelT^zombak and Morel, 1990; Bortoli *et al,* 1998; Yun *et al,* 2001, Tukura *et al,* 2007). In the inorganic dissolved fraction of metals, the H* ions compete with the metals for ligands such as OH, Cl", $CO_3$", HS", and $S^{2}$", sulphates and phosphates (Gundersen *etal,* 2003; Tukura *etal,* 2009). Surface water from Mada River is greatly use for irrigation farming of vegetable crops and the major source of water supply to the Mada Water Works which supply portable water to inhabitants of the part of Nasarawa state. Intensive fishing also takes place in the river, especially during dry season. Research has been reported on trace metal levels in the organs of some fish species from the river (Tukura *et al,* 2011b), but information on the distribution of trace metal forms is scarce. The objective of this work is to determine rainy season and dry season variations in dissolved, suspended and mobile trace metal concentrations in surface water from Mada River.

## MATERIALS AXD METHODS

**Study Area**

M*da River is located at latitude 8° 4' N and xjT'g:tud€ 5* 30 T (Tukura *et al*, 2012). Water flow m the **river** is perennial, with large discharge of wases from point and non-point sources into the r.ver, especially during rainy season. Water from **Vada** River serves as the major source of water to Ma da water works which provides potable water to some inhabitants in the state.

Sampling

Surface water samples were collected from five sampling sites (Fig. 1) at a depth of l-5cm during dry season (November, January, March) and in rainy season (May, July, September). The samples were collected into 1L plastic containers previously soaked in 10% nitric acid solution for 24 h and then washed sufficiently with de-ionized water prior to use.

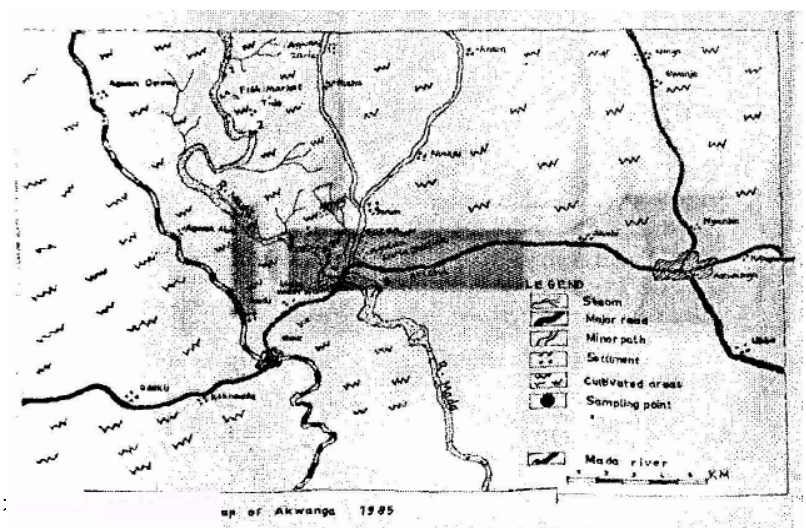


Fig 1: Map showing study **area**

**Sample preparation**

*Dissolved trace metal*

Well-mixed sample of water (50 $cm^3$) was taken from the container and filtered through a 0.45m filter. The solution was then acidified with *2%* nitric acid and preserved for analysis.

*Suspended trace metal*

Unpreserved water sample (50 $cm^3$) was filtered through a 0.45 m membrane filter. The filtrate was transferred into 250 $cm^3$ conical flask and 3 $cm^3$ of concentrated nitric acid was added. The beaker was covered with watch glass and heated gently and cooled. Another 3 $cm^3$ of concentrated nitric acid was added and heated further until digestion was completed. The watch glass and beaker walls were washed down with de-ionized distilled water, filtered and volume made up to 25 $cm^3$ ready for trace metals analysis. *Mobile trace metal*

*Water sample (50 $cm^3$) was decanted from sample vessel, acidified with 2% nitric acid, allowed to stand for 24 h and then filtered through* 0.45/um *filter. '*

