



Heavy Metals Concentration Analysis in Air Particulates of Some Major Towns of Nasarawa State–Nigeria

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Abstract

This work analyzed the presence of seven heavy metals (Cd, Cr, Pb, Mn, Zn, Cu and Ni) measured in fine particulates (PM₁₀) samples collected daily using a Whatman glass fiber filters in five major towns of Nasarawa State, Nigeria, using a high volume respirable dust sampler (APM 460 NL). Ambient air laden with suspended particulates enters the APM 460 NL system through the inlet pipe as the air passes through the cyclone; it is acted upon by centrifugal forces which separate it into fine and coarse particles. The wet digestion method (HNO₃ / HF1) was used for metal analysis by the Flame Atomic Absorption Spectrophotometry (FAAS) method. The mean concentration of PM₁₀ in the study towns was found to range from 40 – 80 µg/m³. FAAS analysis of the PM₁₀ samples shows that the concentrations of heavy metals ranged from 0.018 - 0.064 mg/m³ for Cd, 0.000 - 0.062 mg/m³ for Cr, 0.300 - 0.720 mg/m³ for Pb, 0.110 - 0.184 mg/m³ for Mn, 0.195 - 4.480 mg/m³ for Zn, 0.088- 0.124 mg/m³ for Cu, and 0.000- 0.146 mg/m³ for Ni across the study towns. The concentrations of Cd, Pb and Mn were found to be far above the WHO/EU permissible limit levels of 0.005 mg/m³, 0.050 mg/m³ and 0.150 mg/m³ respectively. Weak correlations were found between the concentrations of the heavy metals. The correlation coefficient R ranged from 0.001 – 0.240 which signified that the sources of metals in the ambient air of the study towns comes from different anthropogenic influences, meteorological factors and vehicular traffic. These results suggested that the people living and working in these towns are exposed to health risk. We do recommend that policy makers should step up regulations to monitor these anthropogenic activities to caution the effects.

Keywords: PM₁₀ concentration, Air Quality, Heavy Metals, Correlation and Concentration.

Introduction

Heavy metals present in trace concentration play a major role in the metabolism and healthy growth of plants and animals. Further their increased concentration may have several toxicological effects on human beings^{1,2}. There are two main sources of heavy metals in ambient air i. natural ii. anthropogenic. The natural sources include the release of metals from rock weathering and dust storms, insect fragments and sea spray into the atmosphere. The anthropogenic sources include discharge of heavy metals into the atmosphere by burning of fossil fuels/ industrial activities, bush burning and incineration of waste. Pollution of the natural environment by heavy metals is a worldwide problem because these metals are indestructible and most of them have toxic effects on living organisms; while some of these elements are essential for humans, at high levels they can also pose toxicological risk². About 4 - 8 percent of deaths occurring annually, in the world, are related to air pollution associated with anthropogenic activities³. The composition of air pollutants can be organic, inorganic or complex mixtures of both. Among the many inorganic pollutants originating from anthropogenic activities, heavy metals are of major concern due to their toxic and potential carcinogenic characteristics. In recent times, studies of air pollution especially in the urban environment have focused largely on respirable

particulates, including seasonal variation and the threat poses to human health^{4,6}. It has been reported that metals absorbed in respirable dust suspended particulates such as those analyzed in this work produces tissue damage of the lungs⁷. The health effects of toxic metals in the air and from road deposited dust is better appreciated if one consider the fact that an active person typically inhaled 10,000 to 20,000 liters of air daily⁸. It is logical to note that this intake increases with vigorous exercise. During inhalation, these pollutants may enter the numerous tiny air sacs deep inside the lungs and also blood stream thereby affecting several other organs than the lungs⁸. The objective of air quality assessment is to gauge the deterioration of air quality caused by anthropogenic activities and to evaluate the efficiency of the measures applied. In view of the increasing evidences of PM₁₀ on human health and environment, not much data on PM₁₀ one of the major components of air particulates pollutants is available for urban area in Nigeria. Information regarding PM₁₀ quality in Nasarawa State major towns which are currently experiencing road construction, infrastructure development and high inflow of vehicular traffic as a result of their proximity to FCT Abuja is not available. This study samples PM₁₀ concentration and also evaluates the levels of some selected heavy metals (Cd, Cr, Pb, Mn, Zn, Cu and Ni) in PM₁₀ samples of some major towns of Nasarawa State, Nigeria.

