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ACCUMULATION OF MERCURY IN SURFACE AND GROUNDWATER OF ANAMBRA STATE,

NIGERIA

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ABSTRACT

Anambra is a state in South Eastern Nigeria; it is the largest industrial city in south eastern Nigeria. 112 water samples were collected and analysed for elemental concentration of mercury using Atomic Absorption Spectrophotometer. Total mercury concentration in surface water was in range of 0.020 - 3.050mg/l and 0.000 - 0.0070mg/l in groundwater sources. Results further showed that 75% of surface waters in the state were enriched with mercury above the maximum permissible limit (MPL) whereas in the groundwater samples mercury concentrations detected were generally below the MPL.

Keywords: Accumulation, Mercury, Surface, Groundwater.

I. **INTRODUCTION**

Mercury presence in surface and groundwater bodies has long been identified as injurious to living organism and exposure to its organic form can cause damage to respiratory, neural and renal system (USEPA, 2012; WHO, 2012; Sadeeq et al., 2013). Sources of mercury are combustion facilities, municipal solid waste incineration, sewage sludge e.t.c. (Clarke, 2011; UNEP, 2002).

Exposure to mercuric compounds through oral, inhalational and dermal routes depends on the levels of toxicity (WHO, 2005; Vupputuri et al., 2005; Costa et al., 2012). In Nigeria, accumulation of mercury in the environment has been researched on. Gustin et al. (2008) noted that anthropogenic impacts with respect to mercury deposition is small compared to natural sources whereas Swain et al. (2007) and John (2013) noted that combustion of fossil fuels and coal burning amounts to 60% pollution. Mercury deposited in the atmosphere may be oxidized as Hg (II) and transformed to MeHg by bacterial activities at and below the sediment/ water interface (Baringer et al., 2013). Atmospheric deposition of mercury has been reported to influence concentration in groundwater sources. higher concentration of filtered mercury were noted by Bradley et al. (2012) in USA.

Industrialization has its own way of inducing mercury in water ways. Mercury is contained in most consumer products such as dry cell batteries, fluorescent light bubls and thermostats, paints, wood preservatives, dental amalgams e.t.c. (Barringer et al., 1997). Subsurface deposition of waste have shown to impart on mercury level in groundwater, products containing mercury often transfuse same in disposing medium hence the conscious attempts by countries in reducing consumption level of mercury by industries (Bradley & Journey, 2012). Industrial and sewage discharges imparts on surface and groundwater quality. Reports abounds on high mercury values of 1 - 18mg/l in water of wells near river Cooum in the Madras urban area of India, this value exceeds the India water quality guideline values of 1mg/l (Somasundaram et al., 1993).

Soil pollution from mercury industrial operation can also affect the quality of water of surface and subsurface sources. Bollen et al., (2008) reported mercury contamination of ground water at a concentration of 230mg/l.

Mercury as an environmental pollutant accumulates in aquatic organism and impacts negatively on health of consumers of organisms. A sizeable number of populace in Nigeria depends on aquatic organisms. High concentration of mercury has been detected in several aquatic species of rivers of many countries. Mercury concentration >10, 000 times value in water have been observed in some aquatic creatures (Ekpo et al., 2007; Galadima and Garba, 2012; Nartey et al., 2011). In freshwater ecosystem, bioaccumulation of mercury is by mercury methylation. Methylmercury (MeHg) is the most common organic form of mercury; it is a potent neurotoxin and biomagnifies in aquatic food web (Stavros et al., 2008; Wolfe et al., 1998; Guebert-Bartholo et al., 2011; Mason, 2012). The incidence of mercury pollution in these organisms further reveals the nature of the various aquatic biotas and hence calls for quick remediation measures.

Anthropogenic activities influences amount of total mercury in aquatic ecosystems; most rivers in Anambra state serves as sinks for most pollutants including mercury. High amount of rainfall in the region also implies continuous runoff of pollutant from various sources to sinks. Very few studies have been conducted on mercury in surface and groundwater in Nigeria and this has led to poor understanding of the fate of mercury in the country. This study was therefore conducted to determine the distribution of Total mercury in surface and subsurface water sources in Anambra state with a view to identifying potential sources of mercury pollution.

