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Seasonal variations of iron (Fe), copper (Cu), zinc (Zn), and lead (Pb) concentrations in selected surface waters of Enugu State of Nigeria

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Abstract

Fe, Cu, Pb, and Zn concentrations were determined using flame atomic absorption spectrometric method (FAAS) in Coal Camp, Asata, and Aria rivers found in Enugu urban in eastern Nigeria. The sampling areas were mapped and sites were chosen in the rivers at intervals of 300m. Analyses were done for four years (2005-2008). Physical assessment of the rivers prior to analyses show heavy dumping of metal scraps from a metal works/market (Tinker) village within the area. Results show average concentrations for Fe, Cu, Pb, and Zn for the four year period to be 0.21-2.66mg/L, 0.18-3.35mg/L, 0.10-1.50mg/L, and 0.18-2.11mg/L, respectively. Flame Atomic Absorption Spectrometric method (FAAS) was used for the analyses. Tolerance limit test at 95% coverage with 95% confidence revealed that only site-5 was free from pollution with these metals. Site-5 also shows negative correlations with the other sites. Normality assumption was not rejected for all the metals determinations, using Kolmogorov Smirnov (KS) test. Undoubtedly, there are strong evidences to believe that the rivers are polluted with Fe, Cu, Pb, and Zn metals.

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Introduction

Increased attention has been accorded to the protection of global water resources since the late 1960s. Awareness of the health effects of polluted water on humans and the increasing demands on the portable water supplies by the ever growing population of Enugu state of Nigeria elicited a much wider recognition of protection. In the developing world of which Nigeria is typical, one of the biggest problems is water scarcity, and the lack of clean supplies (Ekanem, 2007). There is hardly any regular supply of clean water to urban dwellers. When water is scarce, people have to make do with any water at all. In line with that, many people use river water as supplement or substitute for their various domestic needs of which drinking is one. Some of the Enugu city dwellers claim that they boil the water before using for drinking purposes. Granted that boiling may help in reducing the pathogen load of water, it often does not eliminate chemical pollutants such as metals (Dojlido and Best, 1993).

Heavy metals in water have been implicated for a vast many health issues in humans (Ali *et al*., 2005). Cu exposure at levels greater than 1.3ppm can cause gastrointestinal distress, liver and kidney problems, Wilson's disease and corrosion of household plumbing system (Khitoliya, 2004). Copper in association with cadmium, and mercury are known to bind to cell membranes, hindering transport processes through the cell wall. Fe pollution of water is known to come from industrial wastes, corrosion, acid mine water, and microbial action. Fe is essential nutrient but at high concentrations it may cause staining of plumbing fixtures (Nsi and Ogori, 2005). Chemically, Zinc is similar to cadmium and these two metals frequently undergo geochemical processes together (Ogunlaja and Ogunlaja, 2007). Zn and cadmium poisoning in humans come with serious health problems among which are high blood pressure, kidney damage, destruction of testicular tissue, and destruction of red blood cells. Lead poisoning in humans causes severe dysfunction in the kidneys, reproductive system, liver and the brain and central nervous system (Sharma, 2005). Lead is probably not a problem in drinking water, as old lead pipes are no longer in use now. However, rivers and streams receiving effluents from metal works village and domestic waste water are most likely targets for objectionable levels of lead. Coal camp river and its tributaries and recipients cannot run away from Pb contamination, as leaded materials are frequently used in the metal works village close to their banks (Abulude and Orungbemi, 2007).

This work profiles the concentrations of these metals in Coal Camp River over a four year period. This would provide indices for reliable assessment of impacts of these pollution problems and be used to make judgments on levels of impact to the people living in the area. Existing water pollution researches in Enugu area did not reflect any work in this river. Where any record exists, there is none that did yearly time series study to enable meaningful decisions to be taken regarding control.

