

Heavy Metals in the Sediments of the Lower Ikpoba River, Benin City, Nigeria

F. A. OGUZIE

Department of Fisheries, University of Benin, Benin City, Nigeria.

Abstract

Heavy metal concentrations in the sediments of the lower Ikpoba river in Benin City, Nigeria were investigated using the flame atomic absorption spectrophotometry technique and compared with previously determined values for water.

Mean concentration values (in $\mu\text{g g}^{-1}$, dry wt) recorded for metals in sediment samples were as follows: Cd = 1.5; Cr = 0.9; Cu = 1.9; Fe = 7.9; Pb = 3.3; Mn = 4.6; Ni = 3.95 and Zn = 4.7.

Mixed effluent sources, high vehicular traffic density and run-off water from the city's industrial areas are considered to be possible sources of metal contaminants during the dry and rainy seasons. Significant correlations ($P < 0.05$) were observed between metal contents in sediment and water. No significant differences were, however, observed between metal concentrations in dry and rainy seasons ($P > 0.05$).

Introduction

Urbanization and industrial activities in developing countries including Nigeria has gradually led to the deterioration of the quality of the natural environment in recent years. This situation has invariably increased due to the problem of waste disposal.

Several industries in the urban areas have unsanitary habits of disposing solid wastes at dumps without adequate management. Studies have shown that the toxic and hazardous materials from these dumps are transported to inland water bodies where they settle in bottom sediments (Ndiokwere, 1984). The levels of chemicals including those of heavy metals are concentrated in the organic matter of the sediments, which act as a "bank" for the metals (Tada & Suzuki 1982). A significant correlation between the levels of lead, manganese, mercury and nickel, and the organic matter content of bottom sediments was reported by Moore & Sutherland (1981) in a study of a lake contaminated with mine wastes.

In a previous study, Oguzie (1999) discussed the variation of pH and heavy metal concentrations in the lower Ikpoba river water. Information on the heavy metal status of the lower Ikpoba river is incomplete without corresponding data on the sediments.

The aim of this study was to determine the concentration of heavy metals in the sediment of the lower Ikpoba river. This was intended to complement the available information on the heavy metal of the river water.

Materials and methods

Study area

The Ikpoba river from its origin in the Ishan plateau flows from north to south through Benin City, in the Edo State of Southern Nigeria (Lat. $06^{\circ} 5' N$; Long. $05^{\circ} 8' E$). Four sampling zones (Fig. 1) were chosen along the river on the basis of sources and types of effluents. Zone 1 (Temboga) is a collecting point for rubber processing, sand dredging, laundry and land filling effluents. Zone 2 (Bridge) is a collecting point for urban run-off water containing effluents from car wash, dense vehicular traffic, general metal works, battery recharging workshops, and printing houses. Zone 3 (Edo/Bata) serves as a collecting point for slaughter and poultry effluents while zone 4 (Brewery) is a collecting point for brewery effluents.

Sampling Techniques

Sediment samples were collected monthly from April 1991 to June 1992 with a bottom grab sampler (Hydro-Bios). Replicate samples were collected on sampling days around each sampling zone and stored in polythene bags. The samples were dried in a moisture extraction oven at $105^{\circ}C$ and stored in plastic bags. Percent total organic matter of sediment was determined using the modified Walkley and Black method (Piper 1944).

Digestion and Analysis

Sediment samples were digested using the nitric acid-perchloric acid method (Adams et al. 1980). A Varian Techtron Spectr AA 100 (Model, 65) atomic absorption spectrophotometer was used for the analysis of Cd, Cr, Cu, Pb, Mn, Ni and Zn. The concentration of Iron (Fe) was determined by the orthophenantroline method (Allen 1989) with some modifications as described by Oguzie (1999). One way Analysis of Variance, t-test and Pearson's correlation coefficient were used in the statistical analyses at 5% level of significance (Duncan 1955).

