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Trace Metals Concentration Assessment in Urban Particulate Matter in Yenagoa and its Environs

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ABSTRACT: This study was conducted to investigate the distribution and correlation of selected trace elements (Ca, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in Yenagoa, Bayelsa State and its environs. Air particulate matter was collected gravimetrically at five stations (using a high volume portable SKC air check MTXSidekickair sampler (Model: 224-52MTX). The total suspended particulate matter samples were extracted in nitric acid and hydrochloric acid mixture, followed by the quantification of the trace elements by flame Atomic Absorption Spectrophotometric (AAS) method (Model: AA 6600, GBC Avanta PM AAS). The estimated elemental data were then subjected to a set of Multivariate statistical analysis and evaluated for their mutual variations in the urban particles. The concentrations (μgm^{-3}) found in the particulate matter were in of trace elements the order of Ca>Fe>Zn>Ni>Pb>Mn>Cu>Cd>Co>Cr. On the average, the correlation of the trace elements of the study area shows strong correlations between Pb-Ni, Fe-Mn, Co-Ni, Zn-Pb, with correlation coefficients of 0.767, 0.595, 0.508, and 0.791 respectively. Principal component analysis revealed that major sources of trace metals in ambient air of the study areas were mainly emissions from automobile exhaust, industrial emissions and gas flaring.

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Most Nigerian urban cities are confronted with challenges of environmental problems especially atmospheric pollution arising from suspended particulate matter. Concern about air pollution in urban regions is receiving increasing importance worldwide, especially pollution by trace metals (Kabamba et al., 2016). Studies have shown that industrialization and meteorological factors determine the impact of air pollution on a particular location (Mohamade et al., 2016; Pinto et al., 2016 and Gonzalez-Castanedo et al., 2014). Trace elements are released into the atmosphere both from natural and anthropogenic sources namely: resuspended surface dust, combustion of fossil fuels, traffic and industrial activities. One of the most important sources of cadmium, chromium and lead in the urban environment is road traffic (Abiye et al; 2014). High loadings of Pb and Ni are due to emissions from vehicles exhaust (Ragosta et. al; 2002; Kim et. al; 2002; Shah et. al; 2006); while Mn and Fe are mainly contributed by earth crust and windblown soil (Quiterio et al; 2004; Sha et al; 2006; Chakraborty and Gupta, 2009).

Yenagoa, located in Bayelsa State is known for oil and gas production with attendant air quality problems. Recently, the state witnessed significant migration from other parts of Nigeria resulting in an increased wave of construction, commercial and industrial activities. Inorganic component of particulate matters which are mainly trace metals is very important because they are natural constituents of the earth crust and are widely distributed in environmental matrices. At elevated concentrations, all the metals are harmful to living beings including humans (Yasutake and Hiramaya, 1997). The urban population is exposed to the airborne toxic metals that often are well above natural background level (Samura et al; 2003; Zereini et al; 2005; Shridhar et al; 2010). Evident in Niger delta region of Nigeria is the problem of metal particulate air pollution and their role in the oxidation of oxides of sulphur and nitrogen resulting in the formation of acidic aerosols involved in the global acid rain. Many metal ions such as Mn^{2+} , Fe^{3+} , Cu^{2+} , Cr^{3+} , Al^{3+} and Pb^{2+} acts like a catalyst in a reaction in which sulphur (IV) acid is oxidized to tetraoxosulphate (IV) acid. Trace elements including Fe, Va, Ca, Pb, Br and Cl contribute to the formation of photochemical smog (Ward, 2000).

There are reports of total suspended matters and their trace metal concentrations in urban cities (Okuo and Ndiokwere, 2006; Okuo and Okolo, 2013; Abiye *et al;* 2014). There is hardly any such report for Yenagoa and its environs despite the importance of this area in oil and gas activities in Nigeria. Thus, the objective of this study is to determine trace metals concentration in ambient air of Yenagoa and its

environs, major sources of the metals and their enrichment factors.

