ASSESSMENT OF HUMAN HEALTH RISK ASSOCIATED WITH THE PRESENCE OF TRACE METALS IN GROUNDWATER SUPPLIES IN AKWA IBOM STATE, NIGERIA

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ABSTRACT

With the long term dependence on groundwater for drinking and domestic purposes, there is concern for health risk associated with the presence of trace metals in groundwater in Akwa Ibom State. In this study, non-carcinogenic human health risk was computed to assess the adverse health effect on the population. The Hazard Quotient (HQ) via oral ingestion for an adult and a child for each trace metal studied was less than unity indicating no potential risk. However, the calculated Hazard Index (HI) for the state was greater than unity (HI > 1) indicating potential heath implication due to cumulative presence of trace metals in groundwater. HI values were 1.62 and 5.26 for an adult and a child respectively. Multivariate correlation matrix gave good correlation for some metal pairs: Cd-Al, Cr-Al, Cr-Cd, Fe-B, Pb-Cd and Pb-Cr with values (r = 0.766), (r = 0.660), (r = 0.961), (r = 0.946), (r = 0.759) and (r = 0.765) respectively at (P < 0.01) level (2-tailed). This was further confirmed with hierarchical cluster analysis (HCA) where metals were group into three clusters based on inter-metal relationship. Information obtained would be useful in developing human health risk management plan for Akwa Ibom State.

INTRODUCTION

It has become common practice in Nigeria in general and Akwa Ibom in particular that most communities, villages or households abstract groundwater by means of individual borehole from which connections are made to an overhead storage tank. Neighboring households or dwellers in that community or village collect water from the storage tanks for drinking and domestic purpose. Currently, this practice has become an economic venture with borehole owners selling water to the masses with disregard to quality or health risks. Where there is no pollutants seepage, groundwater is generally considered a safer water source than surface waters because of infiltration through several porous soil layers which consequently reduce contamination as well as permit naturally occurring soil bacteria to degrade prevailing pathogenic organisms (Wellender *et al*., 2014). However, contrary to popular belief, inorganic elements derived from rocks or soil within the earth's terrain can leach from the host rocks and soil into the groundwater, at concentrations that render the water unsuitable for consumption (Pelig-Ba, 1998). Similarly, anthropogenic activities may increase the levels of trace metals in groundwater.

Groundwater contamination by trace metals has created substantial concern among environmental health scientists (Phan *et al*., 2013; Buschmann *et al*., 2008; Hoang *et al*., 2010); since it has been known that metallic contaminants may reach groundwater through continuous leaching (Afzal *et al*., 2013). For instance, detrimental health effects due to trace metal contamination of groundwater have been reported to have occurred in many countries including China, Bangledesh, Vietnam, India, etc (Nguyen *et al*., 2009). This study was carried out to assess the human health risk associated with trace metals contamination of groundwater in Akwa Ibom State. Trace metals may be beneficial or detrimental to organisms exposed to them. For essential micro-nutrients such as zinc (Zn), manganese (Mn), and copper (Cu), insufficient uptake leads to deficiency-related health problems while excess uptake may cause toxicity. Exposure to metals such as lead (Pb), cadmium (Cd), mercury (Hg), chromium (Cr), selenium (Se), etc. through drinking water is of serious concern globally because of their links to cardiovascular diseases, kidney-related disorders, neurocognitive effects and various forms of cancer (Packham,1996; Al-Saleh and Al-Doush, 1998; Jarup, 2002).

MATERIALS AND METHODS

Sampling and Chemical analysis

Groundwater samples were collected from 16 local government areas of Akwa Ibom State including: Eket, Essien Udim, Ikono, Ini, Ikot Abasi, Itu, Ibesikpo, Ibeno, Mbo, Mkpat Enin, Nsit Ubium, Obot Akara, Okobo, Oron, Oruk Anam and Uyo, and analysed for trace metals concentrations. The results have been presented in a previous publication (Inam *et al*., 2010). The raw data obtained in that previous study are now used to evaluate the potential human health risk posed by the presence of aluminium (Al), arsenic (As), boron (B), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), lead (Pb) and zinc (Zn), in ground water of the region.

Risk Assessment Process

The United Kingdom Risk Assessment, Toxicology Steering Committee (RATSC, 1999) defines chemical risk assessment as "the evaluation of the potential adverse health effects in humans from exposures to chemicals (Fryer *et al*., 2006). A comprehensive risk assessment process consists of four distinct phases: (i) hazard identification; (ii) exposure assessment; (iii) dose response assessment; and (iv) risk characterization. This basic frame-work for risk assessment is adopted for assessing the health risks to an adult and a child who reside in the studied area and are exposed to the trace elements present in the groundwater through ingestion pathway. The hazard identification process was carried out through the collection of groundwater samples and subsequent determination of the contamination level of the trace elements in the samples which has been reported previously (Inam *et al*., 2010). In order to estimate non-carcinogenic risks, dose-response assessment was done using standard reference dose (RfD) values for the trace metals considered in this study.

