Assessment of heavy metals in air around industrial area of Bonny Island, Rivers State, Nigeria.

ABSTRACT

Heavy metals are naturally found in the environment. However, industrial activities can enhance their concentrations in various environmental media. This is of great concern because of their lethal effects on the ecosystem even in small concentrations. Consequently, the concentrations of Cd, Cr, Pb, Fe, Zn, Cu, Mn and As in $PM_{2.5}$ around industrial area of Bonny Island were investigated. Air samples were collected using the Environmental Monitoring Systems (EMS) High Volume Air Sampler (HVAS). The instrument was set to operate at the specified flow rate for each monitoring period. The filter collected from each of the study stations was prepared for Flame Atomic Absorption Spectrophotometer (FAAS) analysis. The results showed that the concentrations of Cadmium (Cd), Copper (Cu), Lead (Pb) and Arsenic were generally low across the study stations. Whereas Fe, Zn, Cr and Mn had mean concentrations of 36.04 $\mu g/m^3$, 15.57 $\mu g/m^3$, 1.51 $\mu g/m^3$ and 0.60 $\mu g/m^3$ respectively. The heavy metals investigated in this study were distributed in this order: Fe>Zn>Cr>Mn>Cd≥Pb≥Cu≥As. The enrichment factor (EF) of Cd, Cu, Pb, Zn and As, ranged between <1 and <10, the EF of Mn was >100 but <1000 while the EF of Cr was >1000. The concentrations of Cr and Mn obtained in $PM_{2.5}$ exceeded the 8-hour time weighted average (TWA) exposure limit of 1.1 $\mu g/m^3$ and annual average limit of 0.15 $\mu g/m^3$ respectively by the World Health Organization. This implies that the residents of Bonny, especially those who live around the industrial area and vehicular traffic hotspots such as Finima roundabout, Wilbros Junction, etc, might be exposed to high concentrations of Cr and Mn. Hence, regular monitoring of heavy metals around industrial areas and vehicular traffic hotspots is strongly recommended for a healthy environment.

KEYWORDS

Heavy Metals, Pollution, Air Quality, Industrial Area, Vehicular Traffic Hotspot, Bonny Island, Enrichment Factor.

1. INTRODUCTION

Pollution of environmental media by heavy metals has been a major global concern. This is due to their numerous sources, widespread distribution and effects on the ecosystem. Heavy metals are naturally occurring elements characterized by their high atomic mass and density. More recently, the definition has been broadened to include naturally occurring elements with atomic numbers greater than 20 (Ali and Khan 2018; Ali *et al*., 2020). They occur in low concentration and can be found all through the crust of the planet. Some heavy metals like copper, iron, zinc, cobalt, nickel, manganese and molybdenum are broadly grouped into essential trace elements, whose functions are indispensable for various biological processes and driving the entire human metabolism. For example, cobalt acts as the central atom in vitamin B12 complex, it is a key player in the reductive branch of the propionic acid fermentation pathway (Stowers *et al*., 2014). Iron is an essential element of various metabolic processes in humans, including DNA synthesis, electron transport, and oxygen transport (Ems *et al*., 2023). Zinc, a constituent of more than 200 enzymes, plays an important role in nucleic acid metabolism, cell replication, tissue repair and growth through its function in nucleic acid polymerases (Ursula *et al*., 1999; Halstead and Smith, 1970). Copper is an essential nutrient that is widely distributed in food and water and a component of several metalloenzymes that are required for oxidative metabolism, including cytochrome oxidases, ferroxidases, amino oxidases, superoxide dismutase, ascorbic acid oxidase and tyrosinase. Manganese functions both as a cofactor activating many enzymes that form metal-enzyme complexes and as an integral part of certain metalloenzymes. It is also involved in the metabolism of biogenic amines and participates in the regulation of carbohydrate metabolism (Hurley and Keen, 1987). Despite these functions, trace elements are toxic at high concentrations. On the other hand, metals like mercury, cadmium, arsenic, chromium, lead, etc., are classified as non-essential elements. They exert toxic effects at low concentration (Duruibe *et al*., 2007). One of the major concerns about heavy metals is that they may find their way into the food chain through bioaccumulation in plants and animal species, contamination of drinking water sources and the environment. According to Ogundele *et al.* (2017), majority of environmental problems worldwide emanate from toxicity, non-degradability and widespread pollution of heavy metals from industrial, urban and economic growth. Apart from natural sources, heavy metals are released into the environment from mining, coal burning, traffic emission, construction and agricultural activities, petrochemical industries, paper making, refineries, batteries, paints, etc (Liu, 2018; Malakootina *et al*., 2021).