MATERIALS AND METHOD

The study area is Yenagoa and its environs in Bayelsa state. It is located in low lying costal area of Niger delta, with coordinates $N04^{0}.54^{I}$ and E $06^{0}.15^{I}$ obtained using a Global Position System unit (GPS Garmin eTrex® version 3.10). The vegetation is a typical wetland with two seasons (wet and dry). The temperature throughout the year ranges between

28.6°C to 37.5°C respectively. The dry season lasts from November to March and the rainy season from April to October. The predominant occupations are fishing and farming but carried out at small scale; settlement is nucleated. The relative humidity ranges between 61 to 90%. The total area of Yenagoa is 706km², with a total population of 353,344 (NPC, 2006). The following stations (Berger junction, Onopa by government house, Tombia Roundabout, Gbaran-Ubie, and Ogbogoro Village) were selected for monitoring.



Fig 1: Map of Central Yenagoa displaying sampling stations

Table 1: Station, Location, coord	inates, and local activities
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S/No	Sampling	Sampling	Coordinates	Activities	Distance between
	Stations	code			location Ref. AQOV Km)
1	Berger round about	AQBJ	N4 ⁰ 53 22.2'	Pulverization of granite, road construction, vehicular	3.67
			E6 ⁰ 18 40.1'	movement, road traffic	
2	Onopa by Govt House	AQON	N4º56 23.2'	Vehicular movement, road traffic, road construction, residential	4.65
			E6 ⁰ 16 44.1'	activities	
3	Tombia Roundabout	AQTR	N4º50 00.8'	High vehicular movement, road traffic, commercial activities,	9.81
			E6 ⁰ 15 41.2'	open dump site, residential activities, abbatoire, open burning of animal parts	
4	Gbaran-Ubie	AQGU	N4 ⁰ 48 22.4'	Gas flaring, vehicular movement, residential activities	13.58
			E5°54 40.0'		
5	Ogbogoro village	AQOV	N4 ⁰ 54 08.6'	Road construction, few vehicular movements, low residential	0
			E6º14 50.8'	activities	

Sampling Technique: The study was carried out from the month of July 2013 to January 2014. Samples were collected for a period of 7 months to ensure that both wet and dry seasons were covered. Particulate matter samples were collected using a SKC air check MTX Sidekick sampling pump, (224-52MTX Model) by filtration through whatman membrane filters of 25mm with pore size of 3.0μ m for 8 hours (Ogunsola *et al.*, 1994, USEPA, 1999). The high volume sampler operates at a flow rate of 2.2L min^{-1.} A total of 1056L of air was pumped through a filter for 8hrs on each occasion. This sampling unit consists of a filter holder manifold connected to the sampling pump by a Teflon tube. Airborne particulate matter was collected on whatman filter paper. The sampler was installed on top of a building approximately 4.0-6.0m high above the ground level and well cleared from other buildings around. Filter papers were

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equilibrated in a desiccator for 24hours and weighed before and after sampling. Weighing balance meter AE200 was used. Each filter was weighed three times to obtain a constant and accurate weight before recording. Blank filters were also subjected to same condition and weight recorded. All filter handling was done using vinyl gloves to avoid contamination.

*Collection of Sample:*Samples were collected from five different locations for seven months. The particulate matter was obtained by pumping air through the filter paper for 8 hours (Ogunsola *et al.*, 1994, UNEP/WHO, 1994).After sampling, the loaded filter was again desiccated and reweighed to determine the final weight.

Sample Preparation and Instrument Analysis:For the estimation of selected elements, the loaded filter paper was extracted by a mixture of 20ml of high purity 65% nitric acid and of 37% hydrochloric acid (USEPA, 1999). This solution was boiled gently until it approached near dryness to boil off the excess acid and cooled to room temperature and filled to 50ml mark. This was then analyzed by Atomic Absorption Spectrometer (AAS) (Model AA 6600, GBC Avanta PM)

Data Analysis: Basic statistical parameters, multivariate analysis comprising principal component analysis (PCA), correlation matrix (CR) and cluster analysis (CA) were performed on the dataset using SPSS software version 21.0.