Exposure Assessment

The exposure assessment helps to estimate the magnitude of actual and/or potential human exposures to chemical contaminants, the frequency and duration of these exposures and the pathways by which humans are potentially exposed to the contaminants under study (Asante-Duah, 1993). Carrying out exposure assessment involves analyzing contaminant releases; identifying exposed populations; identifying all potential pathways of exposure; estimating point concentrations for specific pathways and estimating contaminant intakes for specific pathways (Lee *et al*., 2008).

Several pathways exist for which humans are exposed to trace elements including food chain, dermal contact, ingestion and inhalation. However, compared to oral ingestion other pathways are negligible (Muhammad *et al*., 2011). This study focuses on the oral ingestion pathway. The chronic daily intake (CDI) through the drinking of groundwater was calculated using the modified equation from Kavcar, *et al*., (2009) and as shown below:

$$CDI = \frac{C \times DI}{BW} \quad (1)$$

were, C, DI and BW represent the concentration of trace metals in water (µg dm^{-3}), average daily intake rate (2 dm^{-3}/day for an adult and 1dm^{-3}/day for a child) and average body weight (72kg for an adult and 10kg for a child) respectively (Inyang, 2013).

Evaluation of Non-cancer (Toxic) Risk

Toxic risks refer to non-carcinogenic harms that would occur as a result of the exposure to contaminants (Lee *et al.*, 2005). The magnitude of harm is estimated in terms of a hazard quotient (HQ) as expressed in the equation from Shah *et al.* (2012) and as shown:

$$HQ = \frac{CDI}{RfD} \quad (2)$$

where, according to USEPA database, the oral toxicity reference dose values (RfD) are 1.8E-01, 3.0E-04, 9.0E-02, 5.0E-04, 3.0E-04, 1.5, 3.7E-02, 8.0E-01, 1.4E-01, 3.6E-02, 3.0E-01 mg/kg-day for Al, As, B, Cd, Co, Cr, Cu, Fe, Mn, Pb, and Zn respectively (USEPA, 2005; Iqbal, Shah and Arhter, 2013). The exposed population is assumed to be safe when HQ<1 (Khan *et al*., 2008; Muhammad *et al*., 2010). The reference dose is the daily dosage that enables the exposed individual to sustain a certain level of exposure over an elongated period of time with detrimental effect. The toxic risk estimates are based on a comparison of actual exposure to the reference dose for the particular chemical involved (Lee *et al*., 2006).

In the case where the potential toxicants are more than one, their interactions must be considered. The toxic risks due to potentially hazardous chemicals in the same medium are assumed to be cumulative. The HQs would then be added to obtain the overall toxic risk, the hazard index (HI) (Kolluru *et al*., 1996) that:

$$HI = \Sigma HQ_i, \qquad i = 1...n. \quad (3)$$

If the calculated HI is less than 1.0, the non-carcinogenic adverse effect due to this exposure pathway or chemical is assumed to be negligible.

Statistical Analysis

The descriptive statistics were performed using Excel 2007 while multivariate and Hierarchical Cluster Analysis analyses were done using the SPSS statistical software package Version 17.0. The inter-metal relationship contributing to the risk was also evaluated using HCA and multivariate correlation matrix.

RESULTS AND DISCUSSION

The results for the physical properties of the groundwater samples have previously been reported by Inam *et al*., (2010). Presented in Table 1 are the Chronic Daily Intake (CDI) calculated for an adult and a child via oral ingestion of trace metals contaminated groundwater in Akwa Ibom State. The chronic daily intake of trace metals through drinking of groundwater in Akwa Ibom State for an adult was less compared to the intake of a child (Tables 1 and 2). Al, Mn, Zn and Fe were the major metals the populace were exposed to as their CDI values in most of the local government areas was greater than 1, while As was insignificant. The graphical distribution of the major trace metals contributing to chronic daily intake of an adult and child is presented in Figures 1 and 2). These four elements were the most important contributors to trace metals intake by the people of Akwa Ibom States that drink untreated ground water. In previous study the mean concentrations of Al and Fe in ground water in Akwa Ibom State were above the maximum limit given by Nigeria standard for drinking water quality (Inam *et al*., 2010). The source of Al in the ground water samples is likely through weathering of the alumino-silicates such as clays, feldspars, micas and other related minerals. High concentration of Al in groundwater may also be attributed to its availability. The dissolved organic matter and fluoride (Edmunds *et al*., 1992) and the presence of chelating agents such as fulvic and humic acids. The later raisea the solubility of Al to several orders of magnitude (Bolt and Bruggenwert, 1978).

This implies that a child living in Akwa Ibom State drinking groundwater containing trace metals is more vulnerable to potential adverse health effects than an adult. Specifically, the risk associated with the computed CDI values between the two targeted age groups show that a child has an average of 3.50 times of been impaired than adult.