It is hoped that the study will form a baseline that can be used by policy makers to achieve better environmental quality and sustainable development in Nasarawa State.

Materials and Methods

Sampler and Analytical Procedures: In this study, the sampling tool employed was the high Volume respirable dust sampler (APM 460 NL) model. This sampling unit consists of an inlet pipe with an in built flow rate meter and a filter adaptor assembly connected to the sampling pump by a cyclone. Airborne particulate matter was collected on a Whatman glass fiber filter papers (GF/A) 8 by 10 inches. The inbuilt gas flow meter has a rating of 0.9 to 1.2 M³/min of air samples.

Before sampling, all unloaded glass fiber filters were dried in desiccators at room temperature and their initial weights were taken.

The particulates were collected on the pre-weighed filter papers after exposure for eight hours and then dried again in desiccators and re-weighed to determine the final weight.

The concentration of the fine particulates in the air was determined from the difference in weight of the filter paper after and before sampling divided by the volume of air sampled^{9,10}.

The sampler was placed at a height of 1.5 meter above ground level to reflect the breathing zone of human.

Fine particulate PM₁₀ concentration was computed from the relation

$$\text{Con } (\mu\text{gm}^{-3}) = \frac{(\text{Final-initial})\text{mass of filter paper}}{\text{Volume of air sampled}} \times 10^6 \quad \text{or} \quad \text{Con } (\mu\text{gm}^{-3}) = \frac{w_2 - w_1}{v} \times 10^6 \quad (1)$$

Where: v = Φ x t, Φ = average flow rate readings in m³/minute and t is sampled time in minutes, 10⁶ is conversion factor from grams to micrograms.

After determining the concentration of the fine particles, the filter papers were stored in desiccators and removed as needed and digested in concentrated nitric acid and hydrofluoric acid and placed in a fume cardboard at a temperature of 150⁰ Celsius. Next to the digestion, the content was filtered through Whatman filter paper number 42 and a standard volume made up of 100 ml with distilled water along with a blank also prepared in same manner. The filtrates were tested for the concentration of Cd, Cr, Pb, Mn, Zn, Cu and Ni using Atomic Absorption Spectrophotometer (Serial NO. AA0904M046) Flame Test to determine the heavy metals concentration in accordance with the user manual from the Multi User Scientific Research Laboratory of the Ahmadu Bello University, Zaria (MUSRL/ABU Zaria).

Because of the proximity of residential houses to the PM₁₀ sources and human exposure, the probability of human effect exists. Thus toxicity potential (TP) are computed as

$$T P = \frac{\text{observed Concentration of metal}}{\text{Permissible limit set by WHO/EU}} \quad (2)$$

T P > 1 is harmful to human^{10,11}.

Study Area: The study area covers five major towns which are Lafia, Akwanga, Keffi, Karu and Nassarawa (all in Nassarawa State- Nigeria). The area is approximately 11120 km² and is located within latitude (7.6⁰-8.3⁰) N and longitude (7.5⁰-8.31⁰) E. The approximate population of the area is 932,118 according to 2006 census figure¹². The climate condition is tropical, characterized by wet and dry seasons. The wet season set in between April and October while the dry season is between November and March¹³. The main human activities in these towns that emit high pollution are the particulate generate from bike, vehicular exhaust, local manufacturing industries, bush/refuse burning and resuspended particle from the unpaved roads.

Sampling Site Selection: Four sites were selected in each of the five towns for study as shown in Table-1.