Enrichment Factor:Enrichment factors(EFs) was calculated using Calciumas reference element to find out the anthropogenic origin of atmospheric trace elements (Arditsoglou and Samara; *et al.*, 2005; Sha and Shahoeni 2008; Shridhar *et al.*, 2010). Usually, Na, K, Al, Mg, Ca, Mn and Fe are used as the reference (Munir *et al.*, 2013a, b). In this analysis,

calcium (Ca) was used as the reference element because it correlated well, the enrichment factor is calculated using the equation:

$$EF_{X} = \frac{\left(\frac{X}{Ca}\right) \text{sample}}{\left(\frac{X}{Ca}\right) \text{crust}}$$

Where EF(x) is the ratio of element to reference material, (X/Ca) Sample and (X/Ca) Crust refer to the mean concentrations of the target element and Ca in atmospheric particulate matter and in continental crust, respectively. The EFs are calculated on the basis of earth crust mean abundance of the metals (Wedepohl, 1995).

RESULTS AND DISCUSSION

Trace Metal Occurrence and Distribution: The mean concentration for different trace metals at various locations (AQBJ, AQON, AQTR, AQGU and AQOV) are shown in (Table 2). On the average, the highest mean concentration (approximated) was found for Ca at 216.76 x $10^{-2}\mu$ gm⁻³, followed by Fe $(65.39 \times 10^{-2} \mu \text{gm}^{-3})$, Zn $(5.80 \times 10^{-2} \mu \text{gm}^{-3})$, Ni $(1.26 \times 10^{-2} \mu \text{gm}^{-3})$ $10^{-2}\mu \text{gm}^{-3}$), Pb (0.53 x $10^{-2}\mu \text{gm}^{-3}$), Mn (0.44 x 10^{-2} $^{2}\mu \text{gm}^{-3}$),Cu (0.43x10 $^{-2}\mu \text{gm}^{-3}$) Cd (0.17 x 10 $^{-2}\mu \text{gm}^{-3}$), Co (0.16 x $10^{-2}\mu \text{gm}^{-3}$), Cr (0.08x10⁻² μgm^{-3}).On the average, the decreasing elemental concentration trend Ca>Fe>Zn>Ni>Pb>Cu>Mn>Cu>Cd>Co>Cr. was: The correlation study between the locations presented in tables 3-7 showed that all locations correlated well, except Gbaran-Ubie and Ogbogoro village which is not unconnected with the marked differences in the activities in these two locations and their distant apart relative to others. On the average, the correlation of the trace elements of the study area shows strong correlations between Pb-Ni, Fe-Mn, Co-Ni, Zn-Pb, with correlation coefficients of 0.767, 0.595, 0.508 and 0.791 respectively.

	Table 2. Statistical summary of trace elements level (μ gm- x 10 ⁻) in air borne particulate matter												
LOCATION	Ca	Cd	Co	Cr	Cu	Fe	Mn	Ni	РЬ	Zn			
AQBJ													
Minimum	27.00	0.00	0.10	-	0.20	0.70	0.00	0.10	0.40	0.30			
Maximum	453.90	0.30	0.20	-	0.40	31.00	0.90	1.20	0.60	7.60			
Mean	169.50	0.14	0.14	-	0.29	12.11	0.39	0.61	0.52	3.00			
SD	139.90	0.10	0.05	-	0.05	10.54	0.39	30.16	0.07	2.82			
AQON													
Minimum	8.10	0.02	0.04	-	0.19	0.74	0.00	0.23	0.28	0.21			
Maximum	297.53	0.09	0.11	-	0.23	348.23	1.38	1.67	0.47	2.27			
Mean	216.76	0.04	0.08	-	0.20	65.39	0.44	0.70	0.34	1.61			
SD	108.72	0.03	0.03	-	0.02	125.90	0.50	0.66	0.07	0.75			
AQTR													
Minimum	52.66	0.09	0.11	0.00	0.38	0.74	0.00	0.21	0.47	0.64			
Maximum	295.33	0.25	0.23	0.15	0.49	17.42	0.49	0.51	0.59	29.06			
Mean	197.69	0.17	0.16	0.05	0.43	6.32	0.18	0.33	0.53	5.81			
SD	81.73	0.07	0.04	0.07	0.04	6.31	0.22	0.11	0.04	10.29			
AQGU													
Minimum	92.16	0.06	0.11	0.00	0.23	0.68	0.00	0.25	0.27	0.53			
Maximum	294.33	0.23	0.17	0.21	0.38	47.94	0.42	3.03	0.36	6.91			
Mean	202.47	0.15	0.15	0.08	0.30	17.06	0.15	1.10	0.32	2.58			
SD	83.62	0.05	0.02	0.08	0.05	15.60	0.17	1.13	0.04	2.65			
AQOV													
Minimum	2.18	0.02	0.06	-	0.15	0.64	0.00	0.19	0.21	0.02			
Maximum	286.83	0.11	0.08	-	0.21	92.84	0.44	3.66	0.32	2.88			
Mean	137.30	0.05	0.07	-	0.18	31.51	0.18	1.26	0.27	1.05			
SD	118.26	0.04	0.01	-	0.03	32.89	0.16	1.45	0.04	1.03			

