X-Ray fluorescence determination of potentially toxic elements in quarry dust from Umuoghara industrial crushing site

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Abstract

Rapid population growth coupled with increasing demand for construction materials like granite and gravel have necessitated the continued growth of quarry activities in different parts of Nigeria. This study was carried out in Umuoghara town, a major quarry industrial zone in Ezza North Local Government Area of Ebonyi State. X-Ray fluoroscopy was used to determine the metal content and concentration of 5 elements (Ni, Cu, Pb, Cd and Zn) in dust samples randomly collected (8 hourly interval) from different locations within the study site on selected days in January to June, 2012. Elemental concentrations in dust samples are as follows: Cd (75.00 mg/kg), Zn (11.62mg/kg), Pb (4.91mg/kg), Cu (1.71mg/kg) and Ni (2.43mg/kg). The data was compared to the elemental composition of urban dust from selected cities in Nigeria and other cities around the world. Overall, the dust samples contained trace metals in comparable quantities that do not pose excessive health threats to both the workers and local inhabitants.

Keywords

X-ray fluorescence; Toxic element; Quarry; Dust.

Introduction

Quarrying of different useful minerals like limestone from underground deposits is an old technology [1]. The Egyptians and the Romans of old used quarried materials in the construction of the huge pyramids, temples, and monuments that still exist today. Backer [2] reported that mineral discovery and development in Nigeria dates back to the pre-historic era. The colonial administration embarked on quarrying in Nigeria for limestone in 1920 in Akamkpa area of Cross River State and its subsequent exploitation led to the establishment of Calabar Cement Company although quarrying has been going on in the area as far back as 1800 at Old Netim Akamkpa Local Government Area [3].

Quarrying activities is associated with dust particles which constitute one of the most invasive and potentially irritating air pollutants [4]. Atmospheric dust occurs in various forms including as fugitive dust from excavation, from haul roads and stone blasting or from point sources such as drilling, crushing and screening. Dust reduces visibility which poses a potent threat to both human health and the environment [4]. The atmosphere can act as a conveyor of metal pollutants, because it is more susceptible to anthropogenic emissions (such as dust) than the terrestrial or aquatic environment [4-5].The impact of dust generated during stone quarrying is influenced by several site conditions including rock properties, size of the quarry operation, proximity to population centres and other nearby sources of dust, moisture, ambient air quality, air currents and prevailing winds. However, dust concentrations, its deposition rates and potential impacts tend to decrease rapidly as the distance from source increases [5].

The increasing demand for housing and quality roads in Nigeria for instance, has resulted to increased quarrying activities and depletions of natural quarry deposits with accompanying environmental and health impacts [7-10].

Many adverse effects of quarrying activities on humans and the environment have been reported [7-13]. Composition and quantity of urban dust are environmental pollution indicators in big cities. Interest in the levels of contaminants associated with urban dust has risen in the last few decades, particularly the concentration and distribution of substances (metals) like lead, copper, cadmium and zinc including their source identification [10]. Studies has identified sources of these metal contaminants as present in urban dust, industrial and commercial activities, road construction and large scale use of coal in power plants and soil [6]. The presence of metals in potentially toxic forms and in potentially toxic concentrations in the soils can lead to the contamination of water supplies and exert phytotoxic effects which may result in trace element contamination of edible crops. Population exposed to these elements develops alterations in their nervous systems with attendant neurophysical consequences resulting to severe health hazards [10-11].

Quarry workers suffer from 'silicosis', through inhalation of minute dust particles (0.1 to 150 μm) high in silica [9, 12]. Other respiratory and skin problems have also being reported among manual stone crushers e.g. in Abia State [13] and pulmonary cases among stone crushers at Umuoghara crushing site in Ezza North Council Area of Ebonyi State [11].

Dust from quarrying have been reported to stall the growth and flowering of crops, by settling on surfaces of leaves thereby interfering with the normal photosynthetic and other exchanges that take place at the leaf and atmosphere interface [9, 12].

Insufficient data in developing countries on the impact of mineral exploration on the environment especially heavy metals pollution has made it necessary for increased studies in this area. Previous reports in Abakaliki e.g. Omaka [10] revealed varying concentrations of metallic contaminants from dust samples collected within the metropolis (Fe: 881.00-1422.33, Pb: 6.17-9.96, Al: 25.48-41.24 and Cu: 18.33-99.33 mg/L respectively).

