ISSN NO. 2320-5407

Journal homepage: http://www.journalijar.com

INTERNATIONAL JOURNAL OF ADVANCED RESEARCH

RESEARCH ARTICLE

Atmospheric trace metal concentrations of Total suspended particulate matter in Isoko land, Southern Nigeria

Oke Michael Aziakpono, E. E. Ukpebor, J.E. Ukpebor and Okungbowa Godwin Nosa
Department of Chemistry, University of Benin, Benin-city, Nigeria.

Manuscript Info

Manuscript History:

Received: 11 September 2013
Final Accepted: 21 September 2013
Published Online: October 2013

Key words:
Trace metals, Enrichment Factor, Atomic Absorption Spectroscopy, and Total Suspended Particulate Matter.

Abstract

Trace metals are one of the most toxic constituents of atmospheric particulates. The baseline concentrations of the trace metals Pb, Ni, V, Cu, Cd, Zn, Cr, Fe, Mn and Co in the particles were collected using a Microdust Pro real time dust monitor (Casella CEL 176000A). Sampling was done for a year in the seventeen (17) sampling sites created in the study area. The samples were collected at a height of between 1.5 – 2.0m on a monthly basis for duration of 8 hours at each site with a flow rate of 2.0Lpm. The particulates samples were collected, characterized and quantified for trace metals concentration using Atomic Absorption Spectrometry (AAS). The concentration of the trace metals were as follows: Fe (0.008382 µg/m^3), Zn (0.007426 µg/m^3), Pb (0.006404 µg/m^3), Cd (0.0013 µg/m^3, Mn- 0.001 µg/m^3, Cu (0.000163 µg/m^3) while Ni, Cr, V and Co were found to be below detection limits.

The rotated component matrix showed that from the two components extracted from PCA, Cd, Cu and Mn loaded positively with the first component, while Pb, Zn and Fe loaded negatively with the first component. For the second component Pb, Zn, Fe and Mn loaded positively while Cd and Cu loaded negatively with the second component, this suggest that two major sources which are vehicular related emissions (60%) and re-suspended road dust (40%) which can be as a direct result of farming activities (Anthropogenic particles). From the source apportionment, it was observed that flow station activities do not directly impair the air quality of Isoko area.

Introduction

The quality of air that we breathe in is determined by the amount of gaseous pollutants and particulate matter present in the air. Among all air pollutants, particulate which can be inhaled into the human respiratory system (**Harrison, R.M.,** 1999) has been found to contribute the most serious health effects including pulmonary and cardiovascular illnesses (**Wallenborn, et al.,** 2009). In terms of adverse effects on human health, particulate matter is perhaps the most important air pollutant. Understanding the composition of atmospheric particulate matter is crucial for so many reasons. Some of the particulate heavy metals are strong triggers for carcinogenesis, teratogenesis and mutagenesis (**Hetland, et al.,** 2001; **Ken, et al.,** 2002). Trace metals are however one of the most toxic constituents of atmospheric particulates. The size and composition of airborne particulates play a very important role in determining their health effects (**Radojevic and Bashkin,** 2007). Pollution resulting from suspended particulate matter and carbon monoxide may place an undue burden on the respiratory system and contribute to increased morbidity and mortality, especially among susceptible individuals in the general population (**WHO Report,** 1968). Besides its effects on health, atmospheric particles have numerous effects. The most conspicuous of these is attenuation and distortion of visibility, they provide active surfaces upon which heterogeneous atmospheric chemical reactions can occur and nucleation bodies for the condensation of atmospheric water vapour, thereby exerting a significant influence upon weather and air pollution phenomena, it also affects the amount of sunlight reaching the ground air (**Pak-EPA/JICA,** 2001b). Air pollution, both natural and manmade affect climate (**Chatwal,** 1997). Particulate

matter has a net detrimental effect upon the environment or upon something of value in the environment (**Manghan,** 1991). The severity of contamination by pollution increases with emission source strength and the atmospheric mixing of the pollutants (**Obioh et al.,** 2005). Municipal waste has been identified as a principal source of particulate occurrence of toxic heavy metals in the respirable fraction pollution (**Wallenborn, et al.,** 2009**; Salvi, S. and S. Holgate**, 1999).