Source Apportionment: To probe the origin of trace metals in Yenagoa and its environs in this study, source apportionment has been performed by applying principal factor analysis (PCA) and computation of enrichment factor. PCA explains the quantitative information of those metals and their corresponding sources (Park and Kim, 2005). The data acquired at the five sampling locations were used to conduct PCA analysis and the result is presented in table 8. Three factors were identified as those contributing to the measured values in each of the locations. At AQBJ (Berger Junction), , Zn, Cu, Ca, Cd, Pb, and Co loaded positively with component 1 and 49.21% variance, Cd, Mn and Ni loaded positively with component 2 and 21.93% variance, while Pb, Co and Ni loaded positively with component 3 and 15.25% variance. At AQON (Onopa) Zn, Cu, Ca, Cd, Mn and Pb loaded positively with component 1 and 52.79% variance; only Co loaded with component 2 (19.1% variance) while Fe and Mn loaded positively with component 3 and 13.42% variance.

 Table 3. Spearman correlation for selected trace elements in air borne particulate matter at AQBJ

Metals	Fe	Zn	Cu	Ca	Cd	Mn	Pb	Co	Ni
Fe	1.000								
Zn	.276	1.000							
Cu	.076	.823	1.000						
Ca	.130	.620	.800	1.000					
Cd	054	.371	.462	.682	1.000				
Mn	213	.029	.449	.713	.779	1.000			
Pb	.011	.791	.670	.422	.632	.206	1.000		
Co	092	.759	.765	.258	.150	038	.761	1.000	
Ni	274	589	542	549	.140	.085	.009	283	1.000

 Table 4.
 Spearman correlation coefficient for selected trace elements in air particulate matter at AQON

Metals	Fe	Zn	Cu	Ca	Cd	Mn	Pb	Co	Ni
Fe	1.000								
Zn	011	1.000							
Cu	.207	.471	1.000						
Ca	.085	.988	.439	1.000					
Cd	063	.559	.928	.527	1.000				
Mn	240	.567	.514	.482	.576	1.000			
Pb	044	.536	.603	.563	.731	014	1.000		
Co	.107	.632	.000	.677	.047	089	.390	1.000	
Ni	337	.547	.774	.498	.905	.390	.847	.161	1.000

At AQTR (Tombia roundabout), Cu, Cr, Ca, Cd, Pb, Ni loaded positively with component 1 while Mn loaded negatively with % variance of 55.51%. Fe, Zn and Mn loaded positively with component 2. At AQGU (Gbaran-Ubie), Ca, Cr, Cd, Pb, Co, Ni loaded positively with component 1 while Zn loaded negatively with 54.61% variance. Cu loaded positively and Mn negatively with component 2 having 20.26% variance while only Fe loaded positively with component 3 with 12.99% variance.

At AQOV (Ogbogoro Village), Fe, Cu, Cd, Pb, and Ni loaded positively with component 1 and 46.74% variance. Zn, Ca, Mn, and Co loaded positively with component 2 and 31.19% variance while Co loaded only with component 3 and 14.80% variance.