Materials and methods

Mapping of study area

Two maps were developed for this work. The first map (map-1) shows the Aria area of Enugu urban towards the north, Ogbete residential area at the west and Uwani area at the south- east. The main river that passes through this area is river Asata. It has two tributary rivers (Ogbete and Akwata rivers) that originate in the precinct of Coal camp Ogbete area, flowing from west to east of the area. The river receives effluent from tinker metal works village, coal camp residential and motor mechanic area. It also receives pollutants from University of Nigeria teaching hospital (UNTH), Ogbete market, Eastern Nigeria Medical Centre, and CIC. All these institutes are within smelling distance of the river's bank. A total of three sampling sites were chosen for the area. Pollution indices as are shown on the map form the basis for the selection of the locations. The sampling locations are about 200-300m from each other. The second map (map-2) shows Ogui in the central/ west, G.R.A. in the north, New- haven in the north-east and Independence layout in the south- east. Aria River originates from the north west of this area and eventually joins Asata River at a confluence near Otigba junction. The two rivers continue as Asata River somewhere into Nyaba River. The river receives effluents from Aria market, Obiagu residential area, New- haven residential area and Artisan goat market. Sampling points were also chosen at intervals of 200-300m.

Table 1. Mean concentrations (mg/L) of Cu in the various sites (four replicates).

year	Site-1	Site-2	Site-3	Site-4	Site-5	Site-6
2005	3.42	0.87	4.24	2.86	0.16	1.44
2006	2.42	0.18	3.22	2.03	0.24	1.46
2007	2.75	0.34	2.84	2.44	0.18	2.21
2008	2.96	0.40	3.11	4.16	0.15	2.11

Table 2. Mean concentrations (mg/L) of Fe in the various sites (four replicates).

year	Site-1	Site-2	Site-3	Site-4	Site-5	Site-6
2005	3.80	4.00	4.21	2.86	0.33	1.22
2006	1.18	0.42	1.44	0.23	0.18	1.34
2007	1.88	0.68	2.45	1.49	0.13	1.62
2008	1.86	2.38	2.55	2.03	0.21	2.86

Table 3. Mean concentrations (mg/L) of Zn in the various sites (four replicates).

year	Site-1	Site-2	Site-3	Site-4	Site-5	Site-6
2005	3.28	1.28	3.09	2.44	0.26	1.32
2006	1.47	0.46	1.34	1.08	0.14	1.33
2007	2.02	0.53	1.89	2.08	0.16	2.03
2008	1.67	1.22	1.72	1.55	0.15	1.37

Table 4. Mean concentrations (mg/L) of Pb in the various sites (four replicates).

year	Site-1	Site-2	Site-3	Site-4	Site-5	Site-6
2005	0.94	1.37	0.86	1.56	0..21	0.92
2006	0.32	0.18	0.42	0.38	0.11	0.36
2007	0.22	0.10	0.34	0.26	0.12	0.28
2008	036	0.24	0.33	0.27	0.40	0.32

Sampling

Samples were collected from each site within a week interval, the same time every month, from December 2004 - October 2008. The collection was done between 7.00hrs – 16.00hrs on the days of sampling. Observations of the sampling sites were made with respect to physical changes and activities during each visit. (Ademoroti, 2002).

Table 5. Upper 95% Parametric Tolerance Limits (mg/l).

Site	Cu	Fe	Pb	Zn
S1	6.11	9.91	5.10	7.20
S2	2.36	12.60	4.34	3.70
S3	7.30	10.04	2.11	6.88
S4	8.87	8.76	4.68	5.63
S5	0.084	0.18	1.08	0.10
S6	4.46	6.61	2.41	3.74
EU MPL	0.10	0.20	0.10	0.05

Samples were collected manually employing a 1-litre polythene beaker tied on a long twine and fitted with a concrete sinker. Four random samples per site were scooped near the surface of the river and stored in labelled 2-litre polythene bottles. The collected samples were delivered to the analytical laboratories for analysis, immediately from the day of the sampling (Ademoroti, 2002 and Kiely, 1998). Turbid samples were filtered through 0.45µm membrane immediately in the lab. Samples that were not analyzed on the same day of collection were stored in the refrigerator set at 4^{o}C. Appropriate preservatives were added to the sample in the event that it was not analyzed immediately (Hirsch et al., 1991). Water samples were digested with HNO_3: HCL (1:3) mixture, prior to AAS determination of the heavy metals.