In the air, heavy metals can accumulate from sources such as mining process, fossil fuels combustion, metallurgical process, incineration activities, industrial plants and windblown soil dust (Adani *et al.*, 2015; Hassanien, 2009; Kampa and Castanas, 2008). Globally, numerous studies have been carried out to determine the concentration of heavy metals in the atmosphere. The results showed that heavy metals pose significant potential hazards to humans and ecosystems due to their long shelf life and stability in the environment, stable degradation, and easy accumulation of acute and chronic toxicity effects (Baltas *et al.*, 2020). In Bangladesh, Rahman *et al.* (2018) assessed the risk to human health from heavy metal contamination through street dust. The study showed that the concentrations of nickel, lead, cadmium, and arsenic were slightly higher than their concentrations in the soil. They also found that lead, zinc, copper, cobalt, and chromium contamination were associated with industrial activity and heavy traffic. In Iran, Farahmandkia *et al.* (2010) assessed the risk to human health from heavy metals contamination in the atmosphere. The result revealed high concentrations of lead and cadmium and they concluded that heavy metals could cause acute and chronic poisoning and many diseases such as neurological disorders, nutritional deficiencies, hormonal imbalances, obesity, abortion, respiratory and cardiac disorders, liver and kidney damage, allergy and asthma, chronic viral infections, decreasing tolerance threshold, infertility, anemia, weakening of the immune system, gene destruction, premature aging, decreasing memory, osteoporosis, hair loss, insomnia, cancers, and death. Similarly, Engwa *et al*. (2019), investigated the mechanism and health effects of heavy metal toxicity in humans, and the result showed they can damage and alter the function of organs such as the brain, kidneys, lungs, liver, and blood, degenerative muscular, physical, and neurological processes such as Parkinson’s, multiple sclerosis, muscular dystrophy, and Alzheimer’s disease. In Port Harcourt, Nigeria, Kalagbor *et al.* (2019), investigated heavy metals in soot samples and cancer risk in Port Harcourt, Nigeria, and reported high concentrations of Pb and Cd. They concluded that the prevalence of these metals in ambient air puts the population in Port Harcourt metropolis at risk of lung, liver, blood and renal cancer, and children are at higher risk. Ede *et al.* (2013); Nkwocha *et al.* (2017), assessed the air quality of Bonny Island but did not investigate heavy metals. Their studies focused on atmospheric gases. Abbey *et al* (2024), evaluated indoor concentrations of heavy metals from heat ventilating air conditioning filter dust in Bonny Island and reported high concentrations of Pb, Cr, Fe, Cu and Zn. However, their study did not consider heavy metal concentrations in the outdoor environment. Generally, there is paucity of information on the concentrations of heavy metals in the atmosphere of Bonny Island especially around the industrial area and vehicular traffic hot spots. It is against this backdrop that the current research aims to investigate the concentrations of heavy metals in the outdoor environment of Bonny Island.

2.0 MATERIALS AND METHODS

2.1 THE STUDY AREA

This study was carried out in Bonny Island, Rivers State in the southern part of Nigeria within the Niger Delta region. The Island is surrounded by the Bonny River to the west and the Atlantic Ocean to the south.

Geographically, Bonny Island is characterized by a tropical climate with high humidity and significant rainfall, particularly during the wet season, which dominates most of the year. The landscape is mainly composed of mangrove swamps, rainforests, and low-lying plains. The indigenous people of Bonny Island are primarily the Ibani, a subgroup of the Ijaw ethnic group. The Ibani people have a long history of seafaring and trade, which dates to pre-colonial times when Bonny was a major trading hub for palm oil and other goods. The population of Bonny Island is diverse due to the influx of people from other parts of Nigeria and expatriates, largely due to the presence of the oil and gas industry. The Ibani culture is rich with traditions, festivals, and a deep connection to the sea. The economy of Bonny Island is dominated by the oil and gas sector. It is home to the Nigeria Liquefied Natural Gas (NLNG) plant, one of the largest of its kind in Africa, which significantly contributes to the Nigerian economy through the production and export of liquefied natural gas. The presence of multinational oil companies such as SPDC, ExxonMobil, etc has brought economic growth and job opportunities to the island, attracting a diverse workforce. Besides industrial activities, fishing continues to be a vital livelihood for many of the island's residents. Small-scale commercial activities such as petty-trading and catering services are common. Fig. 1 is the map of Nigeria showing where the study was carried out in Bonny Island, Rivers State.