Though, much has been reported about particulate matter and its associated health problems, there is no established standard or guidelines as to the levels of particulate matter in the ambient air required to cause hazard.

Gas flaring as one of the sources of particulate matter generation is the careful and regulated burning of natural gases associated with oil exploration. The constant flaring of associated gas has left a destructive effect on the surrounding environment of the Niger Delta Area, where the activities of oil production mainly take place (**E.O. Adeniye, R. Olu-Sule & A. Anyaye, 1983**). Nigeria has an average daily crude oil output in excess of two million barrels per day, with over 200 gas flaring sites. Some of these gas flaring sites have been on continuously for over 20 years.

About 75% of the 22 billion standard cubic feet (SCF) of associated gas produced daily alongside the crude oil in Nigeria is being flared (**Bailey et al**., **2000**). The volume of gas flared in Nigeria is equivalent to one quarter of the current power consumption of the African continent.

The use of coal for power generation in South Africa and gas flaring in the Niger Delta have been traced to be the main sources of carbon dioxide emissions in Sub- Saharan Africa (south of the Sahara). Gas flaring has also been implicated as a major contributor to the accumulation of green house gases in the atmosphere thereby adding to the climate change pandemonium. Continuation of gas flaring is a direct contradiction of the determined stand taken by nations of the world to fight climate change in practical terms.

For neighbouring communities to gas flares, the toxic mixture of substances produced from gas flares have found to have serious health impacts in the form of respiratory illnesses, asthma, blood disorders, cancer, painful breathing and chronic bronchitis (**S. I. Efe, 2006**).

Heavy metals have a variety of effects upon the human body, mostly at the cellular level. While some metals disrupt biochemical reactions others block essential biological processes, including the absorption of nutrients. Some accumulate in the body giving rise to toxic concentration after many years of exposure and yet others such as Argon, Beryllium, cadmium and Chromium are carcinogens (**Friberg et al.,** 1986).

This present study was conducted to investigate the levels of some environmentally significant heavy metals in ambient air particulates in Isoko Land and also to identify these elements which are abnormally enriched in the atmosphere. This preliminary research may help researchers and policy makers in preventing and managing air pollution.

METHODOLOGY

Study Area

This study was carried out in six different oil producing communities in Isoko land (North and South local government areas) of Delta state in the southern part of Nigeria. Isoko land is found in the Niger Delta region of Nigeria in West Africa, occupying an area of about 1,200 square kilometres, with a residual population estimate of over 750,000 people by 2006 census.

Isoko Land is among the most densely populated areas in Nigeria, with an average of 300 persons per square kilometre compared with the average of 198 for Delta State and 130 for Nigeria and this has resulted in shortage of farmland, a shortage also caused by oil exploration activities in the region.

Isoko Land is essentially rural with two semi-urban centres and no urban centre. Isoko land lies within the economic shadow of the vibrant industrial and commercial Warri metropolis.

In between these communities are three flow stations namely: Ogini, Uzere and Olomoro. The study area is located within the co-ordinates of latitude N05^{o} 23’ 0” - N05^{o} 36’ 0” Longitude E006^{o} 8’ 0”- E006^{o} 17’ 0”. The study area has an estimated land mass of 232.56 square kilometer and with a population estimate of 142, 582 people (**NPC** 2006). Ozoro and Oleh are the semi-urban communities while the remaining four communities are rural. The rural dwellers engage themselves in farming, hunting, rubber tapping and rural intra-transportation due to the accessibility of these communities via paved and unpaved roads. The people also engage in cassava processing, smoking of fishes, and their major way of waste disposal is either by burning or indiscriminate dumping of the waste in the

bush. The major means of cooking is through burning of fossil fuel (Fire wood or kerosene). However, as mentioned earlier all these communities are within the proximity of three flow stations where associated gas is being flared on a daily basis. All these afore-mentioned activities are veritable generators of particulate matter in the environment.