Partition coefficients

The log Kj values for suspended/dissolved solids in water is defined as the ratio of the suspended metal concentration (mg/Kg) over the dissolved metal concentration (mg/1) (Sauve *et al,* 2002; Mathieu *et al*, 2004, Okafor and Opuene, 2006), and was calculated based on the formula:

## RESULTS AND DISCUSSION

### Dissolved Trace Metals

Results for the variations in dissolved trace metals concentrations are presented in Table 1. Cd concentration ranged from 0.007 to O.Ollmg/L in dry season and 0.002 to 0.008 in rainy season. The highest Cd concentrations for both seasons were recorded at site 3. Cr concentrations were similar in all sites during rainy season. The highest and the lowest Cr concentrations in dry season were recorded at sites 3 (0.009 mg/L) and 2 (0.073 mg/L) respectively. Cu concentrations in dry season were highest at site 4 (0.026 mg/L), but ranged from 0.007 to 0.009 mg/L during the rainy season. The order of Pb levels according to sites in dry season was site 1 > site 2 > site 3 > site 4 > site 1. During the rainy season Pb concentrations varied from 0.010 to 0.016 mg/L. The highest and the lowest Zn concentrations were obtained at sites 1 (0.281 mg/L) and 5 (0.127 mg/L) respectively. Zn concentration ranged from 0.067 mg/L at site 4 to 0.067 mg/L at site 2 during rainy season. Concentration of Ni varied from 0.009 to 0.016 mg/L in dry season, but did not show site variations during rainy season. Concentration of Fe increased downstream in dry season. However, in rainy season, the highest and the lowest Fe concentrations were recorded at sit 5 (0.811 mg/L) and site 3 (0.755 mg/L) respectively. Mn varied from 0.015 mg/L (site 4) to 0.059 mg/L (site 1) in dry season and 0.005 mg/L (Site 1) to 0.009 mg/L (site 5) during the rainy season.

Suspended Metal Concentrations

The concentrations of metals in suspended particulate fluctuated throughout periods of analysis (Table 2). Cd concentrations varied from 0.001 to 0.004 mg/kg during the periods of analysis. The highest and lowest Cr concentrations in dry season were recorded at sites 5 and 1, respectively. During the rainy season, Cr levels ranged from 0.001 mg/kg at site 4 to 0.329 mg/L at site 5. Order of Cu contents during dry season was site 2 > site 4 > site 5 > site 5 > site 3 > site 1 and site 4 > site 1 > site 5 > site 2 > site 3 in rainy season. During the dry season, concentration of Pb increased from site 1 to site 5, and ranged from 0.140 to 0.050 mg/kg in the rainy season. The level of Zn was highest at site 2 (1.554 mg/L) and lowest at site 1 (0.018 mg/kg) during the dry season, but varied from 0.080 to 0.280 mg/L during the rainy season. The order of variations of Ni according to sites was site 5 > site 4 > site 3 > site 1 > sit 2 and site 5 > site 1 > site 3 > site 4 > site 3 in dry and rainy season respectively. Fe varied from 1.249 mg/L to 2.745 mg/kg in dry season and 0.755 to 7.610 in rainy season. The highest and the lowest Mn concentrations were recorded at sites 2 (0.353 mg/kg) and 1 (0.014 mg/L) respectively, and did not vary during rainy season.