 Table 5.
 Spearman correlation coefficient for selected trace elements in air particulate matter at AQTR

Metals	Fe	Cr	Zn	Cu	Ca	Cd	Mn	Pb	Co	Ni
Fe	1.000									
Cr	442	1.000								
Zn	.432	259	1.000							
Cu	302	.606	360	1.000						
Ca	.040	.779	240	.696	1.000					
Cd	242	.812	.213	.691	.689	1.000				
Min	.495	662	.526	323	260	331	1.000			
Pb	251	.680	.097	.795	.711	.903	186	1.000		
Co	653	.858	283	.629	.621	.715	397	.616	1.000	
Ni	287	.369	065	.908	.426	.665	076	.767	.508	1.000

 Table 6.
 Spearman correlation coefficient for selected trace

 element in air borne particulate matter at AQGU

	Fe	Cr	Zn	Cu	Ca	Cd	Mn	Pb	Co	Ni
Fe	1.000									
Cr	306	1.000								
Zn	.230	573	1.000							
Cu	012	.276	069	1.000						
Са	354	.853	619	.229	1.000					
Cd	.154	.739	741	.448	.756	1.000				
Mn	045	.041	398	713	.171	.092	1.000			
Pb	143	.891	745	.377	.916	.918	.034	1.000		
Co	.153	.664	726	.073	.397	.739	.330	.636	1.000	
Ni	087	.852	387	.446	.784	.709	336	.872	.409	1.000

 Table.7.
 Spearman
 correlation
 coefficient
 for
 selected
 trace
 element in air borne particulate matter at AQOV

Metals	Fe	Zn	Cu	Ca	Cd	Min	Pb	Co	Ni
Fe	1.000								
Zn	.418	1.000							
Cu	.763	.044	1.000						
Ca	016	.658	600	1.000					
Cd	.582	269	.817	561	1.000				
Mn	.101	.600	404	.864	239	1.000			
Pb	.840	.041	.654	112	.757	.016	1.000		
Co	.202	.143	.115	.220	.486	.645	.307	1.000	
Ni	.898	.326	.817	- 163	.565	132	.689	.020	1.000

On the average, Pb, Cu, Cd, Zn, and Ca loaded with PC1 positively: these elements are believed to be originated from automobile and industrial emission (Lee and Hieu, 2011; Okuo *et al.*, 2006). PC2 had higher principal component loading for Fe and Mn, along with considerable contribution from Co. This revealed close association of Fe and Mn in TSP in Urban atmosphere, mainly contributed by earth crust and wind-blown soil from road dust resuspension (Ragosta *et al.*, 2002; Quiterio *et al.*, 2004; Shah *et*

al., 2006). On the other hand, Co, and considerable contribution from Ni and Pb loaded with PC3; these are believed to originate from residual oil combustion (Khodeir et al., 2012). This is in support of studies carried out by Okuo et al., (2006) and Bhawna et al., (2012). Total suspended particulates matters for each location correlated well, an indicator that similar factors are responsible for pollution in the locations. However, Gbaran-Ubie and Ogbogoro village showed a slight variation and this is not unconnected with the marked differences in the nature of activities and their distance apart relative to others. Three components extracted and identified as the major sources of pollution in Yenagoa and its environs are: industrial emissions, emissions from automobile exhaust and gas flaring.

A more comprehensive understanding of the origin of trace elements in atmospheric particulate matter demands developing relationships between airborne TSP and soil, through the Enrichment Factors (EFs). Estimation of EFs is a measure to find out the anthropogenic origin of atmospheric trace elements. The results of EFs can provide useful evidence for the human intrusion of the elements in TSP by using measured element concentrations in particulates (Arditsoglou and Samara, 2005; Zereini *et al.*, 2005; Shah and Shaheen, 2008; Shridhar *et al.*, 2010). The EF value close to unity suggests that the element is dominantly contributed by natural soil dust or the contribution of anthropogenic sources is not significant. The values much higher than 1 may imply

sources other than crustal dust; these sources include human activities (e.g., combustion, automobile and industrial emissions, agricultural activities etc.) and other processes (e.g. forest fires, volcanoes, sea salt). EFs are usually taken as double ratios of the target element and a reference element in aerosols and earth crust. The reference element must be one that is overwhelmingly derived from a natural source.

