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SPATIAL VARIATIONS IN THE CONCENTRATIONS OF SOME METALS IN SEDIMENT OF THE GREAT KWA RIVER, CALABAR, NIGERIA

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ABSTRACT

Spatial variations in the concentrations of some heavy metals (Cadmium) (Cd), Lead (Pb), Chromium (Cr), Nickel (Ni), Copper (Cu), Zinc (Zn), and Manganese (Mn) in some portions of the sediment of the Great Kwa River, Calabar, Nigeria were investigated using Atomic Absorption Spectrophotometer. The mean concentrations of the metals in the three stations investigated revealed the following results: Esuk Ekpo Eyo among the seven metals assessed, Manganese (0.043 $\pm$ 0.004) mg/g was the least in concentration while Lead (0.142 ± 0.046) had the highest in concentration. Esuk Atu recorded heavy metal values in the range of 0.036 ± 0.004 mg/g and 0.144±0.047 mg/g for Manganese and Lead (Pb) respectively. At Esuk Orok the concentration of Lead (0.144±0.047 mg/g) did not differ from the value obtained in station 2 and was still the highest while Manganese still remained the lowest in concentration (0.034 ± 0.004mg/g). There was no significant difference ($P \geq 0.05$) in the values obtained between the metals. The high levels of Cd, Pb, Cr and Ni in the sediments were potentially high in all stations indicating increase in anthropogenic activities around the river locality. Cu, Zn and Mu concentrations were below WHO standards for river sediments while the concentrations of Cd, Pb, Cr and Ni were higher than the recommended values. Monthly variations in the levels of metals were also visible. Pb and Ni were below detectable levels in September while others varied in amounts in other across months. Heavy metals pose serious health threats to life forms even at minute concentrations. The deleterious effects of these metals after long periods of accumulation in aquatic foods cannot be ruled out. It is therefore recommended that all anthropogenic activities which could result in the release of metals into the great Kwa River be prohibited. This will reduce the potential risks on the environment and humans and guarantee the safety of lives and the environment in the long run. Regular monitoring of metal concentrations in the river sediment, water benthos and fish species is equally recommended.

Keywords: Spatial, Variations, Concentrations, Metals, Sediment, Great Kwa River, Calabar, Nigeria

1. INTRODUCTION

Heavy metals exist in water as colloidal particulates and dissolved forms (Adepoju-Bello and Alabi, 2009). Their occurrence in water bodies and sediment are either of natural origin (eroded minerals within sediments, leaching off deposits and volcanism-extruded products) or anthropogenic origin (solid waste disposal, industrial or domestic effluents, harbor channel dredging), (Udosen *et al.*, 2004). Metals pollution and its management has been a major global concern for environmentalists due to their non-biodegradable and hazardous nature.

When heavy metals are accumulated in river sediments at levels above the tolerable limits for aquatic organisms, they become a threat to the organisms, particularly aquatic molluscs, aquatic macrophytes and fishes that derive a greater chunk of their food from sediments. Heavy metals being non-biodegradable can persist in the environment and may become concentrated up to the food chain (Eja *et al.*, 2003), leading to enhanced levels in liver and muscle tissues of fishes, molluscs, (Udofia *et al.*, 2009), aquatic bryophytes (Romeo *et al.*, 2008) and other aquatic biota. This therefore, is an indication that the sediment and water quality of an aquatic ecosystem could determine the qualitative and quantitative levels of heavy metals in tissues of flora and fauna of the ecosystem.

Studying heavy metals distribution and bioavailability in both sediments and the overlying water column is necessary to have a better understanding of interactions between the organisms and their environment. Sometimes (organic or particulate matter of fine grain sizes that is obtained from erosion of surface soil which settles to the bottom of the riverbed) form a significant source of heavy metal pollution in the aquatic environment as a result of changes in pH, redox potential, digenesis of physical perturbation within their primary sedimentary sinks (Akan, *et al.*, 2010).

A high concentration of heavy metals in sediments will invariably increase the volume of suspended sediments and this will in turn reduce light penetration, thereby suppressing the photosynthetic activities of algae, planktons and macrophytes. The occurrences of enhanced concentrations of heavy metals especially in sediments may be an indication of human-induced perturbation (a second influence on a system that causes it to deviate slightly) rather than natural enrichment through geological weathering (Eja *et al.,* 2003; and Akan *et al.,* 2010).