Flame atomic absorption spectrometric determination of the metals

The raw water samples were first digested using HNO_3 and HCL mixture, and analyzed for Fe, Cu, Zn, and Pb, using Flame Atomic Absorption Spectrometric method (FAAS). The wavelength of the lamp discs used for the various metals are; 248nm, 324.7nm, 213.9nm, and 283.3nm, respectively for Fe, Cu, Zn, and Pb, (Nwaedozie, 1998).

Statistical treatment of data

The choices of sampling areas and sites were done with respect to the treatment of the data generated with statistical tests. For each sampling area a representative number of sampling sites were designed, and for each sampling site, random samples were taken for replication (Erin and Mark, 2002). The means of the replicates from each site for each year of analysis were used in designing the yearly means. In view of the fact that any statistical or mathematical model of actual data is an approximation of reality, all statistical procedure require certain assumptions for the method to be used correctly and for the results to have a proper interpretation. Two assumptions used in this work concern the distributional properties of the data and the need for equal variances among subgroups of measurements (Gilroy *et al.*, 1990 and Otti, 1993). For the distributional properties, the following tests for normality were used; Coefficient of Skewness, Shapiro-Wilk test, Kolmogorov-Sminov test and the probability plot correlation coefficient. For homogeneity of variances, Box plots were used. The various parameters determined were compared to EU standards for water with the sampling sites in view (Kiely, 1998).The idea was to check whether the assumption that the site is polluted with respect to the parameter is to be rejected or upheld. The test statistic for this analysis was the Tolerance interval test for an average of 95% coverage with 95% confidence. For all the data sets, Descriptive statistics was used to report the statistical properties of the data (Otti, 1993 and Andronachie and Xiang, 2006).

Results and discussion

Tables 1, 2, 3, and 4 show the mean concentrations of the metal ions over a four year period (2005-2008). Sites 1, and 2 are in Akwata and Ogbete rivers respectively. Sites 3, and 4 are in Asata river. Site 5 was selected from Aria river, and site 6 from a point where Aria river joins Asata river (maps 1, and 2). Cu results for the six sites were 0.33-4.01mg/L in 2005, 0.18-1.44mg/L in 2006, 0.13-2.45mg/L in 2007 and 0.21-2.86mg/L in 2008. Summary results for Fe are presented in table 2, that for Zn in table 3, and Pb in table 4. With respect to Fe, Cu, and Zn in 2005, sites 1, and 3 recorded the highest concentrations. Sites 1, and 2 are tributary to site 3, and they receives effluents from UNTH, Tinker metal works village, and also from Ogbete main market.

The high concentration of Zn may be due to the ZnO component of white paint used by traders working very close to the bank of the river Akwata (site 2). Traders use paints to make marks on their merchandise. There is noticeable metal works also near the river Ogbete (site 1), and good amount of Cu and Fe are expected to contaminate the river (Bassey and Odoh, 2004). Traders also make extensive use of hard nut-grinding machines whose washings form effluents that get to the river; hence heavy Fe contamination was expected in this river. The Fe result did support this. The monthly variations might be related to water flow, which is higher in the raining season than in the dry season (Akueeshi *et al.*, 2003). In the same 2005, Pb concentration was highest in site 4 located in Asata river. This site receives water from site 3. This high level of Pb might be coming from the metal works village and domestic effluents (Dike *et al.*, 2005). With respect to the heavy metals in 2006, only Cu, Fe, Pb, and Zn were detected at worrisome levels within the sampling areas. Sites 1 and 3 show particularly highest levels of these metals.

This is expected, going by the dumping of metal scraps from the Tinker coal camp (Neelima and Dilip, 2005). The levels are in disagreement with world standard for water. However, they were all lower than the results obtained the previous year. Site 5 (from Aria river) recorded least results with respect to all the metals.