Mobile form Metal **Concentrations**

Variations in mobile trace metal concentrations (Table 3) showed that Cd concentration ranged from 0.007 mg/L (site 2) to 0.010 mg/L (site 1) in dry season and 0.002 mg/L (site 1) to 0.006 mg/L (site 4) in rainy season. During the dry season, Cr concentrations was highest at site 3 (0.116 mg/L) and lowest at site 2 (0.006 mg/L), while the highest and the lowest concentrations during rainy season were recorded at sites 2 (0.087 mg/L) and 1 (0.0.018 mg/L). Order of variation of Cu according to sites was site 3 > site 2 > site 1 > site 5 > and site 1 > site 5 > site 4 "> site 2 > site 3 during dry and rainy season, respectively. Pb ranged from 0.101 mg/L at site 1 to 0.160 mg/L at site 4 and 0.011 mg/L (site 3) to 0.811 mg/L (site 4) during dry and rainy season, respectively. Concentration of Zn during the dry season ranged from 0.225 to 0.517 mg/L at sites 5 and 1, respectively. Variations in the concentrations of Ni according to sites was site 2 > site 1 > site 5 > site 3 > site 4 and increased from site 2 to 5 in rainy season. Fe concentration during dry season was highest at site 3 (2.505 mg/L) and lowest at site 1 (0.965 mg/L). During the rainy season, the highest and lowest concentrations were recorded at site 2 (5.301 mg/L) and site 4 (0.243 mg/L) respectively. Mn concentrations varied from 0.033 mg/L (site 4) to 0.060 mg/L at site 1 and 0.007 mg/L at site 3 to 0.129 at site 2 in dry and rainy season respectively. The partition coefficient provides a measure of the relative changes in the affinity of trace metals for the particulate phase (Sauve *et al*., 2002). Log K„ values were less than 1 except for Mn (1.35) during dry season (Table 5). Relatively high log K„ values were observed for Ni (0.63) and Cu (0.56). Pb log K„ value (0.11) was low. The results indicated that log K„ values during the rainy season were higher and greater thanl except for Zn (0.39) and Ni (0.77). Analysis of variance results (ANOVA) for dry and rainyseasons (Table 6) indicated that dissolved and suspended trace metal concentrations were significantly different ($p < 0.05$) during rainy season except for Cd and Cr. During dry season, Pb, Fe, and Ni were significantly different. Zn in suspended particulates and dissolved Ni concentrations were significantly different ($p < 0.05$) from other metals during rainy season. During dry season Zn and Fe in suspended particulates, and dissolved Zn and Ni concentrations were significantly different ($p < 0.05$) from other metals.

Correlation matrixes for dissolved trace metals during rainy season (Table 7) were moderately positive for Cd and Pb (0.5840), Cr and Fe (0.5041), Cu and Fe (0.6723), and Cu and Mn (0.5000). Mn correlated strongly with Zn (0.8970) and Ni (0.8135). Trace metals correlated weakly with pH and TOC. During the dry season (Table 8), correlations of Cd with Cr (0.9682), Zn (0.9682) and TOC (0.9325) were significant. Cr correlated strongly with Mn (0.9682) and also with pH (0.8126). Zn and Mn correlated strongly with TOC. Pb and Mn also correlated positively with pH. Correlation results for suspended trace metal concentrations during rainy season are presented in Table 9. Cr and Cu correlated strongly with Pb (0.9628) and Zn (0.9207), respectively. Cu also correlated significantly with Zn (0.6202). During the dry season (Table 10), correlation between Cu and Fe was perfect. Correlations between Cu and TOC (0.9911) and Fe with TOC (0.7113) were highly significant.

Table 1: Average dissolved trace metal concentrations (mg/l) in surface water (n = 6)