Results

Table 1 shows the variation of percent total organic matter content of the sediment with season at the sampled zones. The total organic matter content varied from 2.05% to 2.63% during the sampling period. Mean percent total organic matter increased from the Bridge (2.26) through Edo/Bata (2.36) and Temboga (2.46) to the Brewery (2.53) where the highest value was recorded. No significant differences were however recorded in the

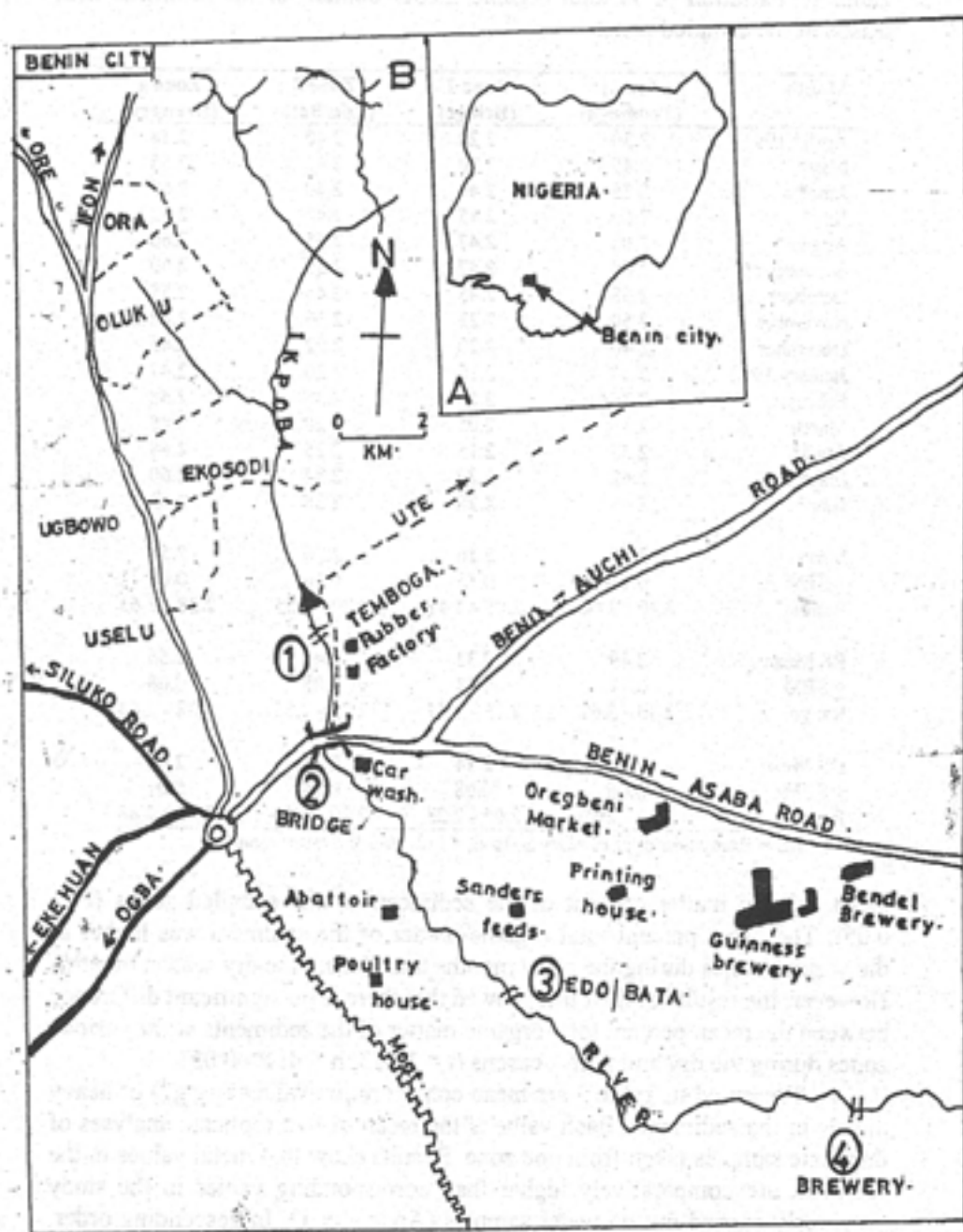


Figure 1. The study area. A. Nigeria showing Benin city; B. The river studied showing four sampling zones. Source: Federal Survey Nigeria 1964.

Table 1: Variation of % total organic matter content of the sediment with season at the sampled zones.

