Research Journal of

# Environmental Sciences

ISSN 1819-3412

Academic Journals Inc.

www.academicjournals.com

Research Journal of Environmental Sciences 1 (5): 220-228, 2007
ISSN 1819-3412


# Assessment of Contamination by Heavy Metals in Sediments of Ase River, Niger Delta, Nigeria

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**Abstract:** As part of assessment Ase river, in dry and wet season of 2006, sediment samples were collected at five locations to determine spatial variation of anthropogenic pollutants. Heavy metal levels (mg $kg^{-1}$) in the sediment were Cd 2.89±2.97, Pb 7.00±10.04, Cr 2.34±2.53, Cu 3.32±2.37, Mn 24.27±9.92, Ni 7.04±7.49, Fe 110.53±101.54 and Zn 12.46±4.56 for dry reason and Cd 2.35±2.71, Pb 6.42±9.03, Cr 21.16±2.19, Cu 3.38±1.72, Mn 21.58±14.93, Ni 5.62±4.22, Fe 86.93±88.36 and Zn 5.63±4.22 for wet season. The results ($p\geq 0.05$) revealed significant spatial and temporal variation in the characteristic levels of heavy metals in the sediments. The variance results from changes in contaminants supply, rate of deposition and erosion as well as seasonal variability in physicochemical conditions. The accumulation pattern of heavy metals in the sediment follows the order Fe> Mn >Zn >Ni >Pb >Cu >Cd >Cr. The levels of heavy metals were similar to levels found in unpolluted sediments and continental crust except for Cd. Such sediment system is at risk of cadmium pollution.

**Key words:** Heavy metals, contamination, sediment, Ase river, Niger Delta, Nigeria

## INTRODUCTION

Bed sediments in rivers not only play an important role in influencing the pollutions of river water but they can also be used to record the history of river pollution. Sediment act as both carrier and potential sources of contaminants in an aquatic environment. Because of anthropogenic activities, industrial and urban wastes are invitasly discharged into water bodies. Consequently, heavy metals are frequently detected in water environment and have gradually become a major concern worldwide (Yu *et al*., 2000).

The contamination of sediment with heavy metals, even in small concentration may lead to serious environmental problem (Loizidou *et al*., 1992). Heavy metals can either be adsorbed onto sediment or accumulate by benthic organism to a toxic levels, the bioavailability and subsequent toxicity of the metals are dependent upon the various forms and amount of the metal bound to the sediment matrices (Yu *et al*., 2000). Synoptically, for the metals, the process of interest in the in a sediment-water system are; decomposition-resuspension, sorption-adsorption, complexation-decomplexation. The chemical and biological processes that affects the mobility depends on environmental factors such as pH, salinity, redox conditions (Gambrell *et al*., 1980).

The Ase river receives discharges from the oil and gas industries, urban water storm, agricultural runoff from the farming communities along the river course. The Ase river forms a major transport channel from inland area to the coastal parts of the Niger Delta, literature on the pollution status of the Ase river appears very scanty. The Ase river serves as fishing sources of drinking water and support activities in the upland areas of Delta. Contamination of the sediment matrix by heavy metals may

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accumulate in fishes and other aquatic resources which may eventually get into human food chains. The primary objective of the present study was to determine the temporal and spatial variation in the concentrations of heavy metals in the sediment with a view of providing information on the extent of contamination.

## MATERIALS AND METHODS

### Description of Study Area

Ase River (Fig. I) is tributary of Forcados River, the western branch of River Niger in the Delta area of Southern Nigeria. Its source is lake Ewuru (6.4°N, 6.30°E) in Oshimili South local area and its