| Element | Site 1 | | Site 2 | | Site 3 | | Site 4 | | Site 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Dry | Rainy | Dry | Rainy | Dry | Rainy | Dry | Rainy | Dry | Rainy |
| Cd | 0.007 | 0.002 | 0.007 | 0.006 | 0.011 | 0.008 | 0.007 | 0.006 | 0.008 | 0.002 |
| Cr | 0.043 | 0.040 | 0.073 | 0.040 | 0.098 | 0.032 | 0.074 | 0.039 | 0.069 | 0.040 |
| Cu | 0.012 | 0.007 | 0.019 | 0.008 | 0.020 | 0.009 | 0.026 | 0.001 | 0.021 | 0.009 |
| Pb | 0.080 | 0.016 | 0.144 | 0.015 | 0.118 | 0.010 | 0.112 | 0.016 | 0.285 | 0.016 |
| Zn | 0.281 | 0.078 | 0.140 | 0.067 | 0.230 | 0.080 | 0.139 | 0.088 | 0.127 | 0.080 |
| Ni | 0.009 | 0.001 | 0.033 | 0.001 | 0.030 | 0.001 | 0.016 | 0.001 | 0.016 | 0.001 |
| Fe | 0.728 | 0.778 | 1.775 | 0.802 | 2.745 | 0.755 | 2.186 | 0.788 | 2.190 | 0.811 |
| Mn | 0.059 | 0.008 | 0.412 | 0.011 | 0.045 | 0.007 | 0.015 | 0.010 | 0.016 | 0.009 |

Table 2: Average suspended trace metal concentrations (mg/kg) in surface water (n = 6)

| Element | Site 1 | | Site 2 | | Site 3 | | Site 4 | | Site 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Dry | Rainy | Dry | Rainy | Dry | Rainy | Dry | Rainy | Dry | Rainy |
| Cd | 0.004 | 0.004 | 0.002 | 0.004 | 0.011 | 0.004 | 0.001 | 0.001 | 0.002 | 0.001 |
| Cr | 0.003 | 0.020 | 0.005 | 0.280 | 0.098 | 0.011 | 0.096 | 0.001 | 0.099 | 0.329 |
| Cu | 0.008 | 0.020 | 0.075 | 0.010 | 0.020 | 0.009 | 0.038 | 0.190 | 0.022 | 0.011 |
| Pb | 0.091 | 0.140 | 0.091 | 0.090 | 0.117 | 0.011 | 0.133 | 0.050 | 0.141 | 0.140 |
| Zn | 0.018 | 0.270 | 1.554 | 0.280 | 0.230 | 0.080 | 1.490 | 0.280 | 1.509 | 0.280 |
| Ni | 0.017 | 0.040 | 0.004 | 0.039 | 0.030 | 0.001 | 0.071 | 0.010 | 0.073 | 0.060 |
| Fe | 1.249 | 4.950 | 2.236 | 5.301 | 2.745 | 0.755 | 2.083 | 6.610 | 2.101 | 7.610 |
| Mn | 0.014 | 0.100 | 0.353 | 0.101 | 0.045 | 0.100 | 0.189 | 0.100 | 0.192 | 0.100 |

Table 3: Average mobile trace metal concentrations (mg/l) in surface water (n = 6)

| Element | Site 1 | | Site 2 | | Site 3 | | Site 4 | | Site 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Dry | Rainy | Dry | Rainy | Dry | Rainy | Dry | Rainy | Dry | Rainy |
| Cd | 0.010 | 0.002 | 0.007 | 0.005 | 0.012 | 0.003 | 0.007 | 0.006 | 0.009 | 0.005 |
| Cr | 0.023 | 0.018 | 0.006 | 0.087 | 0.116 | 0.041 | 0.048 | 0.040 | 0.059 | 0.039 |
| Cu | 0.020 | 0.017 | 0.026 | 0.006 | 0.167 | 0.001 | 0.014 | 0.008 | 0.018 | 0.010 |
| Pb | 0.101 | 0.107 | 0.144 | 0.159 | 0.149 | 0.011 | 0.160 | 0.811 | 0.143 | 0.012 |
| Zn | 0.517 | 0.424 | 0.360 | 0.076 | 0.245 | 0.086 | 0.239 | 0.109 | 0.225 | 0.080 |
| Ni | 0.014 | 0.056 | 0.047 | 0.142 | 0.006 | 0.043 | 0.001 | 0.012 | 0.012 | 0.006 |
| Fe | 0.965 | 1.920 | 2.135 | 5.301 | 2.505 | 0.599 | 1.396 | 0.243 | 1.681 | 0.587 |
| Mn | 0.060 | 0.034 | 0.046 | 0.129 | 0.041 | 0.007 | 0.033 | 0.011 | 0.04 | 0.010 |