Table-1
Sampling Towns and Sites / Coordinates

S/N	Town	Site Names	Coordinate	
			Lat.	Long.
1	Lafia	Rice mill, Doma Road junction, Main Market and GRA Road Construction site	8.3N	8.31E
2	Akwanga	Akwanga motor Park, Jos/Keffi Roundabout, Main market and Lafia Road	8.55N	8.23E
3	Keffi	Angwan Waje, Total Roundabout, Abuja/Kachia Junction and Keffi Main Market	8.51N	7.52E
4	Karu	Karu International Market, New Karu Junction, Abuja express way and Mararaba-Aso road stone crushing site	9.03N	7.60E
5	Nassarawa	Central Motor Park, Toto Junction, Main Market and Bread baking factory	7.59N	7.49E

The four sites were chosen in the 'heart' of the selected towns based on human activities, high population density and traffic volume as carefully observed by the researcher.

volume fraction (ppm) and this were converted to mg/m³ using the relation:

$$\text{Conc (mg/m}^3\text{)} = \frac{PPm \times M_i}{24.5} \quad (3)$$

Abdel-Rahman¹³

Results and Discussion

The monthly mean concentration of PM₁₀ sampled in the study towns from September 2015 to December, 2015 was determined using (1) and presented in Table-2. While the result of the heavy metals concentration analyzed was reported in terms of their

Where: M_i is the molecular weight of the ith metal in g/mol and 24.5 is the quotient of mean mass of air by its density at 25°C¹⁴. The toxicity potential was computed using (2) and presented in Table-3 as follows:

Table-2
Monthly Mean Concentration of PM₁₀ in the Study Towns

Town	Monthly Mean Concentration of PM ₁₀ (µg/m ³)				Mean
	Sept.	Oct.	Nov.	Dec.	
Lafia	55.556	48.157	66.170	124.434	73.579
Akwanga	43.516	61.303	57.870	65.789	57.120
Keffi	56.155	27.027	65.734	71.217	55.033
Karu	70.099	69.615	70.199	103.226	79.035
Nasarawa	38.363	31.153	34.435	57.624	40.394

Source: Field Survey, 2015

Table-3
Mean Concentration of Heavy Metals in the study Towns with their Toxicity Potential

Metals (M _i)	Mean Concentrations in the study Towns (mg/m ³)					Permissible limit set by WHO/EU (mg/m ³)
	Lafia	Akwanga	Keffi	Karu	Nasarawa	
Cadmium	0.041	0.018	0.032	0.064	0.041	0.005
Toxicity potential	8.20	3.60	6.40	12.80	8.20	
Chromium	0.062	0.000	0.000	0.000	0.000	0.500
Toxicity potential	0.12	0.00	0.00	0.00	0.00	
Lead	0.54	0.60	0.30	0.72	0.41	0.050
Toxicity potential	10.80	12.00	6.00	14.40	8.20	
Manganese	0.074	0.161	0.184	0.132	0.110	0.150
Toxicity Potential	0.49	1.08	1.23	0.88	0.73	
Zinc	2.970	4.480	0.195	2.028	2.748	5.000
Toxicity Potential	0.59	0.90	0.04	0.41	0.55	
Copper	0.124	0.091	0.093	0.112	0.088	1.000
Toxicity Potential	0.12	0.09	0.09	0.11	0.09	
Nickel	0.146	0.000	0.005	0.022	0.041	0.050
Toxicity Potential	2.92	0.00	0.10	0.43	0.82	