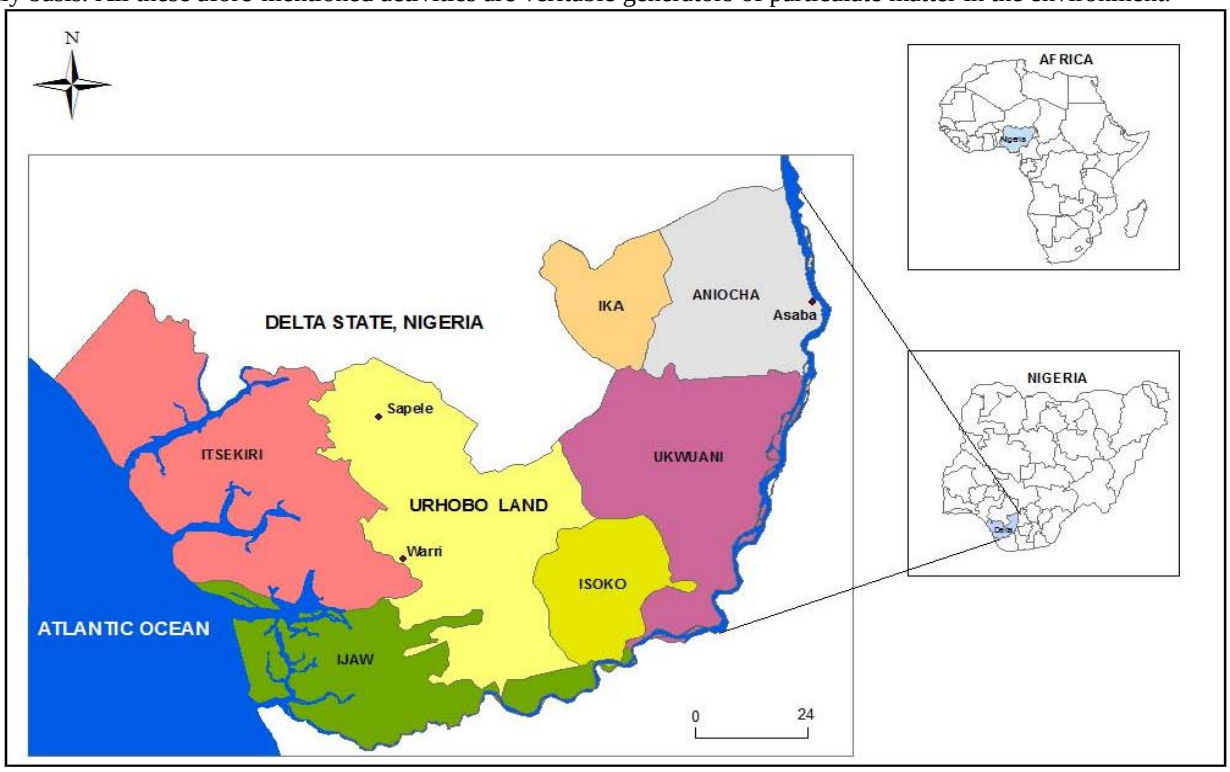


Figure 1: Map of Delta State showing Isoko land.