Month	Zone 1 (Temboga)	Zone 2 (Bridge)	Zone 3 (Edo/Bata)	Zone 4 (Brewery)
April* 1991	2.30	2.20	2.40	2.38
May*	2.45	2.20	2.42	2.55
June*	2.55	2.40	2.40	2.60
July*	2.60	2.45	2.45	2.62
August*	2.62	2.47	2.55	2.60
September*	2.60	2.47	2.55	2.60
October*	2.58	2.45	2.45	2.58
November	2.50	2.23	2.30	2.48
December	2.40	2.20	2.22	2.45
January 1992	2.38	2.10	2.20	2.47
February	2.35	2.10	2.30	2.48
March	2.35	2.05	2.28	2.48
April*	2.35	2.15	2.25	2.48
May*	2.42	2.20	2.34	2.60
June*	2.45	2.28	2.38	2.63
Mean	2.46	2.26	2.36	2.53
± SEM	0.11	0.15	0.10	0.08
Range	2.30 - 2.62	2.05 - 2.47	2.20 - 2.55	2.38 - 2.63
RS Mean	2.49	2.33	2.41	2.56
± SEM	0.11	0.13	0.08	0.08
Range	2.30 - 2.62	2.15 - 2.47	2.25 - 2.55	2.38 - 2.63
DS Mean	2.40	2.14	2.26	2.47
± SEM	0.06	0.08	0.05	0.01
Range	2.35 - 2.50	2.05 - 2.23	2.20 - 2.30	2.45 - 2.48

RS = Rainy Season; DS = Dry Season; * Indicates the rainy months.

mean organic matter content of the sediments at the sampled zones ($P > 0.05$). The mean percent total organic matter of the sediment was higher at the various zones during the rainy months than during the dry season months. However, the results of the *t* test showed that there is no significant difference between the mean percent total organic matter of the sediments at the various zones during the dry and rainy seasons ($t = 1.413$; $n = 4$; $P > 0.05$).

Presented in Table 2 are mean concentration values ($\mu\text{g g}^{-1}$) of heavy metals in the sediments. Each value is the mean of two replicate analyses of duplicate samples taken from one zone. Results show that metal values in the sediment are comparatively higher than corresponding values in the study previously carried out on water samples (Appendix 1). In descending order, metal concentrations in the sediments could be ranked as follows: $\text{Fe} > \text{Zn} > \text{Mn} > \text{Ni} > \text{Pb} > \text{Cu} > \text{Cd} > \text{Cr}$.

The highest mean concentration values of Fe ($9.75 \mu\text{g g}^{-1}$) in the sediments were recorded at Temboga while the highest value for Zn ($6.20 \mu\text{g}$

Heavy metals in sediments of a river

g^{-1}) was recorded at Edo/Bata. Similarly, the highest mean concentration values for Cd ($1.8 \mu\text{g g}^{-1}$), Cr ($1.17 \mu\text{g g}^{-1}$), Cu ($2.27 \mu\text{g g}^{-1}$) and Ni ($4.20 \mu\text{g g}^{-1}$) were recorded at the Brewery while the highest mean concentration of Pb ($4.50 \mu\text{g g}^{-1}$) was recorded at the Bridge. The lowest mean values for Cd ($0.97 \mu\text{g g}^{-1}$), Cr ($0.63 \mu\text{g g}^{-1}$), Fe ($6.08 \mu\text{g g}^{-1}$) and Ni ($3.61 \mu\text{g g}^{-1}$) were recorded at the Bridge. The trend in the distribution of metals in the sediments does not conform with corresponding trend in the water except for Fe, Cd and Cr. However, the highest mean concentration values of Fe, Mn, Ni and Zn in the sediments and water at the various zones appear to follow the same trend.

Table 2. Concentrations of heavy metals ($\mu\text{g/g}$ dry wt) in the sediments at the four zones sampled. Figures in parentheses are zone identification numbers shown in Fig. 1. Mean values in each row and column with the same superscript are not significantly different ($P>0.05$); * Zone with the highest concentration of a particular metal; DS – Dry season; RS – Rainy season.