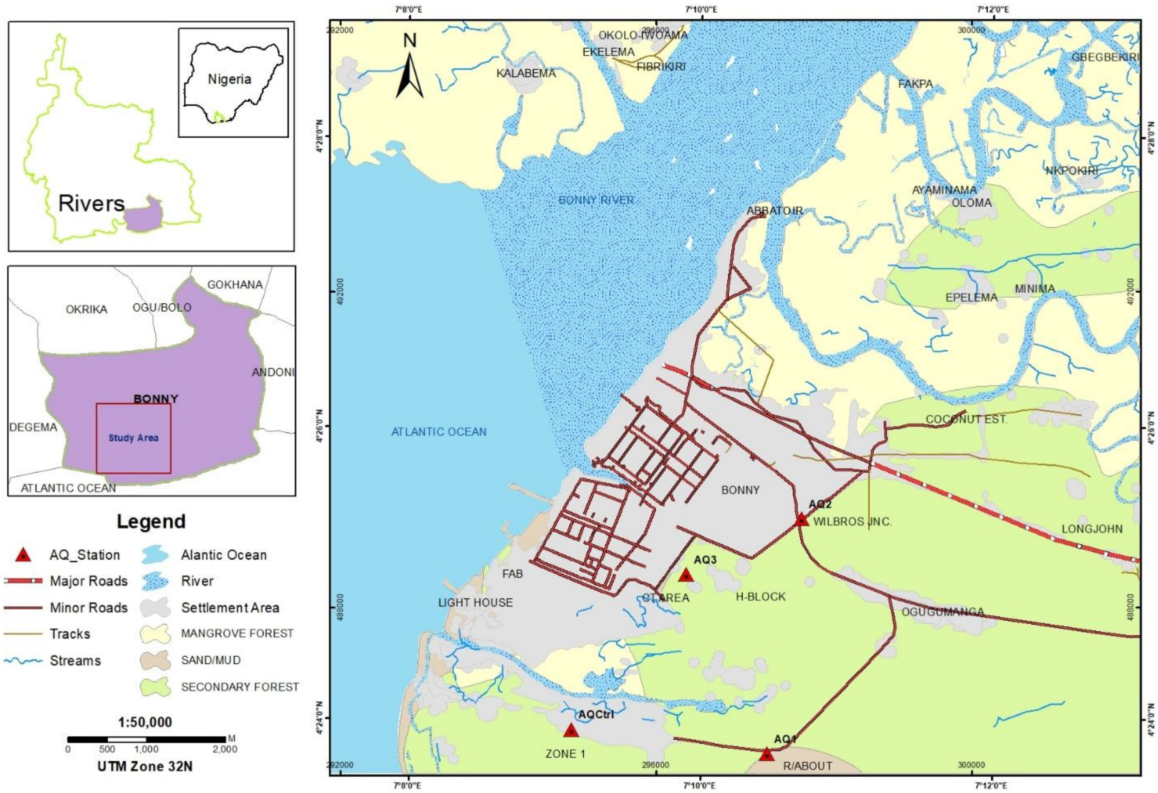

Fig. 1: The map of Nigeria showing the study area in Bonny Island, Rivers State, Nigeria.

Sampling station AQ1 (Plate 1), was at Finima Roundabout with relatively high vehicular density. Adjacent to the roundabout is a car park where passengers board vehicles to different parts of the Island. Activities around this study station included movements of vehicles, restaurants and bakery operations, black market sales of petroleum products such as AGO, PMS, etc. Sampling station AQ2 (Plate 2), was at Wilbros, a popular Junction with high density of vehicles. The major activities around this station included vehicular movements, automobile workshop, welding workshop, automobile spare parts shops, restaurants operations, flaring of gases from nearby flare stacks, etc. Sampling station AQ3 (Plate 3), was in an industrial area with high vehicular movements. Other activities in the area included welding and fabrication, pipe grinding, steel structure erection, civil works, flaring of gases from nearby flare stacks, etc. Control station AQ4 (Plate 4), is a residential area with an assemblage of plant species

Plate 1: AQ1 (Finima Roundabout)

Plate 2: AQ2 (Wilbros Junction)