Table 1: Chronic daily intake (CDI) indices for trace metals via drinking ground water in Akwa Ibom State for an adult

Location	Al	As	B	Cd	Co	Cr	Cu	Fe	Mn	Pb	Zn
Eket	5.77	BDL	7.22E-02	8.33E-03	5.56E-03	5.56E-03	2.58E-01	3.78E-01	1.27	5.83E-02	1.04
Essien Udim	4.21	BDL	5.00E-02	1.67E-03	2.78E-02	8.33E-03	9.22E-01	8.03E-01	3.45	8.61E-02	9.47E-01
Ikono	6.53E-01	BDL	3.33E-02	1.94E-04	8.33E-03	8.33E-03	5.17E-01	1.31E-01	1.31	2.78E-02	5.44E-01
Ini	1.28	2.78E-04	5.00E-02	1.11E-03	8.33E-03	1.67E-02	2.08E-01	3.50E-01	7.92E-01	7.22E-02	2.97E-01
Ikot Abasi	4.58E-01	BDL	1.25E-01	2.78E-04	5.56E-03	5.56E-03	5.86E-01	1.67	4.31E-01	8.61E-02	1.25
Itu	4.21	2.78E-04	1.00E-01	8.33E-03	8.33E-03	1.39E-02	2.67E-01	2.25E-01	1.17	1.17E-01	1.39
Ibesikpo	2.76	BDL	7.50E-01	5.56E-03	2.78E-03	1.67E-02	2.56E-01	8.33E-01	5.64E-01	9.17E-02	1.07
Ibeno	6.30	2.78E-03	4.11E-01	2.78E-03	5.56E-03	1.11E-02	7.22E-02	23.48	3.27	6.39E-02	2.01
Mbo	1.77	BDL	3.61E-02	8.33E-04	5.56E-03	1.94E-03	3.06E-01	1.49	3.53E-01	3.10E-02	6.56E-01
Mkpat Enin	4.00	5.56E-04	5.56E-02	5.56E-04	2.78E-03	5.56E-03	2.67E-01	2.72E-01	4.94E-01	4.72E-02	1.91
Nsit Ubium	5.10	8.33E-04	9.72E-02	1.39E-02	1.11E-03	1.39E-02	3.50E-01	2.33	7.75E-01	2.14E-01	14.07
Obot Akara	1.98	2.78E-04	4.17E-02	8.33E-04	8.33E-03	8.33E-03	4.11E-01	3.41	1.22	4.72E-02	7.83
Okobo	9.25E-01	BDL	4.17E-02	5.56E-04	5.56E-03	8.33E-03	3.81E-01	3.17E-01	3.94E-01	3.61E-02	7.17E-01
Oron	2.49	1.11E-03	5.83E-02	2.78E-03	8.33E-03	2.78E-03	2.61E-01	1.32	6.53E-01	6.39E-02	1.28
Oruk Anam	1.65	BDL	5.56E-02	2.78E-04	5.56E-03	8.33E-03	2.42E-01	1.08E-01	7.19E-01	3.33E-02	6.50E-01
Uyo	9.18	5.56E-04	1.08E-01	5.28E-02	1.11E-02	1.11E-02	3.00E-01	1.22	1.54	6.06E-01	2.733

BDL= below detection limit

Table 2: Chronic daily intake (CDI) indices for trace metals via drinking ground water in Akwa Ibom state for a child

Location	Al	As	B	Cd	Co	Cr	Cu	Fe	Mn	Pb	Zn
Eket	20.78	BDL	2.60E-01	3.00E-02	2.00E-02	2.00E-02	9.30E-01	1.36	4.56	2.10E-01	3.75
Essien Udim	15.17	BDL	1.80E-01	6.00E-03	1.00E-01	3.00E-02	3.32	2.89	12.41	3.10E-01	3.41
Ikono	2.35	BDL	1.20E-01	7.00E-04	3.00E-02	6.00E-02	1.86	4.70E-01	4.73	1.00E-01	1.96
Ini	4.61	1.00E-03	1.80E-01	4.00E-03	3.00E-02	6.00E-02	7.50E-01	1.26	2.85	2.60E-01	1.07
Ikot Abasi	1.65	BDL	4.50E-01	1.00E-03	2.00E-02	2.00E-02	2.11	6.02	1.55	3.10E-01	4.49
Itu	15.14	1.00E-03	3.60E-01	3.00E-02	3.00E-02	5.00E-02	9.60E-01	8.10E-01	4.20	4.20E-01	5.01
Ibesikpo	9.92	BDL	2.70E-01	2.00E-02	1.00E-02	6.00E-02	9.20E-01	3.00E-01	2.03	3.30E-01	3.85
Ibeno	22.67	1.00E-02	1.48	1.00E-02	2.00E-02	4.00E-02	2.60E-01	84.54	11.78	2.30E-01	7.25
Mbo	6.37	BDL	1.30E-01	3.00E-03	2.00E-02	7.00E-03	1.1	5.37	1.27	1.10E-01	2.36
Mkpat Enin	14.42	2.00E-03	2.00E-01	2.00E-03	1.00E-02	2.00E-02	9.60E-01	9.80E-01	1.78	1.70E-01	6.89
Nsit Ubium	18.34	3.00E-03	3.50E-01	5.00E-03	4.00E-02	5.00E-02	1.26	8.40	2.79	7.70E-01	50.66
Obot Akara	7.12	1.00E-03	1.50E-01	3.00E-03	3.00E-02	3.00E-02	1.48	12.29	4.38	1.70E-01	28.20
Okobo	3.33	BDL	1.50E-01	2.00E-03	2.00E-02	3.00E-02	1.37	1.14	1.42	1.30E-01	2.58
Oron	8.97	4.00E-03	2.10E-01	1.00E-02	3.00E-02	1.00E-02	9.40E-01	4.75	2.35	2.30E-01	4.59
Oruk Anam	5.94	BDL	2.00E-01	1.00E-03	2.00E-02	3.00E-02	8.70E-01	3.90E-01	2.59	1.20E-01	2.34
Uyo	33.05	2.00E-03	3.90E-01	1.90E-01	4.00E-02	4.00E-02	1.08	4.40	5.54	2.18	9.84