Heavy metals		Tembosa (1)	Bridge (2)	Edo/Bata (3)	Brewery (4)
Cd	DS	1.43	1.20	1.66	2.36
	RS	1.24	0.85	1.68	1.61
	Mean	1.30 ^{bc}	0.97 ^c	1.67 ^{bc}	1.86 ^{bc*}
Cr	DS	1.11	0.64	0.82	1.22
	RS	1.14	0.62	1.13	1.15
	Mean	1.13 ^c	0.63 ^c	1.03 ^c	1.17 ^{c*}
Cu	DS	1.84	1.96	1.75	2.57
	RS	2.35	1.62	1.32	2.12
	Mean	2.18 ^b	1.73 ^{bc}	1.46 ^{bc}	2.27 ^{b*}
Fe	DS	10.79	7.86	9.50	8.41
	RS	9.23	5.19	7.87	6.90
	Mean	9.75 ^{a*}	6.08 ^a	8.41 ^a	7.40 ^a
Pb	DS	3.16	5.04	3.68	3.51
	RS	2.27	4.23	3.05	2.29
	Mean	2.57 ^b	4.50 ^{ab*}	3.26 ^b	2.70 ^b
Mn	DS	5.17	7.34	6.49	3.24
	RS	4.59	3.33	3.60	4.76
	Mean	4.78 ^{ab*}	4.67 ^{ab}	4.57 ^{ab}	4.25 ^{ab}
Ni	DS	3.26	2.76	3.44	3.54
	RS	4.27	4.04	4.40	4.53
	Mean	3.93 ^{ab}	3.61 ^b	4.08 ^{ab}	4.20 ^{ab*}
Zn	DS	3.72	4.80	7.13	4.36
	RS	3.34	5.34	5.73	3.70
	Mean	4.46 ^b	5.16 ^a	6.20 ^{a*}	3.92 ^{ab}

Among the metals studied, significant correlations were observed between Cu in sediments and Cr in water ($r = 0.665$, $P < 0.05$), Fe in sediments and in water ($r = 0.875$, $P < 0.05$) and between many other metals in sediments and water at various zones. These correlations are given in Table 3.

Table 3: Correlation matrices for Heavy metal concentrations in the water and sediments at four zones of the lower Ikpoba river.

ZONE 1 (Temboga)								
	CDW	CRW	CUW	FEW	PBW	MNW	NIW	ZNW
CDS	0.490*							
CRS	0.053*	0.452*						
CUS	0.267	0.665*						
FES	0.636*	-0.456*	-0.259	0.875*				
PBS	-0.178	-0.087	0.647	0.664*	0.059			
MNS	0.012	0.109	0.541*	0.704*	0.212	0.516*		
NIS	0.243	-0.405*	-0.405	0.652*	0.176	0.719*	0.725	
ZNS	0.014	-0.538*	-0.538*	-0.544*	0.006	0.805*	0.771*	0.560*
ZONE 2 (Bridge)								
CDS	0.457*							
CRS	0.481*	0.990*						
CUS	0.410*	0.995*	0.996*					
FES	-0.102	0.404*	-0.460	-0.413*				
PBS	-0.444*	-0.120	0.164	-0.090	0.146			
MNS	-0.206	0.208	0.159	0.256	-0.126	0.901*		
NIS	0.005	0.255	0.287	0.304	0.403	0.553*	0.628*	
ZNS	0.018	0.470	0.464*	0.450*	-0.422	0.633*	0.761*	0.520*
ZONE 3 (Edo/Bata)								
CDS	0.066							
CRS	0.675*	0.022						
CUS	0.603*	-0.310	0.926*					
FES	-0.216	-0.339	-0.592*	0.456*				
PBS	-0.604*	-0.049	-0.388	-0.247	0.032			
MNS	0.512*	-0.053	-0.377	0.226	0.138	0.955*		
NIS	0.016	0.420	-0.014	-0.126	-0.202	0.353	0.350	
ZNS	-0.200	0.034	-0.183	-0.109	0.053	0.621*	0.681*	0.270
ZONE 4 (Brewery)								
CDS	-0.055							
CRS	0.556*	0.275						
CUS	-0.564*	0.054	-0.622*					
FES	0.257	0.020	0.017	-0.130				
PBS	-0.498*	0.043	-0.709*	0.590*	-0.168			
MNS	-0.506*	0.112	-0.756*	0.742*	-0.104	0.920*		
NIS	0.273	0.014	-0.250	0.208	-0.250	0.589*	0.416	
ZNS	-0.375	0.110	0.498*	0.320	-0.63	0.928*	0.804*	0.510*

CDW - Cd in water; CRW - Cr in water; CUW - Cu in water; FEW - Fe in water; MNW - Mn in water; NIW - Ni in water; PBW - Pb in water; ZNW - Zn in water; CDS - Cd in sediment; CRS - Cr in sediment; CUS - Cu in sediment; FES - Fe in sediment; MNS - Mn in sediment; NIS - Ni in sediment; PBS - Pb in sediment; ZNS - Zn in sediment. Asterisks indicate statistically significant correlations ($P < 0.05$).

On the basis of season, the highest concentrations of Cr, Mn and Ni in sediments were recorded at the Brewery during the rainy season while the

highest concentrations of Cd, Cr, Cu and Ni were recorded in the same zone during the dry season.