Sediments are ecologically important components of the aquatic or marine habitat; it plays a significant role in maintaining the trophic status of any water body. Sediments near urban areas commonly contain high levels of contaminants, which constitutes a major environmental problem faced by many anthropogenically impacted aquatic environments (Marcovecchio *et al.,* 2007). As reported by Shuhaimi (2008), sediments in river do not only play important roles at influencing the pollution but act also as both carrier and sources of contaminant in aquatic environment. The contamination of sediments with heavy metals may lead to serious environmental problem. Heavy metal may adsorb onto sediments or are accumulated by the benthic organisms; their bioavailability and toxicity depends upon the various forms and amount bound to sediment matrices (Chukwujindu *et al.,* 2007).

According to Chukwujindu *et al.,* (2007), pollutants released to surface water from industrial and municipal discharges, atmospheric deposition and run off from agricultural, urban and mining areas can accumulate to harmful levels in sediments. The Great Kwa River runs through farmlands, industrial, commercial and recreational areas such as obufa Esuk, Esuk Atu, Calabar Free Trade Zone, Teaching Hospital, University of Calabar, Satellite Town and Peri-urban areas before it finally empties into Calabar Estuary. Calabar Municipality has no waste treatment facilities, and heavy rains wash human and industrial wastes into the river. Despite increasing anthropogenic influences due to the rapid development of Calabar town in recent times, there is dearth of information regarding the concentrations of metals in the benthos and sediments from the Great Kwa River (Okorafor *et al.,* 2015). This research was aimed at determining spatial variations in the concentrations of some metals in sediment from the Great Kwa River, Calabar, Nigeria. The results obtained were compared to the World Health Organisation (WHO) benchmark to ascertain whether the metals exceeded the threshold limits in the sediment.

2. MATERIALS AND METHODS

2.1 Description of the Study Area

The Great Kwa River is located between latitude $4^0$15” and $4^0$48” North of Equator and longitude $8^0$05” and $8^0$30” East of Greenwich meridian (Eja *et al*., 2003). The river originated from the Oban Hills and has an estimated length of 56km and is about an average of 280m wide. At the Calabar Estuary where the river empties into the Atlantic Ocean, its spreads to cover about 2.8 km (Eja *et al*., 2003). The river is known for a fall along its course known as Kwa fall in Cross River National Park. Its basin spans the Oban Hills (part of the Cross River National Park) and the eastern part of Calabar City (Eja *et al.,* 2003). The climate here is characterized by a long wet season of between April and October yearly (seven months), while the dry season lasts from November to March (five months). The shorelines are lined with mud plates which are exposed during low tides and submerged during high tides; the banks are surrounded by heavy rain forest formation with different species of plants predominantly palm trees, shrubs and grasses.

2.2 Sampling Stations

The samples for the study were collected from three different sampling stations along the length of the Great Kwa River. These stations (which were labeled S1 – S3) were chosen to provide for even spread and to allow for possible generalization to be made about the Great Kwa River.

2.2.1 Station 1 (S1):

This was located at Esuk Ekpo Eyo commonly called Akpabuyo beach by the residents of Akpabuyo Local Government Area of Cross River State. It is situated between longitude $008^0$27’4.9”E and latitude $04^0$55’32.7”N. In this station there is a bridge across the river which allows passage of people and vehicles. The river is turbid. Grasses are found growing along the banks of the river. The distance between this station (S1) and station 2 (S2) is 3 km. The major human activities in this station include sand mining, boat building and fishing.

2.2.2 Station 2 (S2):

This station is called Esuk Atu by the native people. It lies between longitude $008^0$22’00.9”E and latitude $04^0$57’37.3”N. It is close to the permanent site of the University of Calabar Teaching Hospital, some metres away from the Biological Sciences block in University of Calabar. This station spans 2.5km from station 3 and the bed of the river is covered by coarse sand and mud. The vegetation here includes palm trees, elephant grasses and fan palm (*Hyphaene petersiana*). Human activities here are mainly artisanal fisheries and small scale farming. Wastes drained from University of Calabar and the Teaching Hospital is washed into the river at this station.

2,2,3 Station 3 (S3):

This station is called Esuk Orok by the natives living in the area. Esuk Orok is located between longitude 8^0 21'07.7"E and latitude $4^0$56'37.0"N. This station is close to the University of Calabar staff quarters. It is about 2.5km from station 2. Vegetation cover is basically made up of grasses, fan palms (*Hyphaena petersiana*) and Nypa palms. Human activities include small scale farming and artisanal fisheries. Wastes from University of Calabar Staff Quarters and hostels are drained into the river at this station.