BDL= below detection limit

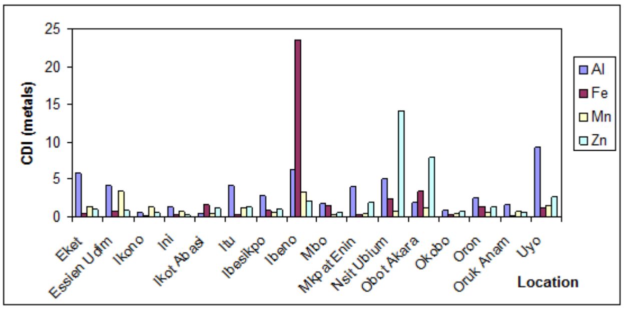

Fig. 1: Distribution of major trace metals (Al, Fe, Mn, Zn) contributing to CDI of an adult drinking groundwater in Akwa Ibom State

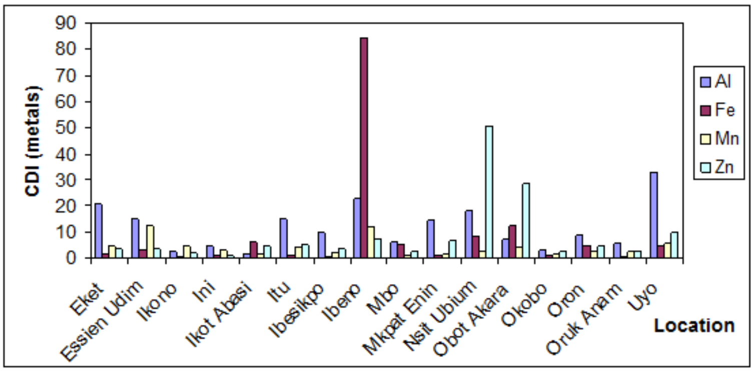

Fig. 2: Distribution of major trace metals (Al, Fe, Mn, Zn) contributing to CDI of a child drinking groundwater in Akwa Ibom State

Evaluation of non-cancer (toxic) risk

The hazard quotient (HQ) helps in the estimation of the magnitude of toxic harm posed to the exposed inhabitants drinking the groundwater containing trace metals. The calculated hazard quotion indices for an adult and a child are presented in Tables 3 and 4 respectively. For all the HQ values computed for the trace metals investigated, none were above unity indicating low or no toxic risk due to drinking groundwater from the study areas.

HI values for a child (0.15 to 0.87) are significantly higher than those of an adult (0.04 to 0.2) and are approaching unity.

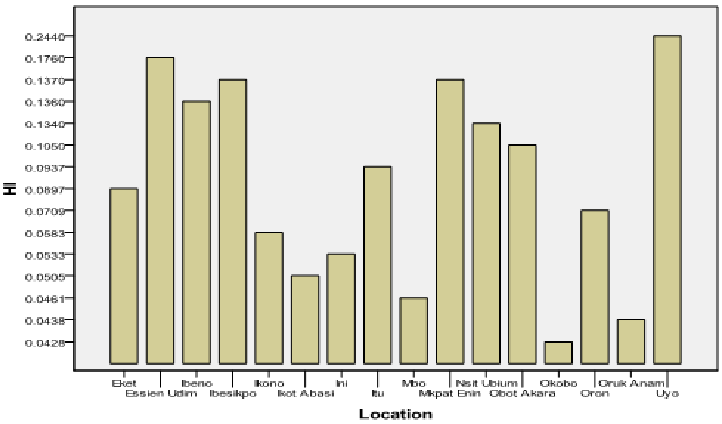

Fig. 3. Hazard index of trace metals for an adult drinking groundwater in Akwa Ibom State

Table 3: Hazard quotient indices of trace metals for a child drinking groundwater in Akwa Ibom State