Several methods have been reported for the determination of metals in dust and soil samples e.g. Flame-AAS, Graphite-AAS, ICP-OES, ICP-MS and XRF [14]. Flame-AAS, used for single element is subject to high chemical interferences. However, inductively coupled plasma mass spectrometry (ICP-MS) though used for multi-element analysis, can only analyse metals after pre-treatment and is also subject to chemical interferences [14]. X-Ray Fluorescence (XRF) was preferred in this study because multi-element determination was possible without sample pre-treatment.

The main aim of this study was to determine the concentrations of selected trace metals in dust samples from Umuoghara quarry site. Other objectives were to investigate the loads of metallic constituents in the top soil within the vicinity of the quarry site, to compare research results obtained with available data on similar studies done on urban dust composition in neighbouring Nigerian cities and major cities globally.

Materials and methods

Study background

Ebonyi State is very rich in solid minerals and deposits of lead and zinc are abundant in the state. The State lies within the lead-zinc field of the Eastern cretaceous belt of Nigeria e.g. Abakaliki and Ishiagu areas where lead and other associated ores are also mined and limestone quarried [15].

Abakaliki is the capital of the present day Ebonyi State in South Eastern Nigeria. It is located at latitude 6°20° N and longitude 8° 06° E. The population of Abakaliki according to 2006 census is 141, 438. The average elevation of Abakaliki is 117m. It has average temperatures ranging from 11°C in January to 14°C in November and average rainfalls in the region of 60mm (May) to 78mm (September) [8]. The area chosen for this investigation is a quarrying site located at Umuoghara Community in Ezza North Local Government Area (LGA) close to Abakaliki, Ebonyi State. Ezza North LGA is made up of rural autonomous communities spread around a land mass of about 58,072 square kilometers. Although pockets of mining have been going on within the area, it was only recently that quarrying activities assumed prominence to compliment the State Government’s drive for more revenue [16].

Description of study area

The major occupations of the inhabitants of Umuoghara are farming, trading and stone quarrying. Stone quarrying is however the most notable economic activity going on in the area. The quarry industry there has about 300 crushers arranged in 4 clusters with about 250 workers found at the site on a daily basis. The workers comprise of both males and females aged between 15-45 years and drawn from both Ebonyi and other neighboring states in Southeastern Nigeria [16]. A map of Abakaliki showing the location of Umuoghara, the sampling site is given in Figure 1. A typical working face of a crushed stone operation showing rubble created by blasting is shown in Figure 2.

Sampling design

About 5 different elements (Ni, Cu, Pb, Cd and Zn) were investigated in the dust samples of the selected study site. The sampling was done on a monthly basis between January and June, 2012 and involved collecting samples from different points within the same quarry site consecutively for 6 months (January-June).