Plate 3: AQ3 (Construction site)

Plate 4: AQC (Control station)

2.3 DATA COLLECTION

Sampling Equipment

Air samples for the determination of heavy metals in the atmosphere were collected using the Environmental Monitoring Systems (EMS) High Volume Air Sampler (HVAS). This is a device that consists of an assemblage of a rotameter, an electrical air pump, a flexible hose and filter cassette. The EMS pump draws a precision-controlled volume of air and airborne contaminants through collection media during the sampling period. It is a high flow rate pump of 1 L/min – 20 L/min. A flowmeter model VFB manufactured by Dwyer Instruments Inc. USA was used to calibrate the flow. The Series Visi-Float VF Flowmeter is a line of direct reading, precision machined, clear acrylic body flowmeter suitable for both gas and liquid applications. The air samples were collected on a 37 mm diameter 3-piece pre-loaded filter cassette with 0.8 µm mixed-cellulose ester filter (MCEF) according to the Occupational Safety and Health Administration (OSHA-21). The filter is a mixture of cellulose nitrate/acetate fibres. It is a 3-piece press-fit cassette which helps prevent leakage around the filter as this will result in a loss of dust that should have been collected on the filter, resulting in a measurement that underestimates the concentration of the aerosol sampled. The membrane filter pore size is 0.8µm to retain even the inhalable aerosols. The inlet and outlet sides of the cassette are marked. MCEF sample cassette was chosen because they can retain particles smaller than their nominal pore size. MCEF membranes are naturally low in metal background and are compatible with dilute bases and acids and aromatic and aliphatic hydrocarbons. The filters are hydrophilic and autoclavable. It meets National Institute for Occupational Safety (NIOSH) and OSHA method specifications for monitoring airborne metals. MCEF is easily digested by dilute nitric acid which makes it ideal for atomic absorption spectroscopic analysis.

Air Sampling

Pump flow calibrations were performed before the commencement of sampling. The flow rate for the pump with a blank sample cassette was measured and recorded as 5 L/min. A constant flow rate of 20 L/min that did not deviate more than ±0.2 L/min was then maintained throughout the sampling period. The exposure time at each sampling station was 2 hours. The filter was attached to the pump that drew air into a 37mm diameter MCE sample cassette. The plug was removed from the cassette inlet and the pump started sampling. The start time was recorded. The pump and sampling train were checked as frequently as practical. At the end of the recording time, the pump was turned off and the end time was also recorded. The filter cassette was removed from the sampling train and the plugs in the inlet and outlet openings of the cassette were replaced. The instrument was set to operate at the specified flow rate for each monitoring period. The filter cassette was replaced after each sampling period and sealed in a Ziploc bag (Plate 5). The filter cassette was weighed before and after sampling to determine the mass of particulate matter collected.

Plate 5: Collected filter cassettes sealed in Ziploc bag after the sampling period

Meteorology

Information on the regional climatic conditions of the study area was obtained from the Nigerian Meteorological Agency (NiMet) and complemented with microclimatic data which were collected using Davis wireless weather station. Davis wireless weather station was installed and allowed to measure various meteorological parameters during the study. The Davis Weather Station has an integrated sensor suite that consists of a rain gauge, temperature, humidity, barometric pressure, wind speed and direction sensors. The integrated sensor suite was carefully mounted on approximately 10 meters pole to represent the average height of cloud formation in the study area.

2.3 Analytical Method

The filter collected from each of the study station was placed into a clean digestion vessel, and a combination of acids (HNO_3 and HCl) was added to digest the particulate matter. The sample was heated gently on a hot plate until complete digestion of the particulate matter was achieved. After digestion, the sample was allowed to cool, filtered and diluted to 100 ml using deionized water to prepare it for Flame Atomic Absorption Spectrophotometer (FAAS) analysis. The FAAS instrument (PerkinElmer AAnalyst 400) was powered on and allowed to stabilize. Then the hallowed cathode lamp for the metal of interest was installed and the wavelength was selected. A calibration blank, followed by calibration standards, was aspirated to establish a calibration standard curve. A reagent blank was carried out to ensure method compliance. The digested sample was aspirated into the flame, where the metal ions were atomized to measure the absorption of light at the selected wavelength. The FAAS instrument provided the concentrations for each metal in the sample after analysis. The metal concentration in the digested solution was converted to mass per volume of air sampled. This was done using the following formula:

$$Conc.\ of\ metal\ in\ Air\ \left(\frac{\mu g}{m3}\right) = \frac{Conc.\ in\ digest\ \left(\frac{\mu g}{ml}\right) \times Dilution\ Volume\ (ml)}{Volume\ of\ air\ sampled\ (m3)}$$