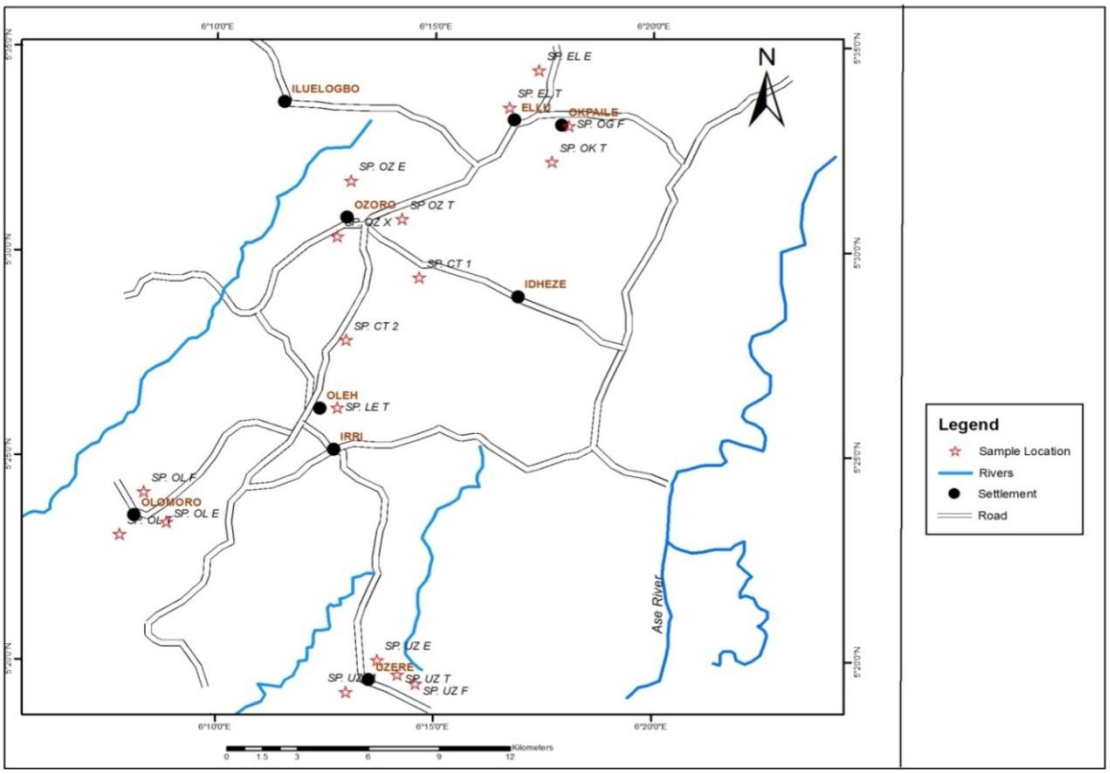


Figure 2: Map of Isoko land showing the various sampling locations.

Table 1: Sampling Sites, description and their Coordinates

S/N	Sampling site	Site code	Co-ordinates
1	Close to Uzere flow station flare tip	SP.UZF	5° 24' 25N, 6° 10' 22E
2	Mango tree along Uzere town entrance from Oleh axis	SP.UZE	5° 24' 9"N, 6° 10' 29"E
3	Close to residential houses opposite Uzere Police station	SP.UZT	5° 35' 25"N, 6° 10' 55"E
4	Front residential house opposite Uzere Daily Market	SP.UZM	5° 35' 15"N, 6° 9' 5"E
5	Close to Ogini flow station flare tip	SP.OGF	5° 35' 25"N, 6° 16' 55"E
6	Front residential house in Okpaile Main Town	SP.OKT	5° 35' 24"N, 6° 16' 55"E
7	This site was created in front of the Catholic church in Ellu just beside the market	SP.ELT	5° 34' 18"N, 6°16' 40"E
8	Front of the Apostolic church, along Ellu/Okpaile road	SP.ELE	5° 34' 43"N, 6° 16' 15"E
9	Front of a residential house Ozoro Entrance Agbaza road Junction	SP.OZE	5° 32' 57"N, 6°13' 38"E
10	Front of an office building Ala Square by Urude quarters	SP.OZT	5° 30' 28"N, 6° 12' 40"E
11	Ozoro Exit (NDC by Express Junction)	SP.OZX	5° 29' 50"N, 6° 11' 30"E
12	Close to Olomoro flow station flare tip	SP.OLF	5° 25' 42"N, 6° 9' 18"E
13	Olomoro Main Town	SP.OLT	5° 25' 8"N, 6° 8' 48"E
14	Olomoro town entrance (Express road Junction)	SP.OLE	5° 24' 56"N, 6° 8' 36"E
15	Front of a residential house at Oleh Town close to Nyaga Market	SP.LET	5° 27' 8"N, 6°12' 12"E
16	Bush along Ozoro/Idheze road at Ozoro axis	SP.CT1	5° 29' 14"N, 6° 13' 58"E
17	Bush along Ozoro/Oleh road at Oleh axis	SP.CT2	5° 26' 28"N, 6° 12' 40"E

Sampling and Experimental Methods

The mass concentrations for $PM_{2.5}$ presented in this paper were monitored by means of Microdust Pro Dust Kit. Precise measurement of respirable airborne particulate matter was carried out through an optical method using the "Microdust pro" monitor (**P. Baltrėnas & M. Kvasauskas**, 2005).

The Microdust Pro measures particulate concentrations using a near forward angle light scattering technique where Infrared light of 880nm wavelength is projected through the sampling volume. The contact of the projected light with the particles causes the light to scatter. The amount of light scattered is proportional to the mass concentration and this is measured by the photo detector. To minimize the uncertainty associated with particle color, shape and refractive index; a narrow angle of scatter (12- 20°) is used.