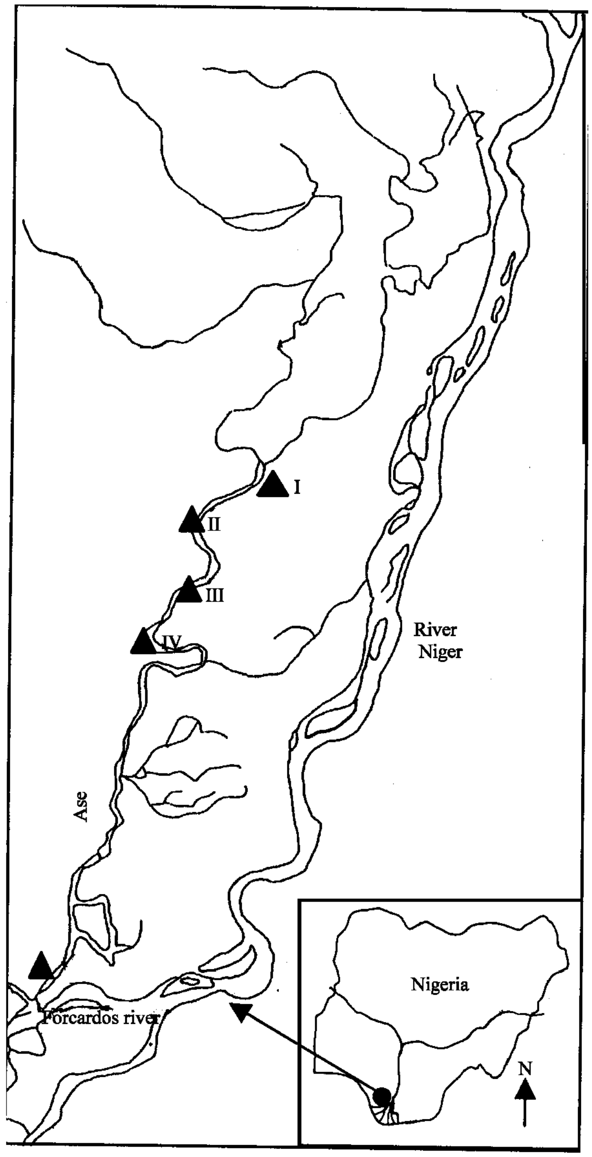


Fig.1: Map of the Ase river showing sampling points

confluence is at Asaba-Ase (5.20°N; 6.17°) in Ndokwa East local government area, Delta State. The length of Ase river is approximately 292 km. Ase River marks the geological boundary of the Sombreiro-Warri formation and the meander belts of the upper deltaic plains of the Niger delta (Short and Stuble, 1968). Other geological characteristics of this area have earlier been described by Allen (1965). The typical tropical climate, consisting of dry and rainy season is governed by the Northeastern and southwestern winds which generally influence the climate of Nigeria (Hare and Carter, 1984). The river served as one of the major slave transport route from the upland to the costal areas in the 18th century.

**Sampling and Analysis**

Sediment samples were collected from 5 different points along the course of the river, the sediment samples was collected into two regime January-March and June-July 2006 representing the dry season and wet seasons, respectively. The bed sediments were collected by scooping up 10 cm of the bed sediment from 10 m away from the riverbank. The sampling sites were established from the upstream section to down stream section of the river;

Site I (Obetim OB). It represent the upstream section, the visible activities in this site are basically swimming, washing and fermentation of cassava.

Site II (Kwale KW), This points is used as jetty by the Nigeria Agip oil Company to ferry their goods across the river.

Site III (Ashaka AS). The most visible activities in this site are basically washing, fermentation of cassava and swimming. The site was used as inland port 18th and earlier 19th century.

Site IV (Igbuku IG): The primary activities in this site are commercial sand dredging, washing and fermentation of cassava.

Site V (Asaba ASE). This is downstream section of the river, it serves as local jetty for transportation of goods from the inland area to the deep coastal area of the Niger Delta. This point is also used as jetty by local petroleum dealers in the coastal zone. The traffic densities of speed boats are quite high in this site.

In our laboratory, the sediment were air-dried at room temperature and subsequently kept for 1 h in an oven at 100°C. These ground in an agate mortal to below 100 mm mesh size and stored at 4°C. The sediment pH, total organic matter and conductivity were analyzed following the procedure described by Radojavic and Bashkin (1999). Total concentration of heavy metals was determined by mineralization of 1.0 gramme of the sediment using aqua-ragia. The digest was subsequently diluted to 50 mL mark using ultra pure distilled water. The concentration of Cd, Pb, Cr, Ni, Cu, Fe Zn in the solution was determined using graphite furnace atomic absorption spectrophotometer equipped with D2 background correction system (GBC scientific equipment SENX AA 1175, Australia).

All acid used were of analytical grade quality control was assured by the use of procedural blanks and spikes. The spike recovery for each element was greater than 94%. All samples were run in triplicates and the relative standard deviation for the triplicate analysis was less than 6%.