Table 4: Mean variations in the concentrations of trace metal forms (n = 20)

| Element | Dissolved (mg/l) | | Suspended (mg/kg) | | Mobile (mg/l) | |
|---|---|---|---|---|---|---|
| | Dry | Rainy | Dry | Rainy | Dry | Rainy |
| Cd | 0.01±0.00 | 0.01±0.00 | 0.01±0.00 | 1.03±0.00 | 0.01±0.00 | 0.00±0.00 |
| Cr | 0.07±0.02 | 0.03±0.00 | 0.10±0.03 | 0.02±0.01 | 0.06±0.01 | 0.04±0.02 |
| Cu | 0.02±0.00 | 0.01±0.00 | 0.05±0.03 | 0.01±0.00 | 0.02±0.00 | 0.01±0.01 |
| Pb | 0.12±0.02 | 0.02±0.02 | 0.13±0.04 | 0.12±0.02 | 0.14±0.02 | 0.13±0.00 |
| Zn | 0.15±0.04 | 0.08±0.08 | 1.13±0.63 | 0.31±0.05 | 0.23±0.09 | 0.08±0.02 |
| Ni | 0.02±0.01 | 0.01±0.00 | 0.04±0.03 | 0.04±0.02 | 0.01±0.00 | 0.19±0.01 |
| Fe | 1.93±0.75 | 0.79±0.02 | 2.89±1.22 | 5.85±0.12 | 1.68±0.62 | 1.53±0.63 |
| Mn | 0.04±0.02 | 0.01±0.00 | 0.17±0.13 | 0.10±0.00 | 0.04±0.01 | 0.02±0.01 |

Table 5: Suspended/dissolved solids metal concentrations partition coefficients ($K_d$)

| Element | Dry season | | Rainy season | |
|---|---|---|---|---|
| | $K_d$ ($Lkg^{-1}$) | $\log K_d$ | $K_d$ ($Lkg^{-1}$) | $\log K_d$ |
| Cd | 10.00 | 1.00 | 0.83 | 0.08 |
| Cr | 0.50 | -0.30 | 1.80 | 0.26 |
| Cu | 18.57 | 1.27 | 2.68 | 0.43 |
| Pb | 5.35 | 0.73 | 5.70 | 0.76 |
| Zn | 3.95 | 0.60 | 7.37 | 0.87 |
| Ni | 1.76 | 0.25 | 3.60 | 0.56 |
| Fe | 1.50 | 0.18 | 7.43 | 0.87 |
| Mn | 4.71 | 0.67 | 11.11 | 1.05 |

Table 6: Analysis of variance (ANOVA) for concentrations of trace metal forms in surface water

| Element | Rainy season Suspended | Rainy season Dissolved | Dry season Suspended | Dry season Dissolved |
|---|---|---|---|---|
| Cd | 0.003[a] | 0.003[a] | 0.006[a] | 0.006[a] |
| Cr | 0.037[a] | 0.030[a] | 0.071[a] | 0.071[a] |
| Cu | 0.023[a] | 0.007[b] | 0.019[a] | 0.019[a] |
| Pb | 0.079[a] | 0.023[b] | 0.115[a] | 0.023[b] |
| Zn | 0.787[a] | 0.079[b] | 0.153[a] | 0.153[a] |
| Fe | 0.003[a] | 0.001[b] | 1.925[a] | 0.021[b] |
| Ni | 0.003[a] | 0.787[b] | 0.021[a] | 1.925[b] |
| Mn | 0.010[a] | 0.009[b] | 0.035[a] | 0.035[a] |

Mean with the same letter along the same row for each season are not significantly different ($p < 0.05$)