II. RESEARCH METHODOLOGY

Description of study area

Anambra is a state in South Eastern Nigeria with a total land area of 4,365square km^2 and a population of four million one hundred and eighty two thousand and thirty two people (4,182,032) (NBS, 2005). The state is bounded in the west by the river Niger, in the south by Imo state, in the east by Enugu state and in the North by Enugu and Kogi states. State lies between latitude 5°44'N and 6°48'N and longitude 6°37'N and 7°20'E. The state is dominated by the Anambra, Niger and Mamu river basins. Most of the rivers – Niger, Idemili, Anambra, Urasi and Mamu are perennial with flows varying from year to year and month to month, with low flow occurring between December and May. Some of the flood plains are endowed with ground water occurring at shallow depths.



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Anambra state is the largest industrial centre in south eastern Nigeria with major industries like mechanical, electrochemical, pharmaceutical and chemical. Climatologically, the mean annual rainfall of the area is about 1800mm, 90% of which is concentrated in the rainy season (Offodile, 2000). Temperature and sunshine hours have little variation throughout the year with mean values of temperature and sunshine hours estimated at average 6hrs respectively.

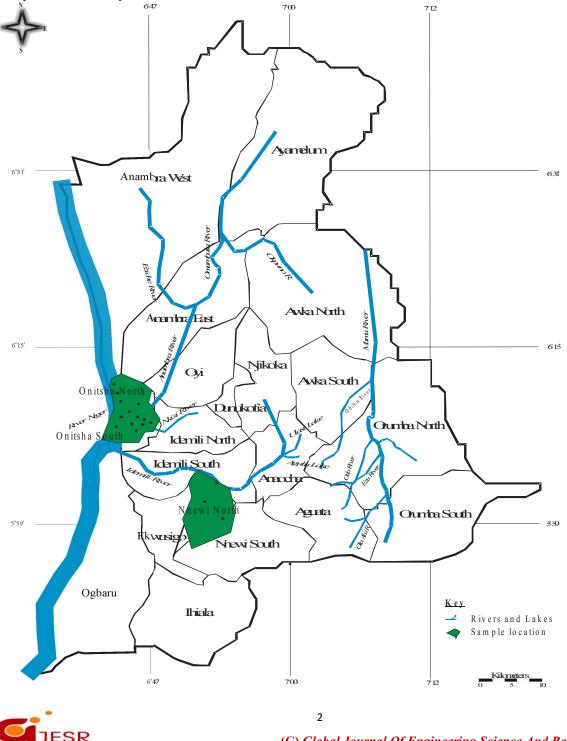
Sampling procedure

Samples of water were collected from 16 sites (rivers and bore wells). A total of six (112) surface and ground water samples were collected from two (2) major cities in the state: Onitsha and Nnewi (Fig. 1.0). Samples were collected using polyethylene bottles soaked with 10% nitric acid and rinsed with de-ionized water prior to use, and labeled indicating source. During course of research, 1 litre plastic sample bottles with screw caps were rinsed with sample water three times and then filled to the brim at a depth of 0.4m below the water surface from each of the sampled points whereas groundwater was collected after well was flushed thrice.

Analytical method

Mercury concentration of samples was determined with the use of UNICAM 969 model atomic absorption spectrophotometer (AAS). This method is based upon the absorption of radiant energy, usually in the ultra-violet and visible regions by neutral atoms in the gaseous state. Calibration was made with mercury standard HgNO₃ (Merch) and procedural blanks were run with each set of sample analysis. Filtration was employed in determination of trace metals in water samples. It involves separating suspended matter from the water with the aid of a cellulose acetate membrane filter of 0.45µm pore size. To avoid contamination from dust during sample preparation, a closed system was adopted for filtration.

Digestion was carried out with 10 ml concentrated nitric (65% HNO₃), heated on a water bath to 80°C for at least 45 min. The solution is removed from the water bath and allowed to cool at room temperature. After cooling the final content is transferred quantitatively to a 25 ml graduated flask and filled up to the mark with deionized water before transfer into bottle for AAS analysis (APHA, 1999). Analyses were conducted using the raw data obtained from the sample analysis. The obtained data were analyzed using SPSS v.18 for descriptive analysis. This provided useful information about water quality variation in sampled locations.



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Figure 1.0 Map Showing Anambra State with Sampled Locations.