## RESULTS AND DISCUSSION

The pH value of Ase river sediment ranged from 4.8 to 6.9 and 4.57-7.30 for wet and dry seasons respectively. The pH values range from weakly acidic to near neutral (Table 1), this is typical of the anaerobic sediment of the Niger Delta. In our previous studies, we have reported similar pH value for Ntwougba creek in the Niger Delta (Iwegbue *et al*., 2006). The Ase river sediment pH may not pose any critical impact on soil reaction. The pH of the sediment are quite high during the dry season than wet season. This might be responsible for high concentrations of heavy metals in the dry season samples. The organic matter content of Ase sediments are generally low. Similar low organic matter content has been reported for some river system in the Niger Delta (Horsfall *et al*., 1999;

Table 1: Range and mean±SD of physicochemical and total heavy metal concentration of Ase river sediments

| | Dry season | | | Wet Season | | |
|---|---|---|---|---|---|---|
| Properties | Mean±SD | Range | CV (%) | Mean±SD | Range | CV(%) |
| pH | 5.27±1.58 | 4.57-7.30 | 30.0 | 5.20±1.32 | 4.8-6.9 | 25.3 |
| EC (μ S $cm^{-1}$) | 2.82±0.99 | 2.54-4.27 | 35.0 | 2.42±0.77 | 1.53-3.29 | 32.2 |
| Organic matter (%) | 1.30±0.33 | 0.7-1.6 | 25.0 | 1.40±0.40 | 0.6-2.0 | 28.3 |
| Cd (mg $kg^{-1}$) | 2.89±2.97 | 0.63-6.91 | 102.8 | 2.35±2.71 | 0.06-5.80 | 115.0 |
| Pb (mg $kg^{-1}$) | 7.00± 10.04 | 1.30-24.79 | 143.5 | 6.42±9.03 | 1.15-22.40 | 140.7 |
| Cr (mg $kg^{-1}$) | 2.34±2.53 | 0.27-6.44 | 108.2 | 2.16±2.19 | 0.48-6.00 | 101.4 |
| Cu (mg $kg^{-1}$) | 3.32±2.37 | 1.19-7.14 | 71.4 | 3.38±1.72 | 1.39-5.87 | 50.8 |
| Mn (mg $kg^{-1}$) | 24.72± 9.92 | 15.20-34.90 | 40.1 | 21.58±14.93 | 7.70-43.50 | 69.3 |
| Ni (mg $kg^{-1}$) | 7.04±7.49 | 0.53-19.86 | 106.4 | 5.62±4.22 | 2.15-12.60 | 75.0 |
| Fe (mg $kg^{-1}$) | 110.53±101.54 | 28.00-250.09 | 91.9 | 86.93±88.36 | 19.51-220.80 | 101.6 |
| Zn (mg $kg^{-1}$) | 12.46±4.56 | 8.35-19.84 | 36.6 | 5.62±4.22 | 2.15-12.60 | 75.1 |

Iwegbue *et al*., 2006). Table 1 also present the mean±SD, range of heavy metal concentrations of Ase river sediment. Figure 2-9 present spatial and temporal variation in the characteristics levels of heavy metals in the Ase river sediments. Analysis of variance (ANOVA) ($p \leq 0.05$) revealed significant spatial variations in the concentrations of the examined heavy metals. This reflects anthropogenic input into the river system and t-test was used for comparison of seasonal mean. The results also revealed significant temporal variations in characteristic levels of heavy metal ($p \leq 0.05$). Temporal variance results from changes in contaminant supply, rate of deposition and erosion as well as, seasonal variability in physical chemical conditions e.g., temperature, microbial activity (Birch *et al*., 2001).

Site V showed elevated concentrations of the examined metals compared to any other site in both seasons. The high concentration of metals at this site may have resulted from the kind of anthropogenic activities going on in the site. Cd, Pb, Ni are higher in this site probably due local spillage of refined petroleum products during the process of transferring from one container to another, runoff from the market and motors park and high daily traffic volume of motorized speed boat, which are the only means of transportation fishermen/inhabitant in these riverine areas. The high lead concentration in this area is as result from the exhaust of motorizd speed boats which uses gasoline as motor fuel. Site 1 showed marked low concentrations of any of heavy metals in the sediment. This area is devoid of any industrial activities. It is therefore the approximates natural background concentration. The heavy metal content of the sediments showed increase concentrations on going from the upstream section of the river to down stream section.