Source: Field / Authors' computation, 2015

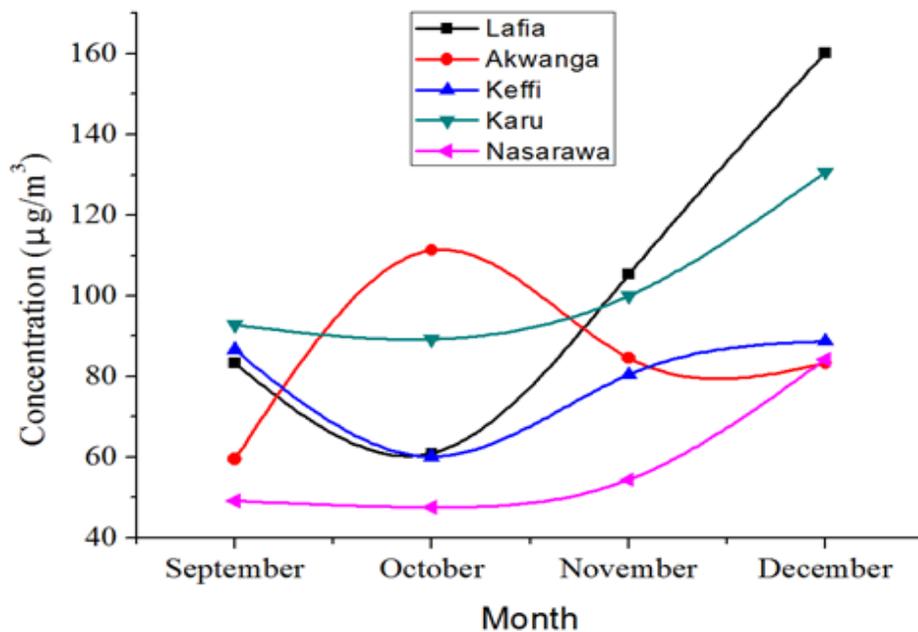


Figure-1
 Monthly mean concentration of PM₁₀ in the ambient air of the study towns of Nasarawa State

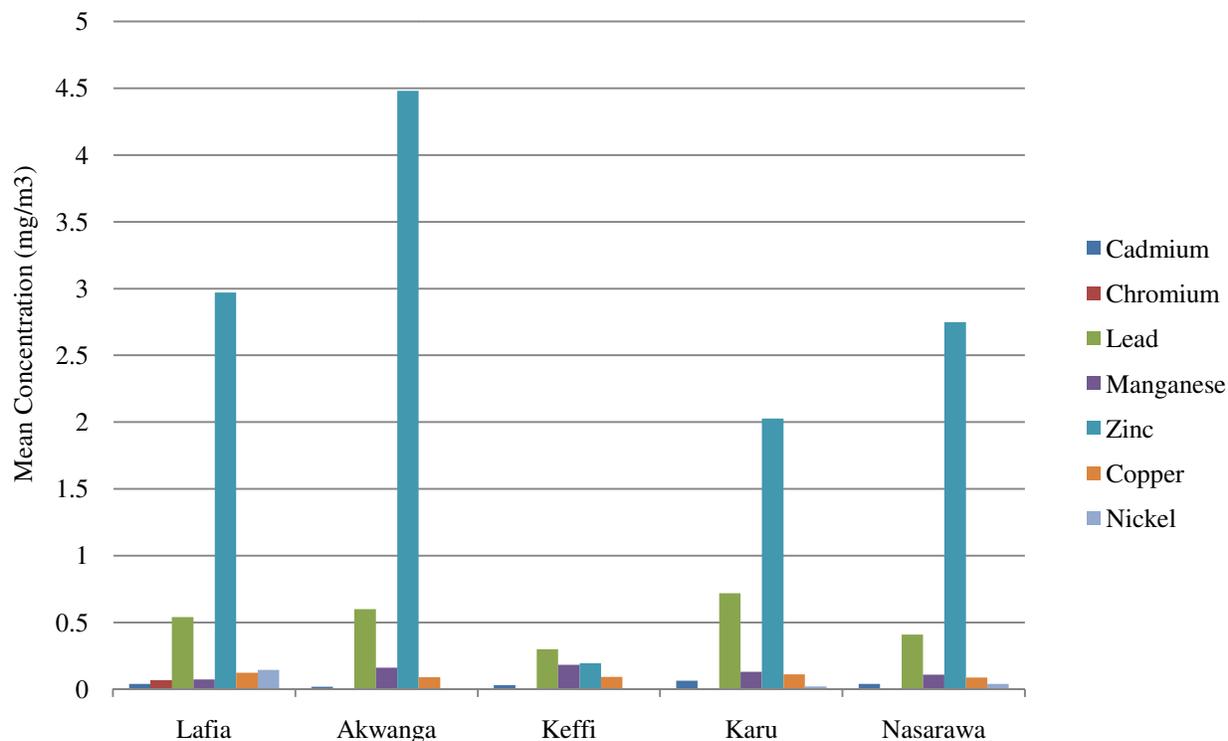


Figure-2
 Mean concentrations of heavy metals in the ambient air of Nasarawa state towns