Location	Al	As	B	Cd	Co	Cr	Cu	Fe	Mn	Pb	Zn	ΣHQ=HI
Eket	1.15E-01	BDL	2.89E-03	6.00E-02	6.67E-02	1.33E-05	2.51E-02	1.70E-03	3.26E-02	5.83E-03	1.25E-02	3.22E-01
Essien Udim	8.43E-02	BDL	2.00E-03	1.20E-02	3.33E-01	2.00E-05	8.97E-02	3.61E-03	8.86E-02	8.61E-03	1.14E-02	6.33E-01
Ikono	1.31E-02	BDL	1.33E-03	1.40E-03	1.00E-01	2.00E-05	5.03E-02	5.88E-04	3.38E-02	2.78E-03	6.53E-03	2.10E-01
Ini	2.56E-02	3.33E-03	2.00E-03	8.00E-03	1.00E-01	4.00E-05	2.03E-02	1.58E-03	2.04E-02	7.22E-03	3.57E-03	1.92E-01
Ikot Abasi	9.17E-03	BDL	5.00E-03	2.00E-03	6.67E-02	1.33E-05	5.70E-02	7.53E-03	1.11E-02	8.61E-03	1.50E-02	1.82E-01
Itu	8.41E-02	3.33E-03	4.00E-03	6.00E-02	1.00E-01	3.33E-05	2.59E-02	1.01E-03	3.00E-02	1.17E-02	1.67E-02	3.37E-01
Ibesikpo	5.51E-02	BDL	3.00E-03	4.00E-02	3.33E-02	4.00E-05	2.47E-02	3.75E-04	1.45E-02	9.17E-03	1.28E-02	1.93E-01
Ibeno	1.26E-01	3.33E-03	1.64E-02	2.00E-02	6.67E-02	2.67E-05	7.03E-03	1.06E-01	8.41E-02	6.39E-03	2.42E-02	4.60E-01
Mbo	3.54E-02	BDL	1.44E-03	6.00E-03	6.67E-02	4.67E-06	2.97E-02	6.71E-03	9.07E-03	3.06E-03	7.87E-03	1.66E-01
Mkpat Enin	8.01E-02	6.67E-03	2.22E-03	4.00E-03	3.33E-02	1.33E-05	2.59E-02	1.22E-03	1.27E-02	4.72E-03	2.30E-02	1.94E-01
Nsit Ubium	1.02E-01	1.00E-03	3.89E-03	1.00E-01	1.33E-01	3.33E-05	3.41E-02	1.05E-02	1.99E-02	2.14E-02	1.69E-01	5.95E-01
Obot Akara	3.96E-02	3.33E-03	1.67E-03	6.00E-03	1.00E-01	2.00E-05	4.00E-02	1.54E-02	3.13E-02	4.72E-03	9.40E-02	3.36E-01
Okobo	1.85E-02	BDL	1.67E-03	4.00E-03	6.67E-02	2.00E-05	3.70E-02	1.43E-03	1.01E-02	3.61E-03	8.60E-03	1.52E-01
Oron	4.98E-02	1.33E-02	2.33E-03	2.00E-02	1.00E-01	6.67E-06	2.54E-02	5.94E-03	1.68E-02	6.39E-03	1.53E-02	2.55E-01
Oruk Anam	3.30E-02	BDL	2.22E-03	2.00E-03	6.67E-02	2.00E-05	2.35E-02	4.88E-04	1.85E-02	3.33E-03	7.80E-03	1.58E-01
Uyo	1.84E-01	6.67E-03	4.33E-03	3.80E-01	1.33E-01	2.67E-05	2.92E-02	5.50E-03	3.96E-02	6.06E-02	3.28E-02	8.76E-01
ΣHQ=HI	1.05E+00	4.10E-02	5.64E-02	7.25E-01	1.57E+00	3.51E-04	5.45E-01	1.70E-01	4.73E-01	1.68E-01	4.61E-01	**5.26E+00**

BDL= below detection limits

Table 4: Hazard quotient indices of trace metals for an adult drinking groundwater in Akwa Ibom State

Location	Al	As	B	Cd	Co	Cr	Cu	Fe	Mn	Pb	Zn	ΣHQ=HI
Eket	3.21E-02	BDL	8.02E-04	1.67E-02	1.85E-02	3.70E-06	6.98E-03	4.72E-04	9.05E-03	1.62E-03	3.47E-03	8.97E-02
Essien Udim	2.34E-02	BDL	5.56E-04	3.33E-03	9.27E-02	5.56E-06	2.49E-02	1.00E-03	2.46E-02	2.39E-03	3.16E-03	1.76E-01
Ikono	3.63E-03	BDL	3.70E-04	3.89E-04	2.78E-02	5.56E-06	1.40E-02	1.63E-04	9.38E-03	7.70E-04	1.82E-03	5.83E-02
Ini	7.11E-03	9.26E-04	5.56E-04	2.22E-03	2.78E-02	1.11E-05	5.63E-03	4.38E-04	5.65E-03	2.01E-03	9.91E-04	5.33E-02
Ikot Abasi	2.54E-03	BDL	1.39E-03	5.56E-04	1.85E-02	3.76E-06	1.58E-02	2.09E-03	3.08E-03	2.39E-03	4.16E-03	5.05E-02
Itu	2.34E-02	9.26E-04	1.11E-03	1.67E-02	2.78E-02	9.25E-06	7.21E-03	2.81E-04	8.35E-03	3.25E-03	4.64E-03	9.37E-02
Ibesikpo	1.53E-02	BDL	8.33E-04	1.11E-02	9.27E-02	1.11E-05	6.91E-03	1.04E-04	4.03E-03	2.55E-03	3.57E-03	1.37E-01
Ibeno	3.50E-02	9.27E-03	4.57E-03	5.56E-03	1.85E-02	7.41E-06	1.95E-03	2.94E-02	2.34E-02	1.78E-03	6.71E-03	1.36E-01
Mbo	9.83E-03	BDL	4.00E-04	1.67E-03	1.85E-02	1.30E-06	8.26E-03	1.86E-03	2.52E-03	8.60E-04	2.19E-03	4.61E-02
Mkpat Enin	2.22E-02	1.85E-03	6.17E-04	1.11E-03	9.27E-02	3.70E-06	7.21E-03	3.40E-04	3.53E-03	1.31E-03	6.38E-03	1.37E-01
Nsit Ubium	2.83E-02	2.78E-03	1.08E-03	2.78E-02	3.70E-03	9.26E-06	9.46E-03	2.91E-03	5.54E-03	5.94E-03	4.69E-02	1.34E-01
Obot Akara	1.10E-02	9.26E-04	4.63E-04	1.67E-03	2.78E-02	5.56E-06	1.11E-02	4.27E-03	8.69E-03	1.31E-02	2.61E-02	1.05E-01
Okobo	5.14E-03	BDL	4.63E-04	1.11E-03	1.85E-02	5.56E-06	1.10E-02	3.96E-04	2.82E-03	1.00E-03	2.39E-03	4.28E-02
Oron	1.38E-02	3.70E-03	6.48E-04	5.56E-03	2.78E-02	1.85E-06	7.06E-03	1.65E-03	4.66E-03	1.78E-03	4.25E-03	7.09E-02
Oruk Anam	9.17E-03	BDL	6.17E-04	5.56E-04	1.85E-02	5.56E-06	6.53E-03	1.35E-04	5.14E-03	9.30E-04	2.17E-03	4.38E-02
Uyo	5.10E-02	1.85E-03	1.20E-03	1.06E-01	3.70E-02	7.41E-05	8.11E-03	1.53E-03	1.10E-02	1.68E-02	9.11E-03	2.44E-01
ΣHQ=HI	2.93E-01	2.22E-02	1.57E-02	2.02E-01	5.69E-01	1.64E-04	1.52E-01	4.70E-02	1.31E-01	5.85E-02	1.28E-01	**1.62E+00**