Cadmium and chromium presented the lowest levels (Table 1). However, cadmium show very high toxicity to both aquatic and terrestrial organisms even at low concentrations (Kennish, 1992). For dissolved cadmium, acute $LC_{50}$ values as low as 35 μg $L^{-1}$ have been demonstrated (Versteeg and Giresy, 1986). Although cadmium is a sulphur seeking metal that tend to precipitate in anoxic sediments, experiments carried out at concentrations lower than value found in this study, show that cadmium can still be assimilated from anoxic sediments with high organic matter content (Griscom *et al*., 2000; Chong and Wong, 2000; Lee *et al*., 2000; Muniz *et al*., 2004). Therefore they can potentially bioaccumulate through dietary uptake.

The total copper concentration range from 1.12-7.14 and 1.39 to 5.87 mg $kg^{-1}$ for dry and wet season, respectively. The results obtained from this study are comparable to value reported for sediment of the Swartkops River estuary, Port Elizabeth, South Africa (Binning and Baird, 2001). Nevertheless, the comparison of contaminant concentration observed during this study with those reported for other areas of the world (Table 2) indicates that levels and ranges of variation of our data are similar to those reported for sites with high anthropogenic activities.

The levels of heavy metals reported herein were below level found in the continental crust (Taylor, 1964) and levels found in unpolluted sediments (GESAMP, 1982. Salomons and Forstner, 1984). However, the mean level of cadmium exceeded levels found is continental crust and that of unpolluted sediment. Such sediment system is at risk of cadmium pollution. The concentration of lead in site V exceeds levels found in unpolluted sediment.

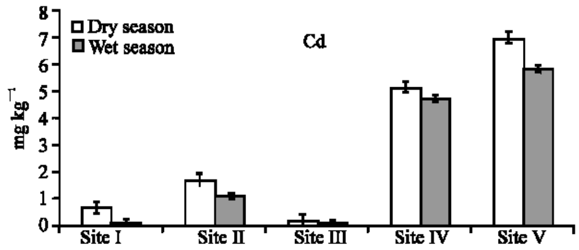


Fig. 2: Temporal and spatial variation in the characteristic levels of cadmium in Ase river sediment

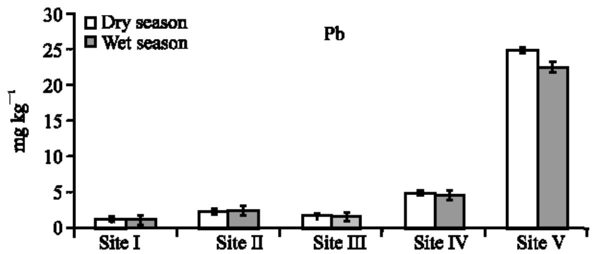


Fig. 3: Temporal and spatial variation in the characteristic levels of lead in Ase river sediment

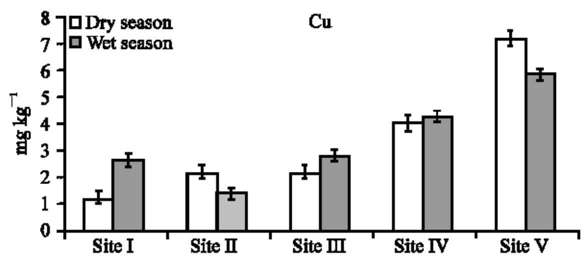


Fig. 4: Temporal and spatial variation in the characteristic levels of copper in Ase river sediment

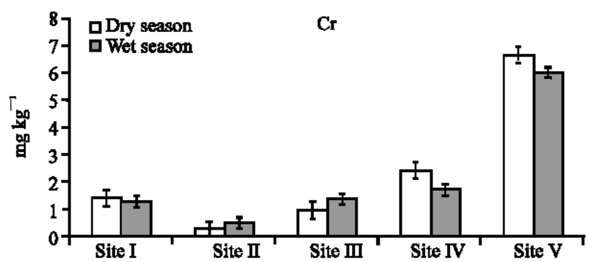


Fig. 5: Temporal and spatial variation in the characteristic evels of chromium in Ase river

Iwegbue *et al.* (2006) reported that mean levels (mg kg$^{-1}$) of heavy metals in post dredged sediment of Ntwuogba creek, Nigeria were 5.92±11.12 for Cu, 4.52±3.70×10$^3$ for Fe, 2.28±2.50 for Pb, 396±236 for Mn, 0.46±0.36 for Ni, 21.88±14.28 for Zn and 0.12±0.10 for Cd. The values of heavy metals reported herein were higher than concentrations previously reported for sediment