2.3 Sample Collection

Sediment samples were collected from the three sampling stations (S1, S2 and S3) using core sampler between the months of June through September, 2014. Sampling was done once a month. The sediments were collected within a depth of 5cm and were put into transparent cellophane bags and taken to the laboratory in an ice-packed cooler. All the samples were packaged and labeled separately.

2.4 Analysis of Samples

All samples were placed in a petri-dish, labelled accordingly and oven dried at 80°C. The dried samples were then ground in glass mortar and pistil to very fine particles. The method of Zheljazkov and Nielson (1996) was adopted for Nitric acid digestion [with slight modification by Hseu (2004)] for the digestion of the sediment samples. Each digested sample was analyzed for Cu, Zn, Cr, Mn, Pb, Cd, and Ni using Atomic Absorption Spectrophotometer (AAS) model VGP 210. During the analysis, three (3) readings were recorded. This is because atoms fluctuate and are never stable. The mean and standard deviation of the three readings were calculated and recorded.

3. RESULTS

3.1 Mean Concentrations of Heavy Metals in Sediment Samples Across Stations

The mean concentrations of heavy metals in sediment across stations are shown in Fig.2. At S1, among the seven metals assessed, Manganese (0.043 ± 0.004) mg/g was the least in concentration while Lead (0.142 ± 0.046) was the highest in concentration. Station 2 (S2) recorded heavy metal values in the range of 0.036 ± 0.004 mg/g and 0.144±0.047 mg/g for Manganese and Lead (Pb) respectively. At S3, the concentration of Lead (0.144±0.047 mg/g) did not differ from the value obtained in station 2 and was still the highest while Manganese still remained the lowest in concentration (0.034 ± 0.004mg/g). Assessment of the levels of individual metals per station revealed that Cd recorded the highest concentration value (0.138 ± 0.44 mg/g) in S1 and the lowest concentration value at S3 (0.123 ± 0.45 mg/g). Pb was higher at S2 and S3 (0.144 ± 0.047) mg/g respectively when with 0.142 ± 0.046 mg/g at S1. Cr recorded the highest concentration values at S2 (0.123 ± 0.023mg/g) and lowest concentration at S3 (0.102 ± 0.016mg/g). The highest concentrations for Ni, Zn and Mn were recorded at S1 while the highest concentration of Cu was recorded at S3. The lowest concentrations of Ni, Cu, and Zn were recorded at S2 while the lowest concentration of Cu was recorded at S2. The lowest concentration of Mn was recorded at S3 0.034 ± 0.004(mg/g). However, the mean values of all the metals assessed did not differ significantly between the metals and within the three stations.

3.2 Concentrations of Heavy Metals in Sediment Samples across Months and Stations

The concentration levels of metals across months and across stations is shown in Table 1. In station 2, Cd level was highest in June (0.392±0.005) mg/g and lowest in August (0.024±0.005) mg/g. in the month of September Pb was below detectable limit (BDL) in all the three stations assessed, however, raised levels were detected in June at S3 where it was highest (0.331±0.004)mg/g. Cr level was highest in June and July at S1 (0.171±0.001) mg/g and was below detectable limit (BDL) in September at S2. Ni level was highest in July at S1 (0.081±0.023) mg/g and was below detectable limit (BDL) in June and September at all the stations. Cu level was highest in July at S3 (0.156±0.010) mg/g and lowest in August at S3 (0.040±0.009) mg/g. Zn level was highest in September at S3 (0.129±0.009) mg/g and lowest in September at S2 (0.012±0.010) mg/g. Mn level was highest in September at S1 (0.054±0.005) mg/g and lowest in July at S1 (0.026±0.006) mg/g.