In 2007, heavy metals were found in amounts that suggest pollution problem. Cu, Fe and Zn are particularly implicated, in this respect. Pb level did not pose any threat, but Pb exceeded 0.1ppm in

December, June, August and November. Since the results are averages for a given distance of the river, a clearer analysis of the level of Pb would be obtained from statistical consideration.

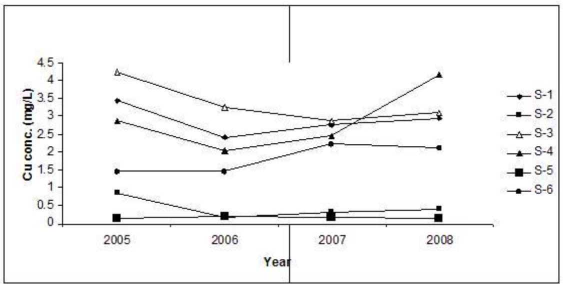


Fig. 1. Trends in Cu concentration at area 1.

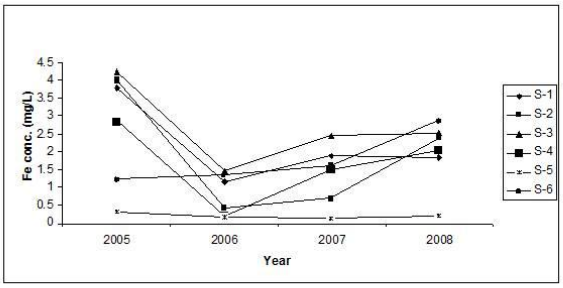


Fig. 2. Trends in Fe concentration at area 1.

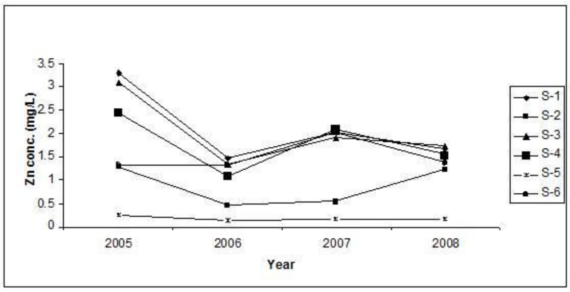


Fig. 3. Trends in Zn concentration at area 1.

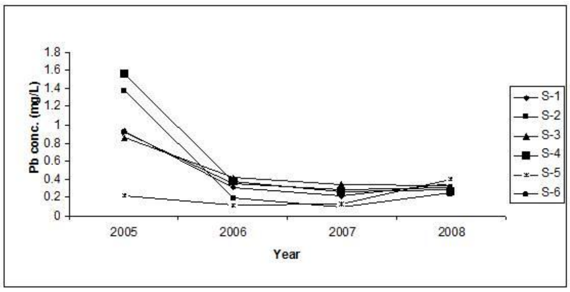
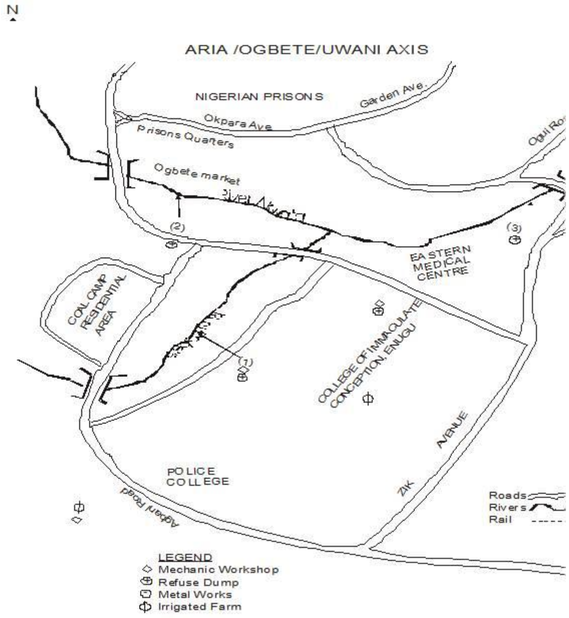


Fig. 4. Trends in Pb concentration at area 1.