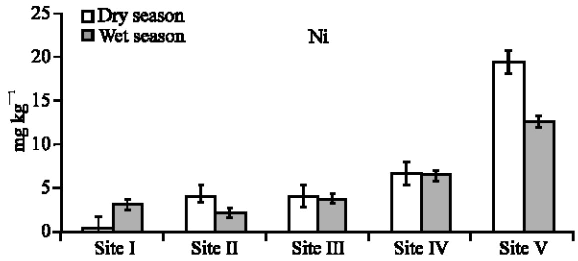


Fig. 6: Temporal and spatial variation in the characteristic levels of nickel in Ase river sediment

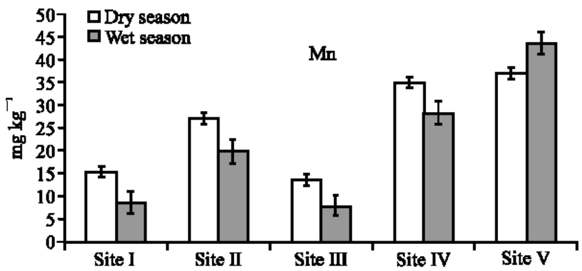


Fig. 7: Temporal and spatial variation in the characteristic levels of manganese in Ase river

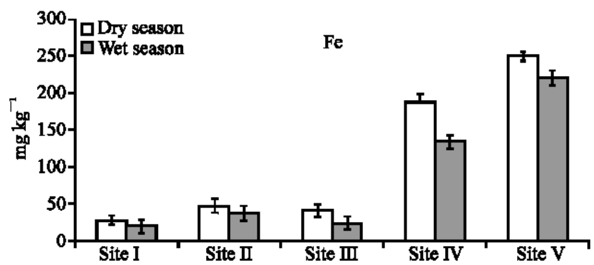


Fig.8: Temporal and spatial variation in the characteristic levels of Iron in Ase river sediment

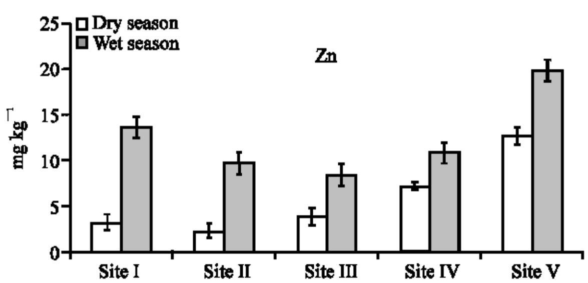


Fig. 9: Temporal and spatial variation in the characteristic levels of Zinc in Ase River Sediment

of a freshwater system in the Niger Delta, except for Fe, Mn and Zn (Iwegbue *et al.*, 2006). Table 3a and b show the intermetallic relation in the sediment of (Ase river) (wet and dry seasons, respectively).

The high degree of association between Cd, Ni, Pb, Cu and Cr is evident and was reported in the literature for urbanized and polluted area (Ruiz, 2001; Spencer, 2002; Muniz *et al*., 2004).

Table 2: Heavy metals concentration of sediments of some rivers/Eaustries in the world

| Country | Cd | Pb | Cr | Cu | Ni | Mn |
|---|---|---|---|---|---|---|
| Nigeria (Ase river) Dry season | 0.63-6.91 | 1.30-24.79 | 0.27-6.44 | 1.19-7.14 | 0.53-19.86 | 15.20-39.40 |
| Wet season | 0.06-5.80 | 1.15-22.40 | 0.48 | 1.39-5.84 | - | 7.70-43.50 |
| USA (St Lucie Estuary) | 14 | 10 | 40 | 26 | 36 | 117 |
| Nigeria (Benin River) | 0.2-0.8 | 3.8-10.00 | 4.50-9.00 | 6.80-3.90 | 2.00-5.80 | |
| South Africa (Swartkpos River Estuary) | 32.9 | 20.3 | 6.8 | - | 1149 | |
| Fresh water reaches | - | 24.7 | 11.9 | 9.5 | - | 119.4 |
| Australia (Cox River) | <1 | 17 | 16 | 18 | 12 | 156 |
| USA (Calcasieu River) | 0.98 | 9.90 | 19.1 | 6.91 | | - |
| Czech (Jihlava River) | 0.62-0.70 | 9.53-19.46 | 8.20-15.44 | 4.49-14.33 | 6.39-8.28 | |
| Zimbabwe (Lake Mcllwaine) | 0.39 | 41.0 | - | | 38.0 | |
| Kenya (Lake Victoria) | 0.55-1.02 | 6.02-69.4 | - | 0.96-78.6 | | 53.1-616 |
| Egypt (River Nile Estuary) | 1.06 | - | - | 85.6 | | 387 |
| Uganda (Lake Edward) | 2.70 | - | | 103 | | $69\times10^3$ |
| Continental Crust | 0.10 | 12.5-20 | | 55 | | 950 |
| Unpolluted sediments | 0.11 | 19 | | 33 | | 770 |