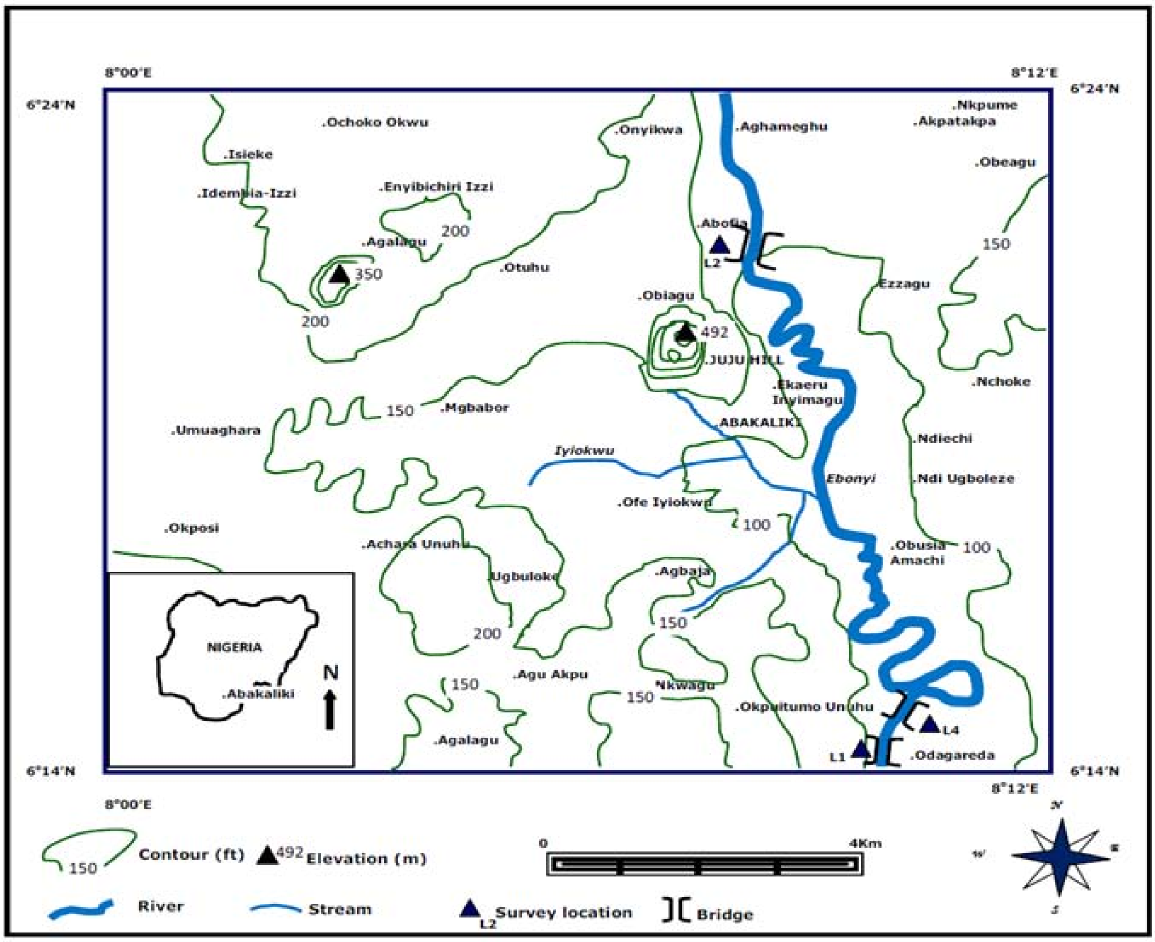

Figure 1. *Map of Abakaliki showing location of Umoghara industrial quarry site [26]*

Sample collection

Quarry dust samples were collected (8 hourly interval) randomly at different points within the study site on selected days in January to June, 2012. The samples were collected using three different 1.0m^2 High Density Polyethylene (HDPE) cut out and placed at different locations within the quarry site. The 1.0m^2 was first rinsed with de-ionized water and soaked in detergent overnight, rinsed with de-ionized water again and soaked in 10% HNO_3 overnight.

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Figure 2. *Working face of a crushed stone operation showing rubble created by blasting [11]*

Sample collection

Quarry dust samples were collected (8 hourly interval) randomly at different points within the study site on selected days within the sampling period. The samples were collected using three different 1.0 m^2 High Density Polyethylene (HDPE) cut out and placed at different locations within the quarry site. The 1.0 m^2 was first rinsed with de-ionized water and soaked in detergent overnight, rinsed with de-ionized water again and soaked in 10% HNO_3 overnight. This cleaning procedure eliminates adsorption onto the surfaces of the containers [17]. All the samples were taken to the laboratory immediately for pre-treatment and analysis. Sampling implements and other work surfaces were always thoroughly cleaned during sample preparation and analysis. To identify the collected samples, the representative sample randomly collected in January was labelled A while that randomly collected during the month of June was labelled B. In addition, a composite sample representing all the six samples randomly collected from January to June was labelled C.

Sample preparation and analysis

Each sample was pulverized to a fine powder using agate mortar and 13mm pellet formed using a CARVER model manual pelletizing machine at a pressure of 6-8 torr. The samples were then taken to the X-Ray Fluorescence (XRF) laboratory at the Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife, Osun State, Nigeria for elemental analysis using X-Ray Fluoroscopy. The pelletized sample was inserted into the sample holder of the X-Ray Fluorescence (XRF) system and was bombarded by the X-Ray tube at a voltage of 25V and current of 50µA for 100 counts or approximately 18 minutes. The characteristic X-Ray of the sample areas were detected by the solid state Si-Li detector system. The spectrum analysis was carried out using the ADMCA and FP-CROSS Software which relates the peak area with concentration.