The monthly mean concentrations of fine particulates (PM_{10}) presented in Table-2 and Figure-2 shows that Karu has the highest concentration of $79.035\mu\text{g}/\text{m}^3$ followed by Lafia town with $73.579\mu\text{g}/\text{m}^3$; these values exceed the $65\mu\text{g}/\text{m}^3$ and $50\mu\text{g}/\text{m}^3$ permissible limit value set by NAAQS and WHO for PM_{10} concentration in ambient air. A careful observation also shows the PM_{10} concentration shows an increasing trend as we move from September and December. This could be attributed to high traffic density and local industries which are sited in Karu as a result of its proximity to FCT Abuja, for Lafia it may not be unconnected to massive ongoing road construction work in Lafia town and also high traffic volume combine with other activities like burning tyres for street protest or for roasting lambs and goats. The increasing trend observed can be attributed to meteorological factors like wind speed and direction. Another reason may be the fact that as we approach December rain had reduced, washout was also reduced and resuspension of dust was enhanced.

These towns are more likely to record human respiratory related diseases like aggravated asthma, aggravated coughing, painful breathing and chronic bronchitis since these diseases are function of PM_{10} pollutant in the ambient air¹⁰. For Akwanga, Keffi and Nasarawa towns, even though the mean concentrations were below the permissible limit cumulative health effects exist¹⁵. The mean concentration of $25 - 124\mu\text{g}/\text{m}^3$ for PM_{10} captured in this study is within the range of literature values presented by many other authors.

Heavy Metals Analysis: Seven heavy metals (Cd, Cr, Pb, Mn, Zn, Cu and Ni) concentrations in the five study towns was determined from September – December, 2015 using Atomic Absorption Spectrophotometer (AAS) flame test and presented in Table-3 and Figure-3. The results show that the sampling techniques and procedures employed give data within the range of literature values published by many other authors.

Cadmium (Cd) is a soft silver-white metal that is usually found in combination with other elements. It is most commonly a byproduct from the smelting of zinc, lead, or copper ores. Cadmium is used in manufacturing (batteries and pigments), metal plating and in plastic industry. It is emitted into the air from burning fossil fuels, incineration of municipal waste materials, and from zinc, lead and copper smelters. Smoking cigarettes is another source of airborne cadmium. The concentration of Cadmium in all the study towns was higher than the permissible limit value of $0.005\text{mg}/\text{m}^3$ as our results ranges from $0.018 - 0.064\text{mg}/\text{m}^3$. The highest concentration was $0.064\text{mg}/\text{m}^3$ obtained from Karu town with Toxicity potential of 12.8, followed by Lafia and Nasarawa $0.041\text{mg}/\text{m}^3$; with toxicity potential of 8.20 while the least value of 0.018 was obtained at Akwanga with toxicity potential of 3.60 (Table-3 and Figure-2). The high concentration of Cd in all the towns especially Karu, Lafia and Nasarawa may be as a result of high vehicular emissions, burning of fossil fuels and municipal waste materials and cigarettes smoking⁵. Exposure to Cd may cause short-term

effects like bronchial and pulmonary irritation when inhaled. A single acute exposure to high levels of Cd can cause long-lasting impairment of lung. Long-term effects may results to kidney failure, softening of the bones (brittle bones), lung damage, weakening of the immune system and abdominal pains⁶.