4. DISCUSSION

Aquatic systems are polluted through anthropogenic activities with chemical pollutants from domestic, agricultural and industrial wastes, which are finally absorbed by aquatic plants and animals (Okorafor *et al.*, 2015). According to Omoregie *et al.*, (2002), heavy metal pollution in aquatic systems is an important environmental problem, since heavy metals are among some of the most dangerous toxicants that bio-accumulate in aquatic plants and animals tissues. Results obtained from this study show that heavy metals including Cd, Pb, Cr, Ni, Cu, Zn and Mn were present in sediments from the three sampling stations of the Great Kwa River. The implication of these findings is that is is likely that, these heavy metals have bio-accumulated in high concentrations in the tissues of plants and animal of this environment. Otitoloju and Otitoloju (2013) reported that the consumption of food such as fish with high levels of heavy metals such as Pb can induce convulsion, abdominal pains, drowsiness, vomiting, kidney and reproductive system malfunctions in humans. In pollution studies, sediment quality is used as an indicator to check contamination as it provides a deeper insight into the long-term pollution state of the aquatic environment (Andem *et al.*, 2015). Sediment being the loose sand, clay, silt and other soil particles which settle at the bottom of body of water (Davies and Abowei, 2009) is a major habitat and major nutrient source for aquatic organisms such as fish, micro-invertebrate and macro-invertebrates (Olubunmi and Olurunsola, 2010). Onyari *et al.*, (2003) described sediments as a ready sink of pollutants where they concentrate according to the levels of pollution. The occurrence of heavy metals such as Cd, Pb, Cr, Ni, Cu, Zn and Mn in the sediments of the Great Kwa River may be attributed to domestic, industrial and farming activities on the shores of the river. The pesticides and other agrochemicals which the farmers use to increase productivity in farms bordering the area may have impacted the river. Heavy metals contamination of the Great Kwa River sediments obtained in this study were in the following order: Mn<Ni<Cu<Zn<Cr<Cd<Pb. Andem *et al.*, (2015) reported the following order (Hg<Co<Zn<Mn<Pb Fe<Ni) for trace metals in the surface sediment of Ona River, Western Nigeria. The difference in the metal content and concentrations in these two rivers may be indicative of the variations in the anthropogenic activities that go on in the vicinity of the rivers.

The values obtained for Pb, Cd, Cr, Zn, Cu, Ni and Mn in this study for the three stations were not significantly different ($P>0.05$). The levels of Cd, Pb, Cr and Ni in the sediments were high in all the stations indicating an increase in the anthropogenic activities in the river locality. Cu, Zn and Mn concentrations recorded in this study were below WHO average levels for river sediment while the concentrations of Cd, Pb, Cr and Ni were higher than the recommended benchmark. Concentration of lead (Pb) was highest in the Great Kwa River sediments and is of serious environmental concern. Andem *et al.*, (2015) explained that age among humans remains a major factor in determining the extent of Pb absorption. Pb gain access into children's bloodstream more than the adults when Pb-contaminated fish is consumed. This, they attributed to the higher rate of detoxification (≈99%) of the metal in adult. Cadmium which recorded second in the order of metal dominance in this study and was present in all the samples in higher concentration when compared with Cd found in sediments from Abuloma River (0.118 mg/kg) and Itu River (0.106mg/kg) as reported by Otitoloju and Otitoloju (2013). Jarup (2003) attributed this to pollutants from industrial and agricultural processes. He asserted that bioaccumulation of Cd results in kidney damage and can also cause a disease condition known as Osteomalacia.

The variability and distribution pattern of heavy metals from one location to another may be due to variation and the volume of the anthropogenic activities, as well as the geological distribution of minerals from one location to the other. This observation is similar to findings of other authors such as Okorafor *et al.*, (2014) in sediments of Akpe Yafe River; Adefemi *et al.*, (2007) in sediment of Major Dams in Ekiti State; Otitoloju and Otitoloju (2013) for Abulomja and Itu River. The concentrations of heavy metals also varied between months, for instance, Pb and Ni were below detectable levels in September. This could be attributed to dilution by rainwater which influences concentrations and heavy metal mobility.

5. CONCLUSION/RECOMMENDATION

Data from sediments of the Great Kwa River has provided information on the impact of different human activities on the river. This research has presented the levels of heavy metals in sediments from the Great Kwa River, Calabar. Heavy metals concentrations show some form of danger posed to aquatic organisms and consumers of aquatic foods and water from the river. Therefore, the possible deleterious effects of these metals after long period of accumulation in aquatic foods cannot be ruled out.

Anthropogenic activities which could result in inputs of metals into the Great Kwa River should be prohibited in order to avoid possible deleterious effects after long periods of accumulation. This will reduce potential environmental and human health risks, as the prolonged exposure to these metals could lead to health complications. Prolonged consumption of high quantities of aquatic foods from the Great Kwa River could pose some health risks, therefore regular monitoring of metals concentrations in the river sediment, water, microphytes, macrophytes, benthos and fish species could be useful and activities around the river should also be monitored to reduce the influx of heavy metals into the river.