Enrichment factor was calculated and the results present in table 9 for these trace elements. The average values for iron, copper, cobalt, nickel and zinc are 2.41, 1.99, 1.14, 4.53 and 5.23 respectively. This shows that they are less enriched (EF<10), while the values for lead, cadmium, manganese, are: 105.87, 63.54 and 70.39 respectively. Lead was highly enriched (EF>100), while cadmium and manganese are moderately enriched (EF between 10 and 100) (Munir et al., 2013a,b). If EF approaches unity, crustal is the predominant source. Lead has the highest EF, followed by manganese and cadmium which is in agreement with Okuo et al., 2011, and Okuo et al., 2006. Road traffic involves the emission of a wide range of trace elements that includes Pb, Cu, Zn and Cd (Gunawardena et al., 2012); Ni and V are tracers for oil combustion (Peltier et al., 2009; Peltier and Lippmann, 2010). Therefore, the EF calculated in this study tend to suggests strongly that combustion sources such as gas flaring and vehicular movement influence trace metal pollution of ambient air of Yenagoa and its environ.

	AOBJ			AQON			AQTR			AOGU			AOOV		
	PC1	PC2	PC3	PC1	PC2	PC3	PC1	PC2	PC1	PC2	PC3	PC1	PC2	PC3	
Eigen value	4.43	1.97	1.37	4.75	1.72	1.21	5.55	1.91	5.46	2.03	1.299	4.21	2.81	1.33	
% Total variance	49.21	21.93	15.25	52.79	19.10	71.89	55.50	19.08	54.61	20.26	12.99	46.74	31.19	14.79	
%Cumulative variance	49.21	71.13	86.38	52.79	71.89	85.30	55.50	74.58	54.61	74.87	87.86	46.74	77 .9 4	92.75	
Ca	0.84			0.83			0.78		0.89				0.84		
Cd	0.66	0.66		0.90	0.84		0.88		0.92			0.88			
Co			0.53				0.86		0.99				0.54	0.78	
Cr	0.95								0.92	0.00		0.05			
Cu				0.81		0.64	0.88	0.60		0.80	0.04	0.95			
Mn		0.81		0.57		0.64	0.51	0.65		0.97	0.34	0.00	0.92		
Ni		0.56	0.55	0.88			0.73	0.02	0.84			0.86			
Pb	0.80		0.51				0.87		0.99			0.85			
Zn	0.89							0.78	0.77				0.81		
	TAB	SLE 9.	Enrichm	nent fact	tor of t	race ele	ments a	t variou	s sampl	ing loca	ations				
ELEMEN	T	AQ)BJ	AQ	ON	A	QTR	A	AQGU	4	AQOV	A	VERA	AGE	
Cadmiun	ı	86	.95	19	.70	5	88.68		78.59		40.78		63.5	4	
Cobalt		1.	40	0.	.65		1.43		1.30		0.91		1.14	ļ.	
Copper		2.	24	1.	.22		2.83		1.93		1.74		1.99)	
Iron		0.	85	1.	.69		2.18		5.74		1.56		2.41	l	
Manganes	se	93	.09	81	.77	-	37.61		87.48		52.02		70.3	9	
Nickel		3.	89	3.	.43		1.77		3.68		9.86		4.53	3	
Lead		148	3.68	77	.42	1	30.07		76.76		96.43		105.8	37	
Zinc		6.	15	2.	.60		10.27		4.46		2.67		5.23	5	
Calcium		1.	00	1.	.00		1.00		1.00		1.00		1.00)	

Table 8.Principal component loadings of selected elements in the air borne particulate matter

Conclusion: In conclusion, present study showed that among the selected trace metals Pb and Cd have high enrichment factor and this is considered serious as these are hazardous to human health. Correlation study along with multivariate PCA evidenced significant anthropogenic contribution of the measured pollutants in the urban atmosphere of Yenagoa. Major atmospheric pollution sources were automobile emissions, industrial emissions, and gas flaring. Lead was highly enriched, while Cadmium and Manganese are moderately enriched. This shows impact of anthropogenic activities in the local atmosphere, which may have adverse health effects on the city dwellers.

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