Table 7: Correlation matrix for dissolved trace metal concentrations in water (rainy season)

| | Cd | Cr | Cu | Pb | Zn | Ni | Fe | Mn | pH | TOC |
|---|---|---|---|---|---|---|---|---|---|---|
| Cd | 1 | 0.0001 | -0.5000 | 0.5840 | 0.0001 | 0.2712 | -0.7563 | 0.0001 | 0.1631 | -0.5000 |
| Cr | | 1 | -0.0292 | -0.7987 | -0.2326 | 0.2949 | 0.5041 | -0.0585 | 0.0057 | -0.7892 |
| Cu | | | 1 | -0.3893 | 0.7339 | -0.0001 | 0.6723 | 0.5000 | -0.6523 | 0.0001 |
| Pb | | | | 1 | 0.0889 | -0.0633 | -0.9028 | -0.0001 | 0.1524 | 0.3892 |
| Zn | | | | | 1 | 0.5126 | 0.0767 | 0.8970 | -0.9149 | 0.0001 |
| Ni | | | | | | 1 | -0.1914 | 0.8135 | -0.7252 | -0.2712 |
| Fe | | | | | | | 1 | -0.0001 | -0.1974 | -0.2712 |
| Mn | | | | | | | | 1 | -0.9785 | 0.0001 |
| pH | | | | | | | | | 1 | 0.1201 |
| TOC | | | | | | | | | | 1 |

Significant at $p < 0.05$

Table 8: Correlation matrix for dissolved trace metal concentrations in water (dry season)

| | Cd | Cr | Cu | Pb | Zn | Ni | Fe | Mn | pH | TOC |
|---|---|---|---|---|---|---|---|---|---|---|
| Cd | 1 | 0.9682 | -1.0000 | 0.1705 | 0.9682 | 0.0001 | -0.3596 | 1.0000 | 0.0001 | 0.9325 |
| Cr | | 1 | -0.9683 | 0.1541 | 1.0000 | -0.0001 | -0.1393 | 0.9682 | 0.0417 | 0.8126 |
| Cu | | | 1 | -0.1705 | -0.9683 | 0.0001 | 0.3596 | -1.0000 | 0.0001 | -0.9325 |
| Pb | | | | 1 | 0.1541 | -0.8525 | 0.1063 | 0.1705 | 0.7264 | 0.1749 |
| Zn | | | | | 1 | -0.0002 | -0.1393 | 0.9682 | 0.0417 | 0.8126 |
| Ni | | | | | | 1 | -0.0001 | 0.0001 | -0.9682 | -0.0001 |
| Fe | | | | | | | 1 | -0.3596 | 0.6179 | -0.6371 |
| Mn | | | | | | | | 1 | 0.0001 | 0.9325 |
| pH | | | | | | | | | 1 | -0.0602 |
| TOC | | | | | | | | | | 1 |

**Significant at $p < 0.05$**

**Table 9: Correlation matrix for suspended trace metal concentrations in water (dry season)**

| | Cd | Cr | Cu | Pb | Zn | Ni | Fe | Mn | pH | TOC |
|---|---|---|---|---|---|---|---|---|---|---|
| Cd | 1 | -0.6124 | 0.4082 | -0.3953 | 0.0490 | 1.0000 | -0.2942 | -0.6875 | 7E-15 | -0.3953 |
| Cr | | 1 | 0.1667 | 0.9682 | 0.5204 | -0.6124 | 0.0801 | -0.1531 | -1.9E-15 | 0.9682 |
| Cu | | | 1 | 0.3227 | 0.9207 | 0.4082 | -0.7206 | -0.6634 | 0.6455 | 0.3227 |
| Pb | | | | 1 | 0.6202 | -0.3953 | 0.0001 | -0.3953 | 0.0001 | 1.0000 |
| Zn | | | | | 1 | 0.0490 | -0.6154 | -0.5394 | 0.6202 | 0.6201 |
| Ni | | | | | | 1 | -0.2942 | -0.6875 | 7.01E-15 | -0.3953 |
| Fe | | | | | | | 1 | 0.2942 | -0.9303 | 0.0001 |
| Mn | | | | | | | | 1 | -7E-15 | -0.3953 |
| pH | | | | | | | | | 1 | 0.0001 |
| TOC | | | | | | | | | | 1 |