Various studies have shown that the monitor "Microdust pro" has the highest level of sensibility for measuring inspirable fractions (particulate matter with a diameter from 0.1 μm to 10 μm).

The Microdust Pro has a Wide measurement range from 0.001 to 2500 mgm^{-3} in single meter, Data-logger with >15,700 readings, Detachable probe, TSP, PM_{10}, $PM_{2.5}$ (Respirable) measurements, Firmware calibration and zero in the field, and simultaneous collection of a gravimetric (filtered) sample of the particulate matter. It is a rugged, hand-held, data-logging meter for the real-time detection of airborne particulate matter, fumes and aerosols. By using both the gravimetric and in situ measurement, two averages are collected over the exposure period. One is from the filter, whilst the other is provided by the averaging function within the instrument. It is then possible to derive the difference in these two figures and correct accordingly. Sampling was done for a year in the seventeen (17) sampling sites created in the study area and sampling was for 8 hours per sampling site and the sampler was placed between the heights of 1.5-2m of human. The Whatman fiber glass filters used were conditioned in a controlled room temperature for at least 24hrs before pre-and post weighing. The sampling was done from July 2011- June 2012. This method has been used and proven to be accurate and reliable. (**P. Baltrėna & J. Morkuniene, 2006; Ruschioni E. *et al.*, 2011; K. Agne, Jorma Pottala & Virginijus Petronis, 2008; Thatcher T. H. *et al.*, 2005**).

Sample Digestion and Measurement:

The following trace metals (Pb, Fe, Zn, Cu, Cd, Mn, Cr, Co, V & Ni) were determined by AAS (Thermo electron corporation Atomic Absorption Spectroscopy, S. series).

The effective fiber glass filter was digested with 20ml 1:1 HNO_3 in a beaker and covered with a watch glass which was concentrated to about 5ml on a hot plate at 150 – 180^oC. 10 ml 1:1 HNO_3 was added to repeat the extraction.

The extract was filtered through a filter paper and the filter paper and the beaker were washed with 0.25M HNO_3. The filterate was transferred and washed into 50ml volumetric flask. The chemical and reagents used for this analysis were analar grade.

RESULTS AND DISCUSSION

Table 2: The mean concentrations of some trace metals in Total Suspended particulate matter in Isoko Land

Site	Pb	Cd	Cu	Zn	Fe	Mn	V	Ni	Cr	Co
SP. UZ F	BDL	BDL	BDL	BDL	0.004	BDL	BDL	BDL	BDL	BDL
SP. UZ E	0.0004	BDL	BDL	BDL	0.003	BDL	BDL	BDL	BDL	BDL
SP. UZ T	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
SP. UZ M	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
SP. OG F	0.0001	0.0001	BDL	0.0001	0.02	0.001	BDL	BDL	BDL	BDL
SP. OK T	0.01	BDL	BDL	0.01	0.02	0.001	BDL	BDL	BDL	BDL
SP. EL T	0.01	BDL	BDL	0.01	0.01	BDL	BDL	BDL	BDL	BDL
SP. EL E	BDL	BDL	BDL	BDL	0.01	BDL	BDL	BDL	BDL	BDL
SP. OZ E	0.01	BDL	BDL	BDL	0.001	BDL	BDL	BDL	BDL	BDL
SP. OZ T	0.01	BDL	BDL	0.01	0.01	BDL	BDL	BDL	BDL	BDL
SP. OZ X	0.02	BDL	BDL	0.01	0.01	BDL	BDL	BDL	BDL	BDL
SP. OL F	BDL	BDL	BDL	BDL	0.0002	BDL	BDL	BDL	BDL	BDL
SP. OL T	0.0001	BDL	BDL	BDL	0.0001	BDL	BDL	BDL	BDL	BDL
SP. OL E	BDL	BDL	BDL	BDL	0.001	BDL	BDL	BDL	BDL	BDL
SP. LE T	0.001	BDL	BDL	0.01	0.02	BDL	BDL	BDL	BDL	BDL
SP. CT 1	BDL	BDL	BDL	0.001	0.001	BDL	BDL	BDL	BDL	BDL
SP. CT 2	BDL	BDL	BDL	0.02	0.02	BDL	BDL	BDL	BDL	BDL

BDL = Below Detection Limit, Detection Limit = 0.0001 $\mu g/m^3$

Enrichment Factor

Calculation of enrichment factor (EF) values helps to determine whether a certain element has additional or anthropogenic sources other than its major natural sources.