BDL= below detection limits

Uyo the capital city of Akwa Ibom state had the highest value of HI (HI=0.88) for a child, indicating the future adverse effect for children. Thus the need for continuous monitoring to safe guide children's health. (Figs. 3 and 4), the HI values did not exceed unity (HI<1) on individual local government basis. However, the sum of the HI values for the 16 cases calculated to approximate the hazard index of the state revealed values which exceeded unity: 1.62 and 5.26 for an adult and a child respectively. This indicates the degrading quality of groundwater supplies in the state and the risk associated with it remain insignificant, computation for the entire state was significant implying serious concerns on usage of untreated groundwater for drinking and other domestic purposes (HI>1).

Statistical Analysis

Analysis of inter-metal relationship provides useful information on metal sources and pathway (Inam *et al*, 2010). Pearson Correlation co-efficient (r) of Hazard Quotient (HQ) contributed by metals are presented in Tables 5 and 6 for an adult and a child respectively showed a strong positive HQ correlation between source metals. Cd-Al, Cr-Al, Cr-Cd, Fe-B, Pb-Cd and Pb-Cr with values (r = 0.766), (r = 0.660), (r = 0.961), (r = 0.946), (r = 0.759) and (r = 0.765) respectively were all positively correlated ($P < 0.01$). This explains a common contribution of the pairs to the HQ evaluation. However, some of the correlations and though positive were not significant and had little or no effect on the effect to consumption of groundwater. Similarly, Fe and Cd were also noted to be positively correlated to B and Al respectively for a child. This further confirmed that the co-existence of these metals pair may impact on the health risk of the adult and child depending on the water source for drinking.

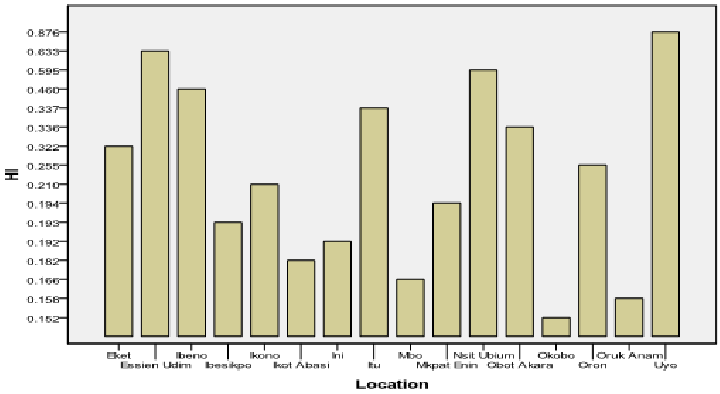

Fig. 4 Hazard index of trace metals for a child drinking groundwater in Akwa Ibom State

Table 5: HQ correlation coefficients for trace metals in ground water in Akwa Ibom State for an adult

	Al	B	Cd	Co	Cr	Cu	Fe	Mn	Pb	Zn
Al	1	.448	.766[a]	.101	.660[a]	-.232	.335	.490	.517[b]	.248
B		1	.093	.188	.090	-.379	.946[a]	.560[b]	-.001	.048
Cd			1	-.048	.961[a]	-.130	-.530	.107	.759[a]	.206
Co				1	.033	.316	-.206	.207	-.057	-.264
Cr					1	-.104	-.036	.130	.765[a]	.640
Cu						1	.353	.290	.009	-.005
Fe							1	.597[b]	-.010	.085
Mn								1	.112	-.037
Pb									1	.471
Zn										1

[a]Correlation is significant at the 0.01 level(2-tailed); [b]Correlation is significant at the 0.05 level (2-tailed).