**Significant at $p < 0.05$**

**Table 10: Correlation matrix for suspended trace metal concentrations in water (dry season)**

| | Cd | Cr | Cu | Pb | Zn | Ni | Fe | Mn | pH | TOC |
|---|---|---|---|---|---|---|---|---|---|---|
| Cd | 1 | 0.6667 | -0.2337 | 0.6124 | 0.1667 | -0.6455 | 0.7386 | -0.3203 | 0.1667 | -0.3612 |
| Cr | | 1 | -0.7834 | -0.1531 | 0.0417 | 0.0001 | 0.9540 | 0.3203 | 0.0417 | -0.8427 |
| Cu | | | 1 | 0.1431 | 0.0390 | -0.3353 | 1.0000 | -0.5281 | -0.0390 | 0.9911 |
| Pb | | | | 1 | 0.1531 | 0.3953 | 0.2638 | 0.1961 | -0.6124 | 0.2212 |
| Zn | | | | | 1 | -0.6455 | 0.1846 | -0.7206 | -0.8750 | -0.0602 |
| Ni | | | | | | 1 | 0.0001 | 0.9303 | 0.3227 | -0.2331 |
| Fe | | | | | | | 1 | -0.3548 | -0.2770 | 0.7113 |
| Mn | | | | | | | | 1 | 0.4804 | -0.4629 |
| pH | | | | | | | | | 1 | -0.0602 |
| TOC | | | | | | | | | | 1 |

Significant at $p < 0.05$

Trace metal concentrations in suspended particles and in dissolved form showed spatial and seasonal variations. Dissolved trace metal concentration increased during dry season and followed a similar trend. Variations in dissolved trace metal concentrations was in the increasing order of Fe > Zn > Pb > Cr > Pb > Cd > Mn. The higher levels of Fe, Zn, Cr and Pb might be due to discharge of solid wastes from residential areas and agriculture runoff which might contain higher levels of these metals (Akanetd.,2010).

The concentration of elements in the dissolved fraction depends on chemisorption onto surface of organic colloids, complexation and/ or chelating by OM present, precipitation of hydroxides (Prendez and Carrasco, 2006). The solubility of trace metals in surface water is predominantly controlled by the water pH, redox potential (Papafilipaki *et al.,* 2008), water temperature and river flow (Xose *et al.*, 2002;

Mean variations results for trace metal forms (Table 4) showed that Cd concentration did not vary irrespective of season and form, except in the suspended partieulate during rainy season. Suspended trace metal concentrations were higher than in the dissolved from during the periods of analysis, except for Cr and Cu, during rainy season and dry season respectively. This may be accounted for by the variation of water physicochQirucal properties, Cr, Cu, Pb, Zn, and Mn forms concentration decreased during the rainy Season. Concentration of Fe also decreased during rainy season, except in suspended particular The relative high flow rate during rainy season may cause dilution of trace metal concentration. When rivpr flow decreases during dry **season, the** concentration of contaminants begin to recover, a **concrnrraring effect of dissolved pollutant OCCUTS in the water due to evaporation (Solai *rt al* , 2010),** which might be responsible for the increase in trace **metal concentrations in dry season. Water pH was** 7.74 ± O.ll in dry season and 6.72 * 0.13 during the rainy season (Tulcura *ft al* ,  2012). A lower water pH increase the competition between metal and hydrogen ion (H*) for binding sites (Tukura *et al.,* 5009) A decrease in pH may allow dissolved metal carbonate complexes to release free metal ion into the water column (Dzombak and Morel, 1990; Tukura *etal.*, 2007).