Results and discussion

The results of the X-ray fluoroscopic analysis of the dust samples from Umuoghara quarry site are shown in table 1. A closer look at table 1 shows that cadmium had the highest concentration, followed by zinc while all other metals investigated were relatively low in concentration when compared to Cd and Zn. This trend shown by Cd and Zn could be as a result of mineralization. The variation in metal concentrations can also be attributed to the differential deposition of these metals in different layers of the soil [7]. Ebonyi State is highly mineralized with abundant deposits of lead and zinc and their associated ores [15].

Descriptive data analysis [mean, median, range, standard deviation (SD), variance, variation coefficient (VC) and skewness] was carried out. VC which is SD/mean and SD was used to reflect the discrete distribution of different element metal concentrations and indirectly indicate the active nature of the selected metal in the environment investigated. Skewness was however used to reflect different distributions of the metals (see table 2).

The concentrations of various metals in the quarry dust (in ppm) shows a wide range of variations: Cd>>Zn>Pb>Cu>Ni (75.00>>11.62>4.91>2.43>1.71) probably as a result of differences in composition of rock layers and dispersion by wind which carries dust containing particles (metals) and scatters them in all directions.

Cadmium (75ppm), zinc (11.62ppm) and lead (4.91ppm) are the three most abundant trace metals in quarry dust from the study site and this may be due to the fact that Ebonyi state lies within the lead-zinc field of the Eastern cretaceous belt of Nigeria [15].

The data from Umuoghara quarry site were compared to similar data from researches on the composition of urban dust in selected locations both locally (Abakaliki, Uturu, Aba, Calabar, Eket and Port-Harcourt) and internationally (Beijing, Calcutta, Istanbul, Zurich, Ottawa Honolulu and Madrid).

Table 1. Descriptive statistics of heavy metal concentration (mg/kg) in quarry dust

Element	Range	Mean	Median	SD	Variance	VC	Skewness
Ni	0.79-5.50	2.43	1.01	2.66	7.07	1.10	1.72
Cu	1.23-2.57	1.71	1.34	0.74	0.55	0.43	1.69
Pb	2.12-8.55	4.91	4.06	3.30	10.88	0.67	1.08
Mn	109.15-193.48	139.62	116.23	46.78	2188.21	0.34	1.69
Zn	7.42-19.33	11.62	8.12	6.68	44.67	0.57	1.71

Range: Minimum – Maximum SD: Standard Deviation VC: Variation Coefficient = SD/Mean

Table 2 compares the data from this present study to comparative data on the urban dust composition of selected cities in Nigeria.

The metallic composition of urban dusts (for example Ni content) in cities like Calabar, Eket and Port-Harcourt are comparatively lower [0.0013ppm (Calabar), 0.0015ppm (Eket), 0.0020ppm (Port Harcourt) than in towns like Umoughara, Abakaliki and Uturu (2.43ppm, 0.03ppm and 0.27ppm respectively) as a result of the relatively high humidity in the coastal cities (Calabar, Eket, Port Harcourt) which results in little or no dry dusty weather conditions all year round. But towns like Abakaliki, Uturu and Umuoghara has relatively higher metallic concentrations in their dust samples which can be accounted for as a result of their dry and dusty weather conditions with little or no humidity [8, 18].

Thus, overall, dust samples from the study site have the highest trace metal levels, followed by those from Uturu and Abakaliki, whereas samples from Aba, Calabar, Eket and Port Harcourt showed negligible concentrations in all the trace metals being measured [8, 18].

Table 2. Comparing the elemental concentration (ppm) of dust samples in present study and selected cities in Nigeria

Town	Cu	Ni	Pb	Zn	Cd	Reference
Umuoghara	1.71	2.43	4.91	11.62	75.00	Present study [a]
Abakaliki	-	0.03	2.00	0.03	0.21	[8] [a]
Uturu	-	0.27	2.30	0.04	0.48	[8]
Aba	0.0030	0.0016	0.0017	0.0136	0.0011	[18] [b]
Calabar	0.0026	0.0013	0.00012	0.0034	0.0011	[18]
Eket	0.0026	0.0015	0.0013	0.0031	0.0015	[18]
Port Harcourt	0.0031	0.0020	0.0015	0.0078	0.0020	[18]

LEGEND - a: average values of metal concentrations (in mg/kg) are used
b: values were originally in $\mu g/m^3$ in the cited reference but converted to mg/kg

A comparison of the elemental composition of urban dust in Abakaliki (the closest city to the study site) with that of major cities worldwide is shown in table 3.