The lowest concentrations of Cd, Cr, Fe, Mn and Ni in sediments were recorded at the Bridge during the rainy season while the lowest concentrations of Cd, Cr, Fe and Ni were recorded in the same zone during the dry season (Table 2).

Temboga and Edo/Bata are zones with intermediate metal concentrations. No significant differences ($P > 0.05$) were observed between the concentrations of metals in the sediments obtained at the various zones during the two seasons of sampling (Table 2). This study shows that Ni appears to be the only metal whose bioavailability is dependent on rainfall.

Discussion

The high mean metal concentrations recorded in the bottom sediments compared to water conforms with previous reports (Gibbs 1977; Ezemonye 1992). The relatively high mean concentrations of Fe and Mn recorded at Temboga may be attributable to the low water pH and dredging operations in the zone as previously reported by Oguzie (1999). Metal enrichment of sediment compared to water is reflected by the sedimentation of metals ions when they compete with H^+ ions for sorption sites in the aquatic environment. The physical process of dredging in the zone could help the release of pore solutions rich in heavy metals into the sediment as reported for Canadian waters by Sly (1977). These metals according to Edginton & Callender (1970) and Chao (1977) have high content of detrital mineral bonds and form complexes that precipitate at river bottom.

The high Zn value recorded in the sediment at Edo/Bata compared to corresponding values in sediments of other zones might suggest the influx of animal dung, excreta and waste from slaughter and poultry set-ups located in the zone. Zn is a product of animal food that is concentrated in excreta which could be flushed into water bodies where they settle in bottom sediments (Forstner & Prosi 1979).

Moderate enhancement of Cd, Cr, Cu and Ni in the sediment obtained at the Brewery may be explained in terms of the relatively high percent organic content of the sediment which according to Oguzie (1996), has a characteristic muddy texture caused invariably by the degradation of brewery products by aquatic insect larvae and tubificid worms.

Sediment samples obtained at the Bridge had the highest mean value of Pb. This suggests the predominance of Pb compounds present in gasoline, fumes from high vehicular traffic and industries in this zone. The burning of gasoline, fossil fuel and open air incineration of refuse were reported by Lagerweff & Specht (1970) as sources of Pb in urban aerosols and roadside dusts that are invariably flushed into the aquatic environment through run-off water and atmospheric precipitation.

The clear trend in the distribution of metals (Fe, Cd and Cr) in the sediment and water suggests strong interactions between these metals. The observed higher concentrations of heavy metals in the sediment and water at the various zones during the dry season than during the rainy season suggests the possible dilution effects by run-off and river water on heavy metals during the rainy season. However, the predominance of Ni in the sediment and water during the rainy season in the present study conforms to earlier studies on the seasonal variations of heavy metals including Ni in the Warri river (Egborge 1991).

The mean concentration values of heavy metals in the lower Ikpoba river sediments are lower than values reported for sediments obtained from the Niger delta by Kakulu & Osibanjo (1988) and those of the Lagos lagoon sediments (Okoye et al. 1991). These low concentrations of heavy metals in the sediments suggest that the river has not yet been subjected to anthropogenic heavy metal contamination as Niger delta and Lagos lagoon.

References

- Adams, T.G., G. T. Atchison, & R.J. Velter 1980.
The impact of an industrially contaminated lake on heavy metal levels in its effluent stream. *Hydrobiologia* 69: 187-193.
- Allen, S.E. 1989.
Chemical Analysis of Ecological Materials. Blackwell Scientific Publications, Oxford. 368 pp.
- Chao, L.L. 1977.
Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. *Proceedings of the American Soil Science Society* 36: 764-768.
- Duncan, D.B. 1955.
Multiple range and multiple F-test. *Biometrics* 11: 1-42.
- Edginton, D.H. & E. Callender 1970.
Minor element geochemistry of Lake Michigan Ferromanganese nodules. *Earth Planets Science Letters* 8: 97-100.
- Egborge, A.B.M. 1991.
Industrialization and heavy metals pollution in Warri river. 32nd inaugural lecture, University of Benin, Benin City 1-26.
- Ezemonye, L. N. 1992.
Heavy metal concentration in water, sediment and selected fish fauna in Warri river and its tributaries. Ph.D. Thesis, University of Benin, Benin City.
- Forstner, V.F. & F Prosi 1979.
Heavy metal pollution in freshwater ecosystems, Biological aspect of freshwater pollution. pp. 129-169, *Proceeding of Joint Research Commission of Environmental Communication*, Ispra, Italy,