Table 6: HQ correlation coefficients for trace metals in ground water in Akwa Ibom State for a child

	Al	B	Cd	Co	Cr	Cu	Fe	Mn	Pb	Zn
Al	1	.449	**.767**[a]	.221	.197	-.222	.335	.489	**.724**[a]	.249
B		1	.094	-.127	.194	-.374	**.946**[a]	.558[b]	.103	.049
Cd			1	.145	.235	-.126	-.053	.107	**.984**[a]	.207
Co				1	.051	**.753**[a]	-.093	**.651**[a]	.213	.121
Cr					1	-.210	.086	.136	.276	.233
Cu						1	-.349	.300	-.045	.001
Fe							1	.596[b]	-.049	.089
Mn								1	.119	-.037
Pb									1	.253
Zn										1

[a]Correlation is significant at the 0.01 level (2-tailed); [b]Correlation is significant at the 0.05 level (2-tailed).

The HCA was used to further analyse the inter-relationship between the metals contributors to the HQ of the study area. As confirmed by two different measures using complete linkages, three clusters were formed by the metals. Figure 5 was derived from absolute correlation method and comprises (i) cluster one which consists of Al, Cd, Cr and Pb; (ii) cluster two consists of B, Co, Cu, Fe and Mn, and (iii) cluster three is made of only Zn. This consolidates the fact that Zn is not significantly correlated to any of the metals. On the three clusters were also formed using Seuclid measures. These include (a) Al, Cd, Cr, Pb and Zn (b) B, Mn and Fe (c) Co and Cu (Fig. 6). The clusters simply revealed that the presence of one metal would have an interactive effect on another.

```
                       Rescaled Distance Cluster Combine
    C A S E      0         5        10        15        20        25
  Label     Num  +---------+---------+---------+---------+---------+

  Cd          3   -+---------+
  Cr          5   -+         +-----------+
  Pb          9   -----------+           +-----------------------+
  Al          1   -----------------------+                       +-+
  Zn         10   -----------------------------------------------+ |
  B           2   -+--------------------+                          |
  Fe          7   -+                    +--------------------+     |
  Mn          8   ----------------------+                    +-----+
  Co          4   ----------------------------------+--------+
  Cu          6   ----------------------------------+
```

Fig.5: Dendrogram showing inter-relationship between metals (Absolute correlation)

```
                   Rescaled Distance Cluster Combine
  C A S E      0         5        10        15        20        25
Label     Num  +---------+---------+---------+---------+---------+

Cd          3   -+-------+
Cr          5   -+       +-----+
Pb          9   ---------+     +-------------------+
Al          1   ---------------+                   +-----+
Zn         10   -----------------------------------+     +-------+
B           2   -+-----------------+                     |       |
Fe          7   -+                 +---------------------+       |
Mn          8   -------------------+                             |
Co          4   -------------------------------+-----------------+
Cu          6   -------------------------------+
```

Fig.6: Dendrogram showing inter-relationship between Metals (Absolute Seuclid)

CONCLUSIONS

The human health risk of trace metals due to drinking of groundwater in Akwa Ibom State has revealed that aluminium (Al), manganese (Mn), zinc (Zn) and iron (Fe) constitute the major trace elements exposed to via ingestion route. Although the hazard quotient was less than unity (HQ<1) indicating no risk, the hazard index for the entire state was greater than unity (HI>1) signifying risk from trace metals ingestion through the drinking of groundwater. In all the computations, children showed greater risk than adults with CDI value 3.5 times greater. The HCA revealed that some trace metal mixtures in the groundwater sources may have pronounced effect than would individual metal. There is need to monitor groundwater supplies and regulate policies to check digging boreholes in already contaminated areas.

REFERENCES

Afzal, M., Shabir, G., Iqbal, S., Mustafa, T., Khan, Q.M. & Khalid, Z.M., 2013. Assessment of heavy metal contamination in soil and ground water at leather industrial area of Kasur, Pakistan. *Clean – Soil Air Water*, 41: 1-7.

Al-Saleh, I & Al-Doush, I., 1998. Survey of elements in household and bottled drinking water samples collected in Riyadh, Saudi Arabia. *Science of the Total Environment*, 216: 181-192.

Asante-Duah, D.F., 1993. *Hazardous Waste Risk Assessment*. Boca Raton, Florida: Lewis Publishers, pp. 21-71.

Bolt, G.H., & Bruggenwert, M.G.M., 1978. *Soil, Chemistry Basic Elements Textbook*, 2nd Ed. Amsterdam: Elsevier Scientific Publishing, p. 34.

Buschmann, J., Berg, M., Stengel, C., Winkel, L., Sampson, M.L., Trang, T.K. & Viet, P.H., 2008. Contamination of drinking water resources in the Mekong delta floodplains: Arsenic and other trace metals pose serious health risks to population. *Environment International*, 34: 756-764.

Edmunds, W.M., Kinniburg, D.G., & Moss, P.D., 1992. Trace metals in interstitial waters from sandstones: acidic inputs to shallow groundwaters. *Environmental Pollution*, 77: 129-141.