At the beginning of the year 2008, the Enugu State Waste Management Authority (ESWAMA) had cleared the solid wastes dumped at various points of the rivers banks. Even though, the state government had introduced a better solid waste disposal option, and hence no more solid wastes were dumped at the rivers banks, the impact has yet to reflect on the pollution parameters. Cu, Fe, Pb, and Zn were detected at levels considered to be higher than acceptable level.



Map 1. Showing Ogbete and Akwata Rivers.

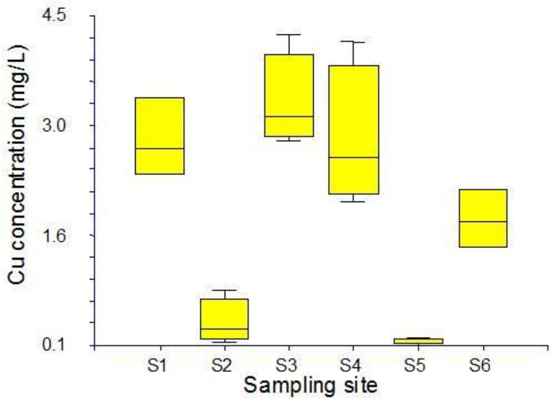
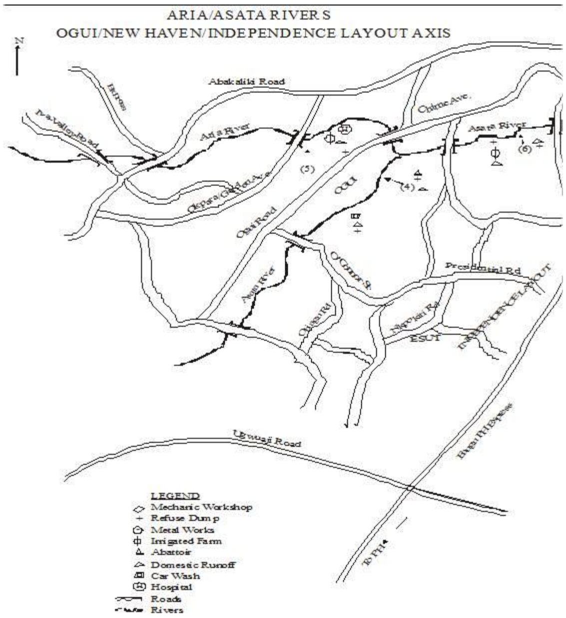


Fig. 5. Box plot for Cu concentration distribution.

From the statistical results for Cu in the analyses area (map1, and map 2), it is found that all the sites are positively skewed. However, the skewness coefficient of sites-1 and 6 are good while others exceeded '1' though, not so much to withdraw confidence in tolerance limit test (table V) (Otti, 1993). The sites are well correlated, except site-5, which had virtually negative correlation with other sites. This is understandable as site-5 come from a different catchment, and is only tributary to Asata river. Assumption of normality of the data was not rejected by (KS) test. Distributional properties was poor (fig 5), especially with respect to site5 and the other sites. Tolerance limit test (table V) reveal that all the sites are polluted except site-5 whose parametric upper tolerance limit of 0.084210 was lower than EU (MPL) of 0.1 (Kiely, 1998). Figure-1 shows the time plot for Cu in A-1. The trends for all the sites follow nearly regular pattern.



Map 2. Showing Asata and Aria Rivers.

The statistical results for Fe in the analyses area reveal that all the sites are positively skewed except site 4 which has a negative skewness. The sites are all well correlated except site-6 which has some negative correlation figures that are of highest severity with site-1 and site-5. Assumption of normality was yes for (KS) and no for (SW). Site 5 did not also follow good distribution with the other sites. This is shown in fig. 6. Tolerance limit test show that only site-5 is not polluted with Fe. Figure 2 shows the year by year trends, and there seems to be a well defined regular pattern in all the sites.