In this work, iron was chosen as the reference element. Iron has been used as reference element in previous studies (**Ediagbonya et al.,** 2012, **Okuo et al**., 2005, **Jian et al**., 2004). Since iron (Fe) has been used as a reference element for an EF evaluation, assuming that the contribution of its anthropogenic sources to the atmosphere is negligible (**Yaroshevsky,** 2006). This study used the EF calculation formula as follows:

EF = (X/Fe) air/(X/Fe) crust

Where EF is the enrichment factor, (X/Fe) air is the ratio of metal and Fe concentration of the sample, (X/Fe)crust is the ratio of metal and Fe concentration of a background.

An enrichment factor close to one would indicate that the relative concentration of a given element is identical to that which is present in the soil. An enrichment factor increase, greater than one indicates that the element is more abundant in the air relative to that found in the soil. For this study, the reference crustal ratios were taken from Wedepohl 1968.

If EF approaches unity, crustal is the predominant source, EFs up to 10 may be considered not to be significantly enriched due to differences in the chemical composition of the local soil and the reference crustal composition. Elements with EFs between 10 and 100 should be considered as enriched and those with EF greater than 100 as

highly enriched, indicating a heavy contribution of non-crustal source (**Buce et al**.; 1975). Cadmium has the highest EF which is in agreement with **Okuo et al** 2011, **Ediagbonya T.** 2011 and **Okuo et al** 2006 and **Lovenzini et al** 2006.

Table 3: Typical concentration ranges of some trace metals in the atmosphere (µg/m^3) (Misoslav, 2006)

Element	Urban	Background
Fe	0.1 – 10	0.04 – 2
Pb	0.1 10	0.02 – 2
Mn	0.01 – 0.5	0.001 – 0.01
Cd	0.0005 – 0.5	0.0001 – 0.1
Zn	0.02 – 2	0.003 – 0.1
V	0.02 – 0.2	0.001 – 0.05

Table 4: The descriptive statistics of trace metals in total suspended particulate matter (µg/m^3) and enrichment factor in Isoko Land

Element	Min	Max	Mean	SD	Enrichment Factor
Fe	0.0001	0.02	0.008076	0.007698	1
Zn	0.0001	0.02	0.00568	0.005676	4.4387
Pb	0.0001	0.02	0.005963	0.005623	16.5669
Cd	0.0001	0.001	0.0025	0.000367	117.2185
Mn	0.0001	0.001	0.001	0.00085	0.05776
Cu	0.0001	0.001	0.000325	0.00045	0.5079
Ni	BDL	BDL	BDL	BDL	
Cr	BDL	BDL	BDL	BDL	
V	BDL	BDL	BDL	BDL	
Co	BDL	BDL	BDL	BDL	

Source identification of particulate matter

In this essay, to find a common metal source, factor analysis was carried out which includes correlation coefficient of metal concentration and principal component analysis with Varimax rotation and cluster analysis.

Table 5 shows the inter-elemental correlation between the trace metals. Elements positively correlated shows that an increase in one element gives rise to a corresponding increase in the other element; while negatively correlated elements shows that an increase in one element gives rise to a corresponding decrease in the other element. From the table above most of the elements have positive correlation with each other suggesting that they are from different sources.

Table 5: Inter-elemental correlation matrix of total suspended particulate matter in Isoko Area.

	Pb	**Cd**	**Cu**	**Zn**	**Fe**	**Mn**
Pb	1.00	-0.154	-0.147	0.149	0.188	0.229
Cd	-0.154	1.00	0.980	-0.069	-0.102	0.211
Cu	-0.147	0.980	1.00	-0.115	-0.215	0.220
Zn	0.149	-0.069	-0115	1.00	0.655	0.098
Fe	0.188	-0.102	-0.215	0.655	1.00	0.412
Mn	0.229	0.211	0.220	0.098	0.412	1.00