Table 2: Continued

| Country | Fe | Co | As | Hg | Zn | References |
|---|---|---|---|---|---|---|
| Nigeria (Ase river) Dry season | 28-.250.08 | - | - | - | 8.35-19.84 | This study |
| Wet season | 19.51-220.8 | - | - | - | 2.15-12.60 | |
| USA (St Lucie Estuary) | 17 | 19 | - | - | 40 | |
| Nigeria (Benin River) | 198.70-504.9 | | | | 6.7-11.7 | Iheyen (2001) |
| South Africa (Swartkpos River Estuary) | - | - | - | - | 35.9 | Binning and Baird (2001) |
| Fresh water reaches | | | | | 24.7 | |
| Australia (Cox River) | 2.3 | 13 | | | 48 | Birch *et al.* (2001) |
| USA (Calcasieu River) | - | - | 0.724 | <0.05 | 35.6 | Beck *et al.* (1990) |
| Czech (Jihlava River) | | | | | 46.48-102.82 | Spurny *et al.* (2002) |
| Zimbabwe (Lake Mcllwaine) | 350 | - | | 0.28 | 100 | Grieichus (1978) |
| Kenya Lake Victoria | $1.18\times10^3$-$52.9\times10^3$ | | | | 2.54-265 | Onyari and Wandinga (1989) |
| Egypt (River Nile Estuary) | $0.46\times10^3$ | | | | | |
| Uganda (Lake Edward) | $69\times10^3$ | | | | | Bugenyi (1982) |
| Continental Crust | $56.0\times10^3$ | | | 0.08 | 70 | Taylor (1964) |
| Unplluted sediments | $41.0\times10^3$ | | | 0.05-0.3 | 95 | GESAMP (1982) Salomons and Forstners (1984) |

Table 3a: Intermetallic relationship in the sediments of Ase river (Dry season)

| Elements | Cd | Pb | Cu | Cr | Ni | Mn | Fe | Zn |
|---|---|---|---|---|---|---|---|---|
| Cd | - | - | - | - | - | - | - | - |
| Pb | 0.84 | - | - | - | - | - | - | - |
| Cu | 0.94* | 0.95* | - | - | - | - | - | - |
| Cr | 0.86 | 0.97** | 0.94* | - | - | - | - | - |
| Ni | 0.87 | 0.98** | 0.98** | 0.94* | | - | - | - |
| Mn | 0.94* | 0.69 | 0.82** | 0.67 | 0.74 | - | - | - |
| Fe | 0.99** | 0.85 | 0.96* | 0.89* | 0.89* | 0.88 | - | - |
| Zn | 0.90** | 0.96** | 0.98** | 0.99** | 0.96** | 0.72 | 0.77 | - |

*Significant, **Highly significant

Table 3b: Intermetallic relationship in the sediments of Ase River (wet season)

| Elements | Cd | Pb | Cu | Cr | Ni | Mn | Fe | Zn |
|---|---|---|---|---|---|---|---|---|
| Cd | - | - | - | - | - | - | - | - |
| Pb | 0.80 | - | - | - | - | - | - | - |
| Cu | 0.87 | 0.85 | - | - | - | - | - | - |
| Cr | 0.76 | 0.98 | 0.90* | - | - | - | - | - |
| Ni | 0.88* | 0.96* | 0.96* | 0.97** | - | - | - | - |
| Mn | 0.96* | 0.89* | 0.79 | 0.82 | 0.89* | - | - | |
| Fe | 0.97** | 0.91* | 0.92* | 0.89* | 0.96* | 0.97* | - | - |
| Zn | 0.64 | 0.89* | 0.76 | 0.90* | 0.83 | 0.73 | 0.77 | - |

*Significant, **Highly significant

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