III. RESULTS AND DISCUSSIONS

Some selected ground and surface water sources in study areas were tested for mercury presence. Seven (7) samples from each of the ground and surface water (16 No.) sources were collected for analysis. The sampling locations are depicted in Table 1.

Sample	Names of Borewell water sources	Sample	Names of surface water sources
Codes		Codes	
B1	Edna Table Water, Onitsha	W1	River Niger upstream
B2	Kizzy water, Onitsha	W2	River Niger river bed
B3	Delina water, Nnewi	W3	Nwangene lake
B4	Bettics water, Nnewi	W4	River Niger Otumoye surface
B5	St. Joseph water, Onitsha	W5	River Niger Otumoye bed
B6	Bany water, Onitsha	W6	River Niger Creek surface
B7	Borehole at Onitsha south	W7	River Niger Creek bed
B8	Life Brewery, Onithsa	W8	Mili Ele stream, Nnewi

Surface Water

Mean concentration of Mercury metal is given in Table 2. Mean mercury concentration in surface water of Anambra state ranged from 0.055 ± 0.011 mg/l – 1.973 ± 0.222 mg/l. Surface water sample at River Niger creek surface had the highest value. A careful examination of results shows that 25% of sampled locations had concentration above the WHO maximum permissible limit of waste water into the environment (MPL) of 1mg/l (WHO, 2011). The boxplots in Figure 2.0, gives a comparative analysis of mercury concentration in the sampled water; mercury concentration from surface sampled sources of River Niger upstream and River Niger creek surface are almost normally distributed, presence of outlier shows presence of extreme values. It was noticed that the values in River Niger river bed and River Niger otumoye surface were normally distributed with a slight positive skewness and no outlier; this implies an almost evenly distributed value of concentration in sources.

Nwangene lake, River Niger otumoye bed and River Niger creek bed had highest variability amongst sampled sources. Nwangene lake and River Niger Otumoye bed were negatively skewed unlike River Niger creek bed. Value of Q1, Q3 and interquartile range for Nwangene lake, River Niger otumoye bed and River Niger creek bed are 1.43, 1.01, 0.07; 2.27, 1.99, 1.12 and 1.36-3.05, 0.76-1.99 and 0.07-1.36 respectively. Variation of concentration in sampled locations is depicted in Figure 2.

Surface water samples (mg/l)										
	W1	W2	W3	W4	W5	W6	W7	W8		
Mean	1.203± 0.134	0.055 ± 0.011	1.973± 0.222	$\begin{array}{c} 0.057 \pm \\ 0.006 \end{array}$	1.562± 0.199	1.531± 0.300	0.513± 0.216	1.717± 0.075		
Variance	0.126	0.001	0.344	0.000	0.277	0.629	0.325	0.039		
Minimum	0.910	0.020	1.360	0.040	0.760	0.090	0.070	1.400		
Maximum	1.970	0.090	3.050	0.080	1.990	2.610	1.360	2.000		
Borehole water samples (mg/l)										
	B1	B2	B3	B4	B5	B6	B7	B8		
Mean	0.000 ± 0.000	0.000± 0.000	0.000± 0.000	$\begin{array}{c} 0.000 \pm \\ 0.000 \end{array}$	0.0017± 0.0016	0.0009 ± 0.0002	0.0025 ± 0.0008	${0.0027 \pm \atop 0.0008}$		
Variance	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000		
Minimum	0.000	0.000	0.000	0.000	0.000	0.000	0.0010	0.000		
Maximum	0.000	0.000	0.000	0.000	0.0017	0.0020	0.0070	0.0060		

ND (0.000 mg/l) – Not detected

Appreciable quantities of mercury were detected in surface water sources. The high presence of plastic industries, medical waste, and electronic components in study locations might have induced concentration values.