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For the case of Cd, Abakaliki showed Cd enrichment (78mg/kg) and was comparatively higher than Cd levels in urban dusts of Ottawa (0.37mg/kg), Beijing (1.67mg/kg), Calcutta (3.12mg/kg), Istanbul (3.85mg/kg), Islamabad (5.00mg/kg) and Oslo (1.4mg/kg). Copper is not found in appreciable quantities in Abakaliki urban dust, hence there is no basis for comparison with that of other cities. In all cases, the Ni level (39mg/kg) in Abakaliki urban dust was found to be comparatively lower than that of the rest of the cities cited (Honolulu, 177mg/kg; Beijing, 72mg/kg; Calcutta, 42mg/kg; Oslo, 41mg/kg) except in the case of Ottawa (15.2mg/kg), Istanbul (38mg/kg) and Islamabad (23mg/kg). The Pb level in Abakaliki urban dust (260mg/kg) was higher than Pb levels in urban dusts of Ottawa (39.1mg/kg), Honolulu (106mg/kg), Beijing (126mg/kg), Islamabad (104mg/kg) and Oslo (180mg/kg). Abakaliki urban dust showed comparatively poor Zn enrichment (39mg/kg) hence, in all cases, the Zn levels of urban dusts in all the cities sited were comparatively higher (Ottawa, 112.5mg/kg; Honolulu, 434mg/kg; Beijing, 167mg/kg; Calcutta, 159mg/kg; Istanbul, 1039mg/kg; Islamabad, 106mg/kg; Oslo, 412mgkg) [8, 19-25].

Table 3. Comparison of metallic concentrations (in mg/kg) found in urban dust from Abakaliki and other selected cities worldwide

City/Country	Cd	Cu	Ni	Pb	Zn	Reference
Abakaliki (Nigeria)	78	-	39	260	39	[8]
Ottawa (Canada)	0.37	65.8	15.2	39.1	112.5	[19]
Honolulu (USA)	-	167	177	106	434	[20]
Beijing (China)	1.67	42	72	126	167	[21]
Calcutta (India)	3.12	44	42	536	159	[22]
Istanbul (Turkey)	3.85	227	38	222	1039	[23]
Islamabad (Pakistan)	5	52	23	104	106	[24]
Oslo (Norway)	1.4	123	41	180	412	[25]

Conclusion

The data obtained from this study compared favourably with data from similar studies conducted in selected cities in Nigeria and other cities globally. There is no aggravated increase in trace metal levels in the study area hence, no major health risks are being faced by inhabitants living in this area. Finally, results obtained from this research would now provide significant reference data for future studies within Umuoghara and other parts of Ebonyi State.

References

1. Ekmekci M., *Impact of quarries on Karst groundwater systems, hydrological processes in Karst, Terrenes*, Antalya Symposium and Field Seminar, 1993, 207, p.3.
2. Baker J. R., *A study of the world borne tailings in Zimbabwe*, South African Institute of Mining and Metallurgy, 1981, 1(1), p.197-198.
3. Crysanthus C., *Evaluating baseline data for trace elements, pH, organic matter content and bulk density in agricultural soils in Nigeria*, Water, Air and Soil Pollution, 1996, 86, p. 13-34.
4. Langer W. H. (online), *Potential impacts of quarrying stone in karst-a literature review*. Available at: http://geology.cr.usgs.gov/pub/ofrs/OFR-01-0484/ (accessed 9/02/2014).
5. Howard B., Cameron I., *Dust control: Best practice environnemental management in mining*, Environment Australia, 1998.
6. Zuzana H., Jaroslav M., Miroslav K., Vitezslav., *Identification of factors affecting air pollution by dust aerosol PM10 in Brno City, Czech Republic*, Atmospheric Environment, 2008, 42, p. 8661-8673.
7. Adie G.U., Etim E.U., *Assessment of toxic heavy metal loading in topsoil samples within the vicinity of a limestone quarry in South Western Nigeria*, African Journal of Environmental Science and Technology, 2012, 6(8), p. 322-330.
8. Chiemeka I.U., *Determination of the metal content and concentration of quarry dust in air at Ugwuele, Uturu and Abakaliki, Nigeria*, International Science Research Journal, 2011, p. 78-81.
9. Madhaven P., Sanjay R., *Budhpura 'ground zero, sandstone quarrying in India*, India Committee of the Netherlands, Netherlands, 2005, p. 32.
10. Omaka O.N., *Atmospheric and metallic pollutants and their impacts on the environment: case study of Abakaliki Metropolis*, Journal of Applied and Natural Sciences (JANS), 2010, 4(1), p. 24-29.
11. Nwibo A.N., Ugwuja E.I., Nwambeke N.O., Emelumadu O.F., Ogbonaya L.U., *Pulmonary problems among quarry workers of stone crushing industrial site at Umuoghara, Ebonyi State, Nigeria*, The International Journal of Occupational and Environmental Medicine, 2012, 3, p. 178-185.
12. Durvasula R., *Occupational health information systems in developing countries-India: A*