Heavy metals in sediments of a river

- Gibbs, R.J. 1977.
Mechanism of trace metal transport in rivers. *Science* 180: 71-73.
- Kakulu, S.E. & O. Osibanijo 1988.
Trace heavy metal pollutional studies in sediments of the Niger Delta area of Nigeria. *Journal of the Chemical Society of Nigeria* 13: 9-15.
- Lagerweff, J.V. & A.W. Specht 1970.
Contamination of roadside soil and vegetation with Cd, Ni, Pb, Zn. *Environmental Science and Technology* 10: 483-586.
- Moore, J.W. & D.L. Sutherland 1981.
Distribution of Heavy metals and Radio nuclides in sediments, water and fish in an area of Great Bean Lake contaminated with mine waste. *Archives Environmental Contamination and Toxicology* 10: 324-338.
- Ndiokwere, C.L. 1984.
An investigation of heavy metal content of sediments and algae from the River Niger and Nigerian Atlantic coastal water. *Environmental Pollution (B)* 7: 247- 254.
- Oguzie, F. A. 1996.
Heavy metals in fish, water and effluents of the lower Ikpoba river in Benin. Ph.D. thesis, University of Benin, Benin City, Nigeria 153 p.
- Oguzie, F. A. 1999.
Variation of the pH and heavy metal concentrations in the lower Ikpoba river in Benin City, Nigeria. *African Journal of Applied Zoology* 2: 13-16.
- Okoye, B.C.C., O.A. Afolabi & E.A. Ajao 1991.
Heavy metals in the Lagos lagoon sediments. *International Journal Environmental Studies* 37: 35-41.
- Piper, C.S. 1944.
Soil and Plant Analysis. Inter-Science Publishers, Inc. New York.
- Sly, P.G.A. 1977.
A report on studies of the effects of the dredging and disposal in the Great Lake with emphasis on Canadian waters. *Science Series*. C.C.I.W., Burlington. 1-38.
- Tada F. & S. Suzuki 1982.
Adsorption and desorption of heavy metals in bottom mud of urban rivers. *Water Research* 16 (10): 1489-1494.

Appendix 1. Concentration values of heavy metals (mg/l) in water at the 4 zones sampled. Figures in parentheses are zone identification numbers shown in Fig. 1. Mean values in each row and column with the same superscript are not significantly different ($P>0.05$); * Zone with the highest concentration of a particular metal; DS - Dry season; RS - Rainy season. Source: Oguzie (1996).

Heavy metals		Tembosa (1)	Bridge (2)	Edo/Bata (3)	Brewery (4)
Cd	DS	1.09	0.95	0.89	1.29
	RS	0.645	0.47	0.79	0.38
	Mean	0.80 ^{bc}	0.63 ^c	0.83 ^{bc*}	0.68 ^{bc}
Cr	DS	0.47	0.36	0.64	0.44
	RS	1.64	0.28	0.35	0.53
	Mean	0.59 ^{c*}	0.34 ^c	0.54 ^c	0.50 ^c
Cu	DS	1.36	1.40	0.80	1.16
	RS	1.44	1.24	1.07	1.29
	Mean	1.41 ^{b*}	1.30 ^b	0.98 ^{bc}	1.25 ^b
Fe	DS	5.13	4.00	4.72	3.79
	RS	4.78	2.76	4.03	3.49
	Mean	4.61 ^{a*}	3.17 ^a	4.26 ^a	3.59 ^a
Pb	DS	0.82	0.72	0.84	0.44
	RS	0.83	0.92	1.00	1.01
	Mean	0.83 ^{bc}	0.85 ^{ab}	0.95 ^{bc*}	0.82 ^{bc}
Mn	DS	4.83	5.52	2.55	2.83
	RS	4.58	2.46	1.65	2.39
	Mean	4.70	3.60 ^a	1.95 ^{ab}	2.54 ^{ab}
Ni	DS	1.14	1.40	2.12	2.61
	RS	2.14	1.93	2.36	2.28
	Mean	1.81 ^{ab}	1.75 ^{ab}	2.28 ^{ab*}	2.44 [*]
Zn	DS	1.52	1.71	1.67	0.80
	RS	0.94	1.04	1.37	1.02
	Mean	1.14 ^b	1.27 ^b	1.47 ^{b*}	0.95 ^{bc}