Chromium (Cr) is a steel-gray solid with a high melting point. It is used to make steel and other alloys, and its compounds either in form of chromium (III) or chromium (VI) are used in chrome plating, manufacturing dyes and pigments, preserving leather and wood, and treating water in cooling towers. It occurs naturally in the environment as Cr^{3+} or Cr^{6+} . Cr^{6+} is more commonly produce by industrial processes. Exposure to Cr occurs mainly by inhalation of airborne chromium from ferrochrome production, ore refining, cement-producing plants, leather tanneries, brake lining and catalytic converters from automobiles and even eating food and drinking water. Short-term effects of Cr^{6+} inhalation includes shortness of breath, coughing, wheezing. Cr^{6+} is more toxic than Cr^{3+} and the inhalation of both may cause gastrointestinal effects including abdominal pain vomiting and hemorrhage. While long-term effects of Cr^{6+} inhalation include respiratory tracts infections including perforations and ulceration of the septum, asthma, pneumonia, bronchitis. Pregnancy and child birth complications are also linked to Cr^{6+} exposure¹⁶. The concentration of Cr determined in all the study towns shows that Cr is present only in Lafia with a concentration of $0.062\text{mg}/\text{m}^3$. This value is less than the permissible limit value of $0.5\text{mg}/\text{m}^3$ and hence toxicity potential of 0.12 (Table-3 and Figure-2). The present of Cr in Lafia only may be due to the unique nature of fossil fuel burning, numerous Cr waste disposal sites, Cr manufacturing and processing plants, and dyes and pigments manufacturing plants⁴.

Lead (Pb) had it largest source in the atmosphere traceable to leaded gasoline combustion. In nature it occurred as bluish – gray metal that is found in a small quantity in the earth crust. Pure lead is insoluble in water; however, the compounds of Pb vary in solubility. Its primary used is in batteries manufacturing, it is also used in producing metal products including sheet lead, solder and pipes, paint ammunition and cable covering. The average concentration of lead determined in the study towns ranged from $0.30 - 0.72\text{mg}/\text{m}^3$. This value exceed the permissible limit value of $0.05\text{mg}/\text{m}^3$ and hence the computed toxicity potential ranges from 6.00 – 14.40 (Table-3 and Figure-2). This can be attributed to storage batteries, pollution from car exhaust, old painted buildings and cable sheathing. Other activities that can deposit Pb in air that were observed in the study towns are oil leakages from motor cars and motor cycles, wind – blown from mechanical workshops, burning of tyres for street protest. Short-term effects of exposure to lead include headaches, nerve problems, irritation and impaired neurobehavior in children. Long-term effects can results to severe mental and physical impairment. Others are kidney dysfunction, memory loss and anemia. Children and babies are at highest risk to these effects¹⁷.

Manganese (Mn) is a metal that is found naturally in air, water, soil and in living systems. Biologically, it is an essential mineral and is required for the functioning of a number of enzymes families. But at higher levels it can be toxic to a number of organ systems especially the central nervous system where it accumulates within the basal ganglia of the brain. The concentration of Mn determined in all the study towns ranges from 0.110 – 0.184mg/m³ and the toxicity potential computed also ranges from 0.49 – 1.23 (Table-3 and Figure-2). The toxicity potential was less than unity for all the study towns except for Keffi and Akwanga where it was 1.23 and 1.08 respectively. The present of Manganese in PM₁₀ sample higher than the permissible limit value of 0.15mg/m³ by the WHO and EU in Keffi and Akwanga can be attributed to anthropogenic activities within these towns like numerous ferroalloy production facilities, coke ovens and power plants, welding rods and use of organic manganese fuel additives.

Copper (Cu) is a reddish metal that occurs naturally in rocks, soil, water, sediments and at low levels in air. It also occurs in plants and animals and is an essential element to all living organisms including human at low levels of intake. At much higher levels toxic effects can occur. Long- term exposure to copper can cause nose, mouth and eyes irritation, liver and kidney damage and even death. The concentration of Cu determined in all the study towns ranges from 0.088 – 0.124 mg/m³ (Table-3). These values are far less than the permissible limit value of 1 mg/m³ set by WHO, and all the toxicity potential computed shows no cause for alarm. The consistent occurrence of Cu implies that the particulates sources can be traceable to suspended soils and dust, construction work, rock weathering and residential activities.