The statistical results for Zn in the analyses area show that the sites correlated with each other appreciably well, except with site-6. Normality of the data set was not rejected by the (KS) test; hence parametric tolerance limit test was performed. Results show that all sites except site-5 are polluted with Zn. Box plot (fig.7) upheld the assumptions of equal variances in the data, as the length of the boxes are not far from each other. Fig 3 shows the time series plot. Sites 1, 2, 3, and 4 show decreases in Zn concentration between 2005 and 2006, increases in 2007, and corresponding decreases by the end of 2008.

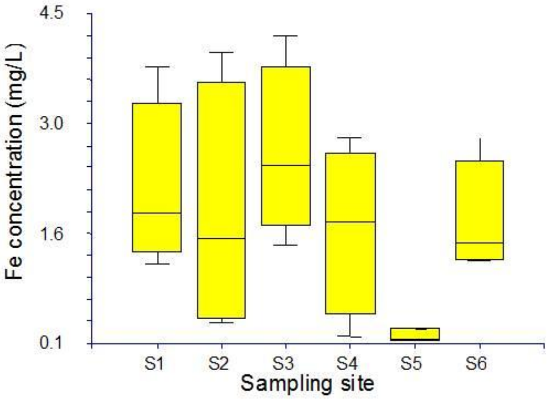


Fig. 6. Box plot for Fe concentration distribution.

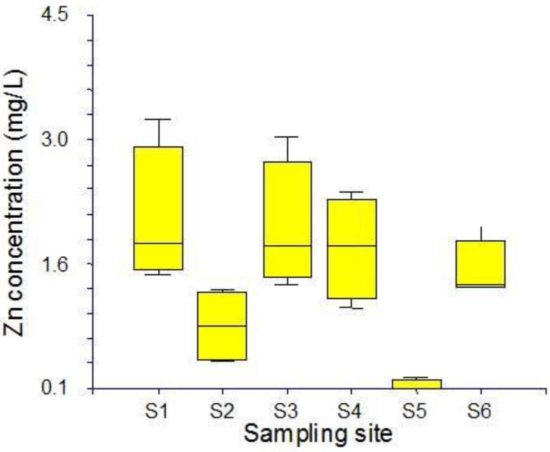


Fig. 7. Box plot for Zn concentration distribution.

Statistical test for Zn data show some significant difference for ten correlations and no significance for five correlations. The t-test at 5% of probability was applied and the related correlations are linear (Erin and Mark, 2002). SK and SW tests rejected normality hence no much confidence was placed on the tolerance limit test. Box plot (fig 8) supported this idea of non-normality as box lengths of site-2 and site 4 were more than three times the box length of site-5 (Andrnachie and Xiang, 2006). However, based on the tolerance limit test, at 75% confidence, all the sites are polluted with lead. Figure 4 shows the yearly trends in Pb concentrations. All the sites show decreases in Pb concentrations between 2005 and 2006. Between 2006 and 2008, there was negligible decrease in the amount of Pb in the water bodies. Site 5 showed slight increase in Pb concentration by the end of 2008.

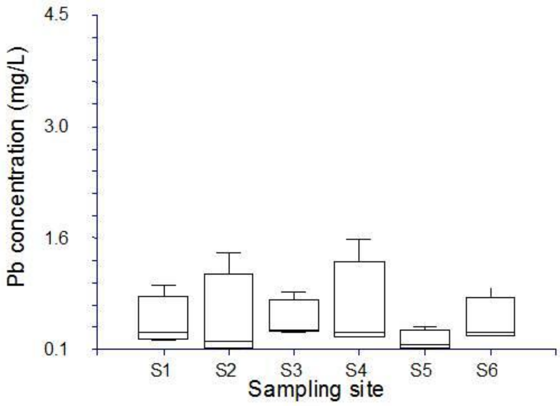


Fig. 8. Box plot for Pb concentration distribution.

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