Concentrations of trace metal forms generally increased downstream which could be due to the contribution of stream inputs containing soil colloidal particulate materials released either by soil along the river bank or by water runoff. The decreased in metal concentrations between site 2 and 3 might have occurred by exchange between water and suspended solids and subsequently deposition between the sites. Suspended trace metal concentrations were below the world average (WA) values (Martins, 1979). The results in this study were comparable with those reported by MathieueraZ. (2005),Kucuksezginef *al.* (2008). K.J depends on the nature of suspended solids, geochemical parameters of the water and specific characteristics of each element (EPA, 2005; Xguyen *etal.,* 2005).The log $K_d$ values for suspended/dissolved solids trace metal concentrations were greater than 1 during rainy season. The partition coefficient results indicated the relative affinity of each metal sorption to the OM in the solid phase as compared to complexation with dissolved organic matter in water. The competition of complexation by dissolved OM and sorption/precipitation to the solid phase can also explain the apparent higher sorption of Cu and Pb during rainy season (Sauve *et al.*, 2003). The K^ for Cu was highest in dry season and Mn in rainy season. These results suggest that the mechanism controlling trace metals portioning in Mada River does not vary significantly. The results in this study are consistent with those reported by Sauve *et al.* (2003) andMathieuef flZ. (2004). Lower log$K_d$ values suggest lower affinity of organic sediments to sorb metals. Dissolved ligands present in sediment pore waters (e.g., dissolved OM, anthropogenic organic acids) can complex with metals, reducing their propensity for sorption in proportion to the concentration of the ligands (Sauve *et al.,* 2003). Seasonal differences may be attributed to variations in water chemistry. Large influx of wastes into the water body during the rainy season may also be contributory from farmlands. As some trace metals may originate from similar sources and have similar reactivity's towards biological and non-biological particles, it is probable that some of them may have their particle bond and dissolved concentration closely related to each other. Significant relationships of metals in suspended particles were obtained. Such significant relationship profiles could be due to the fact that suspended particles are constantly interacting with trace metals and hence depending on the kinetics and reversibility of such reactions, the concentrations of metals in suspended particulates may not change significantly during a limited period of time (Eckard, 1996; Okafor and Opuene, 2006), In the dissolved phase, no strong correlations between trace metals were obvious, which concords with the results reported by Munksgaard and Parry (2001), and Okafor and Opuene (2006). The observed strong correlations of some metal concentrations with pH and TOC implies that variation in the level of any of these *parameters would affect the suspended and dissolved metal levels (Tukura* et al., *2007). Significant inter-relationship existed between the concentrations of certain metals in dissolved and suspended phases, suggesting similar sources for and/or similar geochernical processing controlling such metals (Mahallapaefa/., 2010).*

## *CONCLUSIONS -•*

*Dissolved, suspended and mobile trace metal concentrations water showed spatial and temporal changes. Fe concentration predominated in all the forms. Trace metal concentrations increased downstream. Suspended trace metal concentrations were higher than in the dissolved form irrespective of season, except for Cr during rainy season and Cu during dry season. Trace metal levels generally decreased during rainy season due to dilution of water. Suspended trace metal concentrations were below the world average Values. The log K,, values for suspended/ dissolved solids trace metal concentrations were greater than 1 during rainy season. This implies relative affinity of each metal sorption to OM in the solid phase as compared complexation with dissolved OM in water Strong correlations among metals suggest the same sourrp, mechanism and fate. Significant ircuTwlativne of metals With pH and TOC imply that Variation in their levels would affect the metal contents,*

## *ACKNOWLEDGEMENTS*

*The author^ cxprrs* then gratitude to Education Ti u*it Fund (ETF), Nigeria, for the financial support the success of the reseai ch work. We also staff of National Research Institute of Chemical and Technology (NARTCT), Zaria, Nigeria, for ihelr support during the AAS analysis*

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