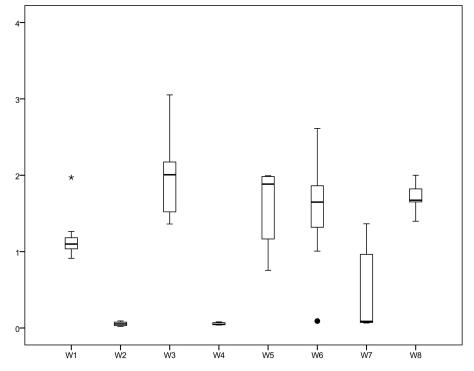


Figure 2 Boxplots of measured values of mercury in surface water, Anambra state

Ground Water

Mercury in the groundwater sources was generally below the MPL (Table 2) and this accounts for the no detection values in table. Mercury concentrations in ground sources are typical for subsurface water values. Similar mercury subsurface values of 0.002 mg/l have been noted in Sweden and 0.002 - 0.004 mg/l in the U.S.A. The boxplots in Figure 3.0 shows that the median concentration value for borehole sample is highest for Life brewery (0.003 mg/l). Life brewery also demonstrates the greatest variability with an interquartile range of 0.003 mg/l and the distribution is negatively skewed. Borehole Bany water had Q1 as 0ppm, Q3 as 0.002 mg/l, median as 0.001 mg/l with range of 0 - 0.002 mg/l. Concentrations in borehole Edna water – Bettics water were not detected while St. Joseph and Borehole at Onitsha south were positively skewed with outliers appearing at 0.011 mg/l and 0.007 mg/l respectively. Also, mercury concentration in water of Bany water and Life brewery, departed from a normal distribution only in the skewness in contrast to St. Joseph water and Borehole at Onitsha south which departed both in skewness and outliers.

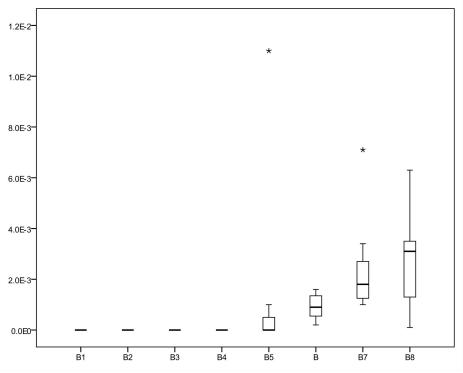


Figure 3 Boxplots of measured values of mercury in boreholes, Anambra state

Consumption of very high mercury-rich diet has a potential of impairing fetal growth and well being (USEPA, 2001). Mean values of mercury in surface water sources were in the increasing order: W2 ($0.055\pm0.011 \text{ mg/l}$) < W4 ($0.057\pm0.006 \text{ mg/l}$) < W7 ($0.513\pm0.216 \text{ mg/l}$) < W1 ($1.203\pm0.134 \text{ mg/l}$) < W6 ($1.531\pm0.300 \text{ mg/l}$) < W5 ($1.562\pm0.199 \text{ mg/l}$) < W8 ($1.717\pm0.075 \text{ mg/l}$) < W3 (1.973 ± 0.222) whereas in borehole sources mercury concentration were in the increasing order: B1-B4 (ND – 0.000 mg/l) < B6 ($0.009\pm0.002 \text{ mg/l}$) < B5 ($0.0017\pm0.0016 \text{ mg/l}$) < B7 (0.0025 ± 0.0008) < B8 ($0.0027\pm0.0008 \text{ mg/l}$).

CONCLUSION AND RECOMMENDATIONS



[Ezeabasili, 2(1): January, 2015]

This exploratory research focused on assessing mercury concentration in surface and subsurface waters in Anambra state, Nigeria. Mercury levels in surface waters were generally above the permissible limit while in ground water mercury concentration was below. Mercury is highly toxic at low concentration. Research conducted by Ajiwe et al (2002) shows a high mercury content of about 8mg/l in fresh water in study locations. Results from the groundwater analysis showed mercury limits below MPL, the detection in some of the samples should be a source of concern to stakeholders taking into concern the extreme toxicity of some of the metal species, this should foster constant monitoring of metal in water bodies. Uptake of mercury from air into aquatic biota should be a major string of concern, trace concentration of mercury in ground water sources need not be ignored as there may be more shocking revelations. Disposal of untreated sewage should be discouraged and development of appropriate strategy to curb upsurge in level of mercury in these water sources are paramount if the desired health status and developmental goals are to be attained.

Measure should be taken to restrict commercial activities in mercury as already been witnessed in developed nations (USEPA, 2012). Further researches on the speciation of mercury in the study location should be conducted to ascertain the prevalence of the most lethal organic compound, this will help in taking measures to prevent and mitigate its effect by adopting appropriate technology.

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