case study. 4th Takemi Symposium on International health in the Third World: problems and policies, Boston, Harvard School of Public Health. 1990.

13. Ugbogu, O.C., Ohakwe, J., Foltescu, V., *Occurrence of respiratory and skin problems among manual stone quarry workers,* African Journal of Respiratory Medicine, 2009, p. 23-26.
14. Patanaik, P., *Handbook of environmental analysis* (*2nd ed.*): *chemical pollutants in air, water, soil and other chemical wastes.* Boca Raton, Florida, CRC Press, 2010, p. 89-98.
15. Ebonyi State Ministry of Information and State Orientation. *Dairies Publication*, Abakaliki, Nigeria, Abakaliki Government House Printing Press, 2013.
16. Ebonyi State Ministry of information and state orientation. Documentary Diary on Ezza North LGA. Abakaliki, Nigeria, Abakaliki Government House Printing Press, 2011.
17. Garrison, V., Lamothe S. and Plumlee G. *Trace-metal concentratrations in African dust: Effects of long-distance transport and implications for human health*. 19th World Congress of Soil Science: soil solutions for a changing World, Brisbane, Australia, 2010.
18. Uno, U.A., Ekpo, B.O., Etuk, V.E., Etuk, H.S. and Ibok, U.J. *Comparative study of levels of trace metals in airborne particulates in some cities of the Niger Delta Region of Nigeria*, Environment and Pollution, 2013, 2(1), p. 110-121.
19. Rasmussen, P.E., Subramanian, S.K., Jessiman, B.J. *A multi-element profile of house dust in relation to exterior dust and soils in the city of Ottawa, Canada*, The Science of the Total Environment, 2001, 267, p. 125-140.
20. Sutherland, R.A., Tolosa, C.A. *Multi-element analysis of road deposited sediment in an urban drainage basin, Honolulu, Hawaii*, Environmental Pollution, 2000, 110, p. 483-495.
21. Han, L., Zhuang, G., Cheng, S., Wang, Y., Li, J. *Characteristics of re-suspended road dust and its impact on the atmospheric environment in Beijing*, Atmospheric Environment, 2007, 41, p. 7485-7499.
22. Chatterjee, A. and Banerjee, R.N. *Determination of lead and other metals in residential area of greater Calcutta*, The Science of the Total Environment, 1999, 227, p. 175-185.
23. Sezgin, N., Ozcan, H.K., Demir, G., Nemlioglu, S., Bayat, C. *Determination of heavy metal concentrations in street dusts in Istanbul E-5 highway*, Environment International, 2003, 29, p. 979-985.

24. Yasir, F., Tufail, M., Tayyeb, J.M., Chaudhry, M.M., Siddique, N. *Road dust pollution of Cd, Cu, Ni, Pb and Zn along Islamabad Expressway, Pakistan,* Microchemistry Journal, 2009, 92, p. 186-192.
25. De Miguel, E., Llamas, J.F., Chacon, E., Berg, T., Larssen, S., Royset, O. and Vadset, M. *Origin and pattern of distribution of trace elements in street dust: unleaded petrol and urban lead,* Atmospheric Environment, 1997, 31(17), p. 2733-2740.
26. Omaka O.N., Offor I.F., Nwabue F.I., Onyekezini K. and Mba C.C. *Analyses of species of phosphorus in four selected streams within Abakaliki Metropolis, Nigeria*, British Journal of Applied Science and Technology, 2014, 4(8), p.1285-1295.