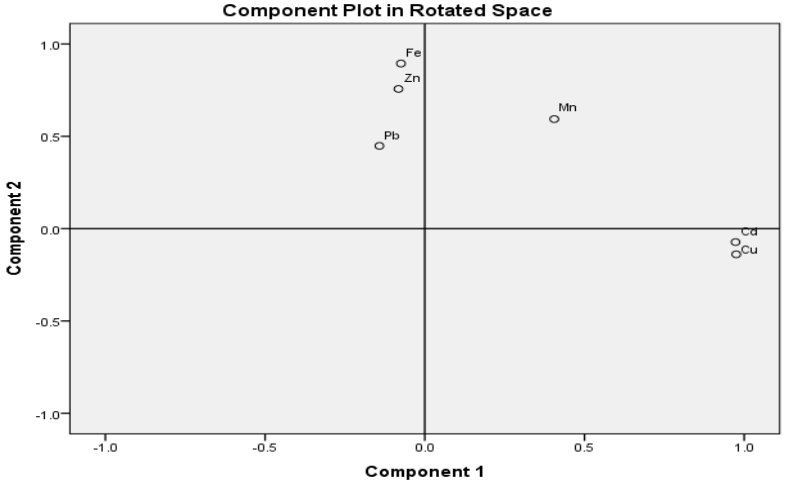
The rotated component matrix in table 6 showed that from the two components extracted from PCA; Cd, Cu and Mn loaded positively with the first component, while Pb, Zn and Fe loaded negatively with the first component. For the second component Pb, Zn, Fe and Mn loaded positively while Cd and Cu loaded negatively with the second component, this suggest that two major sources which are vehicular related emissions (60%) and re-suspended road dust (40%) .

Cluster analysis separated the data into two groups. ANOSIM showed that the groups are separated (R=0.72, P=0.0002). The PCA with varimax rotation extracted two components which explained 67.40% of the total variance.

Table 6: Rotated Component Matrix of TSP in Isoko land

	Component	
	1	**2**
Pb	-0.142	0.448
Cd	0.973	-0.073
Cu	0.975	-0.139
Zn	-0.082	0.757
Fe	-0.075	0.894
Mn	0.405	0.593

Figure 3: Rotated Component Plot



CONCLUSION

This study on the trace metal concentration of airborne particulate matter collected from Isoko land in southern, Nigeria, revealed a relatively high particulate mass but low baseline levels of trace metals.
Enrichment factor (EF) analysis proved useful in identifying the sources and their contributions to particulate matter and indicated that the background atmosphere in the studied communities is highly affected by anthropogenic pollution. Two major sources were identified, which are vehicular related emissions (60%) and re-suspended road dust (40%) which can be as a direct result of farming activities (Anthropogenic particles). From the source apportionment, it was observed that flow station activities do not directly impair the air quality of Isoko area. The levels of pollutants obtained in the study have provided baseline information about the regional pollution pattern and intra regional atmospheric cycle of the pollutants.

ACKNOWLEDGEMENT

We gratefully acknowledge the support of Dr. Chris Oke, Dr. T.F. Ediagbonya, Mrs. Esther Oke, Rev. Laura Odioko and Bishop (Dr.) Pius Odioko for their immeasurable support.

REFERENCES

Adeniye E.O., Olu-Sule R., Anyaye A. (1983). Environmental and Socioeconomic impacts of oil spillage in the Petroleum producing of Riverine Area in Nigeria: The Petroleum Industry and the Nigerian Environment. Proceedings of 1983 International Oil Seminar, NNPC, 3:130-35.

Agne k., Jorma Pottala, and Virginijus Petronis (2008). Research of dustiness on graveled roads in Lithuania. Environmental Engineering . The 7th International Conference
Bailey W., Crabree M., Tyrie J., Elphick J., Kuchuk F., Romano C., Roodhart C. (2000) Water Control; Oil field review: Shell International Exploration and Production Newsletter, 70:17-19.

Baltrėnas, P. and Kvasauskas, M. (2005) Experimental investigation of particulate concentration using mass and optical methods. Journal of Environmental Engineering and Landscape Management, Vol XII, No 2. Vilnius: Technika, 2005, p 57–64.

Baltrėnas P. and Morkuniene J. (2006). Investigation of particulate matter concentration in the air of Zverynas district in Vilnius, J. Environ. Eng. Landsc. Manage. 14(1):23 - 30.

Chatwal G.R.(1997). Encyclopedia of Environmental Air Pollution, vol. III, New Delhi Animal Publication.