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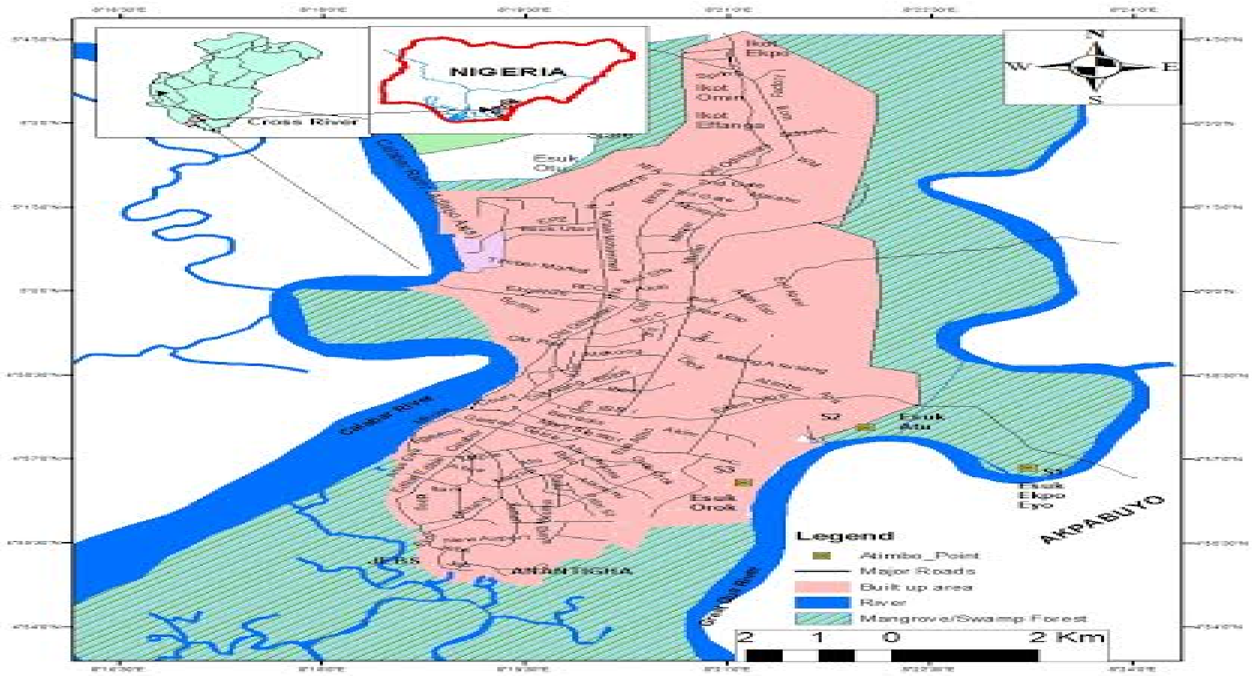