Zinc (Zn) is a bluish-white metal which is present in air, soil, water and all the food that we eat. In air it attaches to dust and can be removed by washout or rainout process into the soil and water bodies. It is an essential element needed by all living things including human and is commonly found in our nutritional supplements. However, taking too much of it can have toxicological effects. Inhaling zinc in large amount as zinc dust or fumes from smelting or welding can cause short-term disease known as metal fume fever which can attack the lungs and rise body temperature¹⁷. The concentration of Zn determined in all the study towns ranges from 0.195 – 2.970 mg/m³. These values are less than the permissible limit value of 5 mg/m³ set by WHO and hence the computed toxicity potentials were all less than unity. The concentration of Zn was highest in Akwanga and least in Keffi (Table-3 and Figure-2).

Nickel (Ni) is a strong, lustrous, silvery white metal that is a staple of our daily lives and can be found in air combined with oxygen or sulphur and with air particles with sediments or may be removed by washout. It also occurs in iron containing ores. Anthropogenic sources of nickel are high-temperature metallurgical operations, cooling towers, coal combustion, steel production, nickel metal refining, incineration of municipal

waste and other natural process such as soil dust, forest fires and sea salt spray. Exposure to Nickel can cause Ni dermatitis consisting of itching of the fingers, hands and forearms. Lung and nasal cancers have also been reported from exposure to nickel refinery dust and nickel subsulfide¹⁸. The concentration of Ni determined in all the study towns ranged from 0.000 – 0.146 mg/m³ and the computed toxicity potentials also ranges from 0.00 – 2.92 (Table-3 and Figure-2). The concentration of Nickel was higher in Lafia and least in Akwanga where it was not detected. The occurrence of Ni may be as a result of coal combustion, nickel metal refining facilities and incineration of municipal waste. The most common adverse health effect of Ni in human is an allergic reaction such as skin rash. Cancer of the lung and nasal sinus have been reported when workers breathed dust containing high levels of Ni compounds while working in Nickel processing plants⁶.

In addition to analysis of the concentrations of the heavy metals in the PM₁₀ samples of the study towns, it was found that a weak correlation existed between the concentrations of the metals examined in all the study towns. This signifies that the sources of the metals in the ambient air of the study towns are unique. The correlation coefficient R is described by the relation:

$$R = \frac{n\sum C_i C_j - \sum C_i \sum C_j}{\sqrt{[n\sum C_i^2 - (\sum C_i)^2][n\sum C_j^2 - (\sum C_j)^2]}} \quad (4)$$

Where: n is the number of pairs of data and C_i, C_j are the concentrations of two metals correlated. The correlation coefficient is between 0.001 – 0.24. The highest value of R (4) is 0.24 which was found for Cd/Ni while the least value of R (4) was found for Cr/Zn. Also it was found that the highest human health effects arise mostly from contribution of Cd and Pb metal in the PM₁₀ samples of all the study towns.

Conclusion

The monthly mean of PM₁₀ concentrations were found to be within the range of 40 – 80 µg/m³ in the study towns. The highest concentration was measured in Karu Followed by Lafia. The result of the analysis showed that the average Cr, Zn and Cu determined in all the study towns from September – December, 2015 were below the WHO and EU Standards.

However, the reverse was the case for Pb, Cd and Mn as their values were extremely higher than the WHO and EU Standards. For Ni the result was fairly good in all the study towns except for Lafia where the value was higher than the WHO Standard. The weak correlation between the concentrations of the heavy metals showed that the distribution of the heavy metals in the study towns has come about as a result of different anthropogenic influences, meteorological factors and vehicular emissions. We do recommend that policy makers should step up regulations to monitor the anthropogenic activities that emit these heavy metals in the environment so as to reduce their health effects.

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