Ediagbonya T.F., Ukpebor E.E., Okieimen F.E. and Okungbowa G. E. (2012) Comparative study of TSP, Inhalable Particles and Respirable Particles in Urban and Rural Areas in Niger Delta Region of Nigeria. Greener Journal of Physical Sciences Vol. 2 (3), pp. 089-096,

Efe S.I. (2006). Particulate pollution and its Health Implications in warri Metropolis, Delta State, Nigeria. Env. Anal. 11, 1339-1351

Friberg, L., Nordberg, G.F., Vouk, V.B., 1986. Handbook on the Toxicology of metals. Elsevier, Amsterdam.

Harrison, R.M., 1999. Understanding our Environment. The Royal Society of Chemistry, UK.

Hetland, R.B., O. Myhre, M. Lag, D. Hongve, P.E. Schwarze and M. Refsnes, 2001. Importance of soluble metals and reactive oxygen species for cytokine release induced by mineral particles. Toxicol., 165: 133-144.

Jian Zheng ab , Mingguang Tan a, Yasuyuki Shibata a, Atsushi Tanaka b, Yun Li a, Guilin Zhang a, Yuanmao Zhang c, Zuci Shan c (2004). Characteristic of Lead isotope ratios and elemental concentration in PM 10 fraction of air borne particulate matter in Shanghai after the phase out of leaded gasoline, Atmospheric environment 38, 1191-1200.

Ken, D., B. David, C. Anna, D. Rodger, M. William, R. Louise, T. Lang and S. Vicki, 2002. The pulmonary toxicology of ultrafine particles. J. Aerosol. Med., 15(2): 213-220. 19.

Manghan S.E. (1991). Environmental Chemistry, 5 th Edition, chapter Lewis Publisher Chelsea Milligan, U.S.A.

National Population Commission (NPC) (2006). Population Census of the Federal Republic of Nigeria **(**Abuja, Nigeria: NPC).

Obioh I. B., Olise F.S., Owoadi O.K., Olaniyi H.B. (2005). Chemical characterization of suspended particulate along air corridors of motorways in two Nigerian cities. J. Appl. Sci. 5(2):347-350.

Okuo, J. M., & Okolo, P. O. (2011). Levels of As, Pb, Cd and Fe in suspended particulate matter (spm) in ambient air of artisan workshops in Benin City, Nigeria. Bayero Journal of Pure and Applied Sciences, 4(2), 97-99.

Okuo James M and Ndiokwere CL (2005). Elemental concentration of total suspended particulate matter on relation to air pollution in Niger Delta: A Case Study of Warri: Trends in Applied Science Research 1(1): 91-96.

Pak-EPA/JICA, 2001b. 2 Cities Investigation of Air and Water Quality. http://www. environment. gov. pk/pub-pdf/FbadGujwla-std.pdf.

Radojevic, M. and Bashkin, V.N., 2007. Practical Environmental Chemistry. The Royal Society of Chemistry, London, UK.

Ruschioni E., Di Napoli M.D., Rivaroli L.R., Talone A., Cannistrà E., Giani A., Giovagnoli M., Nugari, (2011). Conservation and environmental conditions in a temporary storage area of Palazzo Soliano in Orvieto, Firenze Art 2011, pp. 88-96

Salvi, S. and S. Holgate, 1999. Mechanisms of particulate matter toxicity. Clinical and Experimental Allergy, 29: 1187-1194.

Thatcher T.H., McHugh NA, Egan RW, Chapman RW, Hey JA, Turner CK, Redonnet MR, Seweryniak KE, Sime PJ, Phipps RP (2005). Role of CXCR2 in cigarette smoke–induced lung inflammation. Am. J. Physiol. Lung Cell Mol. Physiol. 289:L322-L328.

Wallenborn, J.G. M.J. Schladweiler, J.H. Richards and U.P. Kodavanti, 2009. Differential pulmonary and cardiac effects of pulmonary exposure to a panel of particulate matter-associated metals. Toxicology and Applied Pharmacology, 241: 71-80. A. Hussain, 2008.

Wedephol K. H. (1968). Origin and distribution of the elements, L.H. Ahren Ed., Pergimon Press, London, England. P99.

WHO Report (1968). Research into Environmental Pollution WHO Technical Report Series 406.