Figure 1: Map of Great Kwa River showing sampling stations

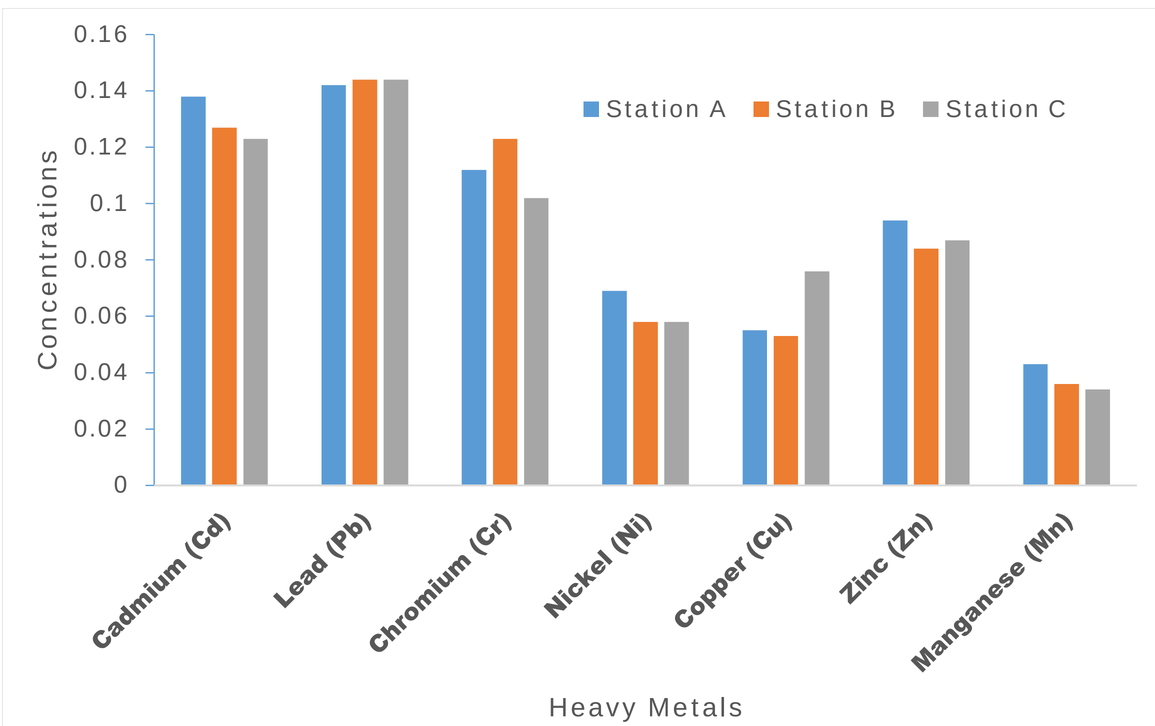

Figure 2: Mean concentrations of heavy metals in sediment samples across stations of the Great Kwa River

Table 1: Mean monthly concentrations of heavy metals in sediments samples from the Great Kwa River

Months	Heavy metals (mg/g)	Sampling Stations		
		S1 (Esuk Ekpo Eyo)	S2 (Esuk Atu)	S3 (Esuk Orok
June	Cd	0.390 ± 0.003	0.392 ± 0.005	0.380 ± 0.002
	Pb	0.325 ± 0.003	0.330 ± 0.001	0.331 ± 0.004
	Cr	0.171 ± 0.001	0.154 ± 0.043	0.151 ± 0.018
	Ni	BDL	BDL	BDL
	Cu	0.055 ± 0.01	0.051 ± 0.008	0.154 ± 0.118
	Zn	0.028 ± 0.002	0.031 ± 0.005	0.025 ± 0.008
	Mn	0.045 ± 0.004	0.035 ± 0.008	0.032 ± 0.012
July	Cd	0.050 ± 0.010	0.043 ± 0.010	0.031 ± 0.004
	Pb	0.063 ± 0.003	0.480 ± 0.006	0.050 ± 0.002
	Cr	0.171 ± 0.023	0.154 ± 0.043	0.151 ± 0.018
	Ni	0.081 ± 0.008	0.065 ± 0.005	0.065 ± 0.008
	Cu	0.049 ± 0.017	0.059 ± 0.007	0.156 ± 0.010
	Zn	0.109 ± 0.017	0.088 ± 0.029	0.118 ± 0.004
	Mn	0.026 ± 0.006	0.028 ± 0.007	0.031 ± 0.004
August	Cd	0.038 ± 0.007	0.024 ± 0.005	0.038 ± 0.007
	Pb	0.039 ± 0.007	0.054 ± 0.006	0.050 ± 0.002
	Cr	0.060 ± 0.005	0.063 ± 0.004	0.067 ± 0.009
	Ni	0.056 ± 0.008	0.051 ± 0.005	0.052 ± 0.003
	Cu	0.052 ± 0.011	0.042 ± 0.011	0.040 ± 0.009
	Zn	0.080 ± 0.017	0.096 ± 0.011	0.080 ± 0.024
	Mn	0.043 ± 0.007	0.035 ± 0.010	0.043 ± 0.009
September	Cd	0.072 ± 0.005	0.050 ± 0.007	0.037 ± 0.005
	Pb	BDL	BDL	BDL
	Cr	0.044 ± 0.010	BDL	0.038 ± 0.003
	Ni	BDL	BDL	BDL
	Cu	0.062 ± 0.010	0.059 ± 0.006	0.053 ± 0.009
	Zn	0.0159 ± 0.03	0.012 ± 0.010	0.129 ± 0.009
	Mn	0.054 ± 0.005	0.046 ± 0.004	0.031 ± 0.008.

BDL = Below Detectable Level

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