Escobar, A. S., Pereira,M.M. & Cerqueira, H. S., 2008. Effect of iron and calcium over USY coke formation. *Applied Catalyst A*, 346:194-199

Fryer, M., Collins, C.D., Ferrier, H., Colvile, R.N. & Nieuwenhuijsen, M.J., 2006. Human exposure modelling for chemical risk assessment: a review of current approaches and research and policy implications. *Environmental Science & Policy*, 9: 261-271.

Hoang, T.H., Bang, S., Kim, K.-W., Nguyen, M.H. & Dang, D.M., 2010. Arsenic in groundwater and sediment in the Mekong River delta, Vietnam. *Environmental Pollution*, 158: 2648-2658.

Inam, E., Kim, K.-W., Ebong, G. & Eduok, U., 2010. Trace elements in ground and packaged water in Akwa Ibom State, Nigeria. *Geosystem Engineering*, 13(2): 57-68.

Inyang, H.I., 2013. *Beyond Contaminant Concentration Measurements: use of data in contaminant migration analyses and environmental risk assessment*. A paper presented at an invited lecture at the University of Uyo, Nigeria. January, 4. 2013.

Iqbal, J., Shah, M.H. & Akhter, G., 2013. Characterization, source apportionment and health risk assessment of trace metals in freshwater Rawal Lake, Pakistan. *Journal of Geochemical Exploration*, 125:94-101.

Jarup, L., 2002. Cadnium overload and toxicity. *Nephrology Dialysis Transplantation*, 17(Suppl. 2): 35-39.

Kavcar, P., Sofuoglu, A. & Sofuoglu, S.C., 2009. A health risk assessment for exposure to trace metals via drinking ingestion pathway. *International Journal of Hygiene and Environmental Health*, 212: 216-227.

Khan, S., Cao, Q., Zheng, Y.M., Huang, Y.Z., Zhu, Y.G., 2008. Health risk of heavy metals in contaminated soils and food crops irrigated with wastewater in Beijing, China. *Environmental Pollution*, 152: 686-692.

Kolluru, R.V., Bartell, S.M., Pitblado, R.M. & Stricoff, R.S., 1996. *Risk Assessment and Management Hanbook*. New York: Mc-Graw-Hill.

Lee, J.-S., Chon, H.-T. & Kim, K.-W., 2005. Human risk assessment of As, Cd, Cu and Zn in the abandoned metal mine site. *Environmental Geochemistry and Health*, 27: 185-191.

Lee, J.-S., Lee, S.-W., Chon, H.-T. & Kim, K.-W., 2008. Evaluation of human exposure to arsenic due to rice ingestion in the vicinity of abandoned Myungbong Au-Ag mine site, Korea. *Journal of Geochemical Exploration*, 96: 231-235.

Lee, S.-W., Lee, B.-T., Kim, J.-Y., Kim, K.-W. & Lee, J.-S., 2006. Human risk assessment for heavy metals and As contamination in the abandoned metal mine areas, Korea. *Environmental Monitoring and Assessment*, 119: 233-244.

Muhammad, S. Shah, M.T., & Khan, S., 2010. Arsenic health risk assessment of drinking water and source apportionment using multivariate statistical techniques in Kohistan region, northern Pakistan. *Food and Chemical Toxicology*, 48: 2855-2864.

Muhammad, S. Shah, M.T., & Khan, S., 2011. Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan. *Microchemical Journal*, 98: 334-343.

Nyugen, V.A., Bang, S., Viet, P.H. & Kim, K.-W., 2009. Contamination of groundwater and risk assessment for arsenic exposure in Ha Nam province, Vietnam. *Environment International*, 35: 466-472.

Packham, R.F., 1996. Drinking Water Quality and Health, In R.M. Harrison (Ed.), *Pollution Causes, Effects and Control*. United Kingdom: The Royal Society of Chemistry, pp. 52-65.

Pelig-Ba, K.B., 1998. Trace elements in groundwater from some crystalline rocks in the upper regions of Ghana. *Water, Air, and Soil Pollution*, 103: 71-89.

Phan, K., Phan, S., Huoy, L., Suy, B., Wong, M.H., Hashim. J.H., Yasin, M.S.M, Aljunid, S.M., Sthiannopkao, S. & Kim, K.-W., 2013. Assessing mixed trace elements in groundwater and their health risk of residents living in the Mekong River basin of Cambodia. *Environmental Pollution*, 182: 111-119.

RATSC (Risk Assessment, Toxicology Steering Committee), 1999. *Risk Assessment Approaches Used by UK Government for Evaluating Human Health Effects of Chemicals*. Institute for Environmental and Health, UK.

Shah, M.T., Ara, J., Muhammad, S., Khan, S. & Tariq, S., 2012. Health risk assessment via surface water and sub-surface water consumption in the mafic and ultramafic terrain, Mohmand agency, northern Pakistan. *Journal of Geochemical Exploration*, 118: 60-67.

US EPA (US Environmental Protection Agency), 2005. Guidelines for carcinogen risk assessment. Risk Assessment Forum, Washington, DC. EPA/630/P-03/001F.

Wellender, E.K., Ailes, E.C., Yoder, J.S., Roberts, V.A. & Brunkard, J.M., 2014. Contributing factors to disease outbreaks associated with untreated groundwater. *Groundwater*, 52(6): 886-897.