2.4 Enrichment Factor (EF)

Enrichment factor was used to determine the source of the elements in the study area, whether natural or anthropogenic, and it was calculated according to Liu *et al*., 2018; Turekian and Wedepohl, 1961 as follows:

$$EF = \frac{[Cx/C_{ref}]Sample}{[Cx/C_{ref}]Background}$$

where the concentration of the element of interest is C_x, and the concentration of a reference element for the purpose of normalization is C_{ref}. The selection of reference elements should meet certain criteria, such as having stable chemical properties which are less influenced by human activity (Liu *et al*., 2018). For this reason, Fe, Mn, Al and Se can be used as reference elements. In this study, Fe being one of the most abundant elements with relatively stable chemical properties, was used as the reference element. The standard of enrichment factor is presented in Table 1.0.

Table 1.0: The Standard of Enrichment Factor

Level	EF	Degree of Enrichment	Source
1	<1	No enrichment	Crust and Soil
2	1<10	Minimal enrichment	Natural & Anthropogenic factors
3	10<100	Moderate enrichment	Anthropogenic factors
4	100<1000	Significant enrichment	Anthropogenic factors
5	1000	Extremely high enrichment	Anthropogenic factors

Source: (Liu *et al*., 2018)

2.5 Quality Assurance and Control

Quality assurance and quality control (QA/QC) measures were adopted and applied consistently throughout all phases of the data gathering in accordance with OSHA requirements to ensure a high level of reliability of results. The QA/QC measures adopted are as stated below:

- The equipment was correctly calibrated and checked prior to use.
- The collection device inlet was oriented in a downward vertical position to avoid gross contamination from airborne debris falling into the collection device.
- Blank and duplicate analyses were carried out to ensure analytical integrity.
- Written analytical standard operating procedures (SOPs) were followed during analysis.

The results obtained from the Laboratory analysis were compared with national standards (Federal Ministry of Environment and Environmental Guidelines and Standards for the Petroleum Industry in Nigeria) as well as the World Health Organization (WHO) guidelines (Table 2.0).

Table 2.0: National and WHO Air Quality Guidelines

Metals	EGASPIN Guidelines for (µg/m^3) (2018)	WHO Guidelines (µg/m^3)	FMEnv Guidelines (µg/m^3) (2001)
Cd	NS	0.005	0.005
Cr	NS	1.1	NS
Cu	NS	NS	NS
Fe	NS	NS	NS
Mn	NS	0.15	NS
Pb	1.0	0.5	1.00
Zn	NS	NS	NS
As	NS	NS	NS

Legend: EGASPIN = Environmental Guidelines and Standards for the Petroleum Industry in Nigeria; WHO = World Health Organization; FMEnv = Federal Ministry of Environment; NS = Not Stated

3.0 RESULTS AND DISCUSSION

3.1. Results

3.1.1 Heavy Metals Concentrations in the Study Area

The concentrations of Cadmium (Cd), Copper (Cu), Lead (Pb) and Arsenic were generally low. Whereas Fe and Zn concentrations were obtained across the three study stations and at the control. Cr concentration was relatively high at AQ1 and AQ3 but very low at AQ1. Moreover, Mn had relatively high concentration at AQ2 and AQ3 but was very low at AQ1. Apart from Fe and Zn, the concentration of Cd, Cr, Cu, Mn, As and Pb obtained at the control was generally below equipment detection limit of <0.001 (Table 3.0).

Table 3.0: Metal concentration at different locations

	Sample Stations				
Metals	**AQ1 (µg/m^3)**	**AQ2 (µg/m^3)**	**AQ3 (µg/m^3)**	**mean (µg/m^3)**	**AQC (Control)**
Cd	0.001	0.001	0.001	0.001	<0.001
Cr	2.33	0.001	2.21	1.51	<0.001
Cu	0.001	0.001	0.001	0.00	<0.001
Fe	17.13	50.25	40.75	36.04	22.38
Mn	0.001	0.875	0.92	0.60	<0.001
Pb	0.001	0.001	0.001	0.001	<0.001
Zn	12.38	15.13	19.21	15.57	15.13
As	0.001	0.001	0.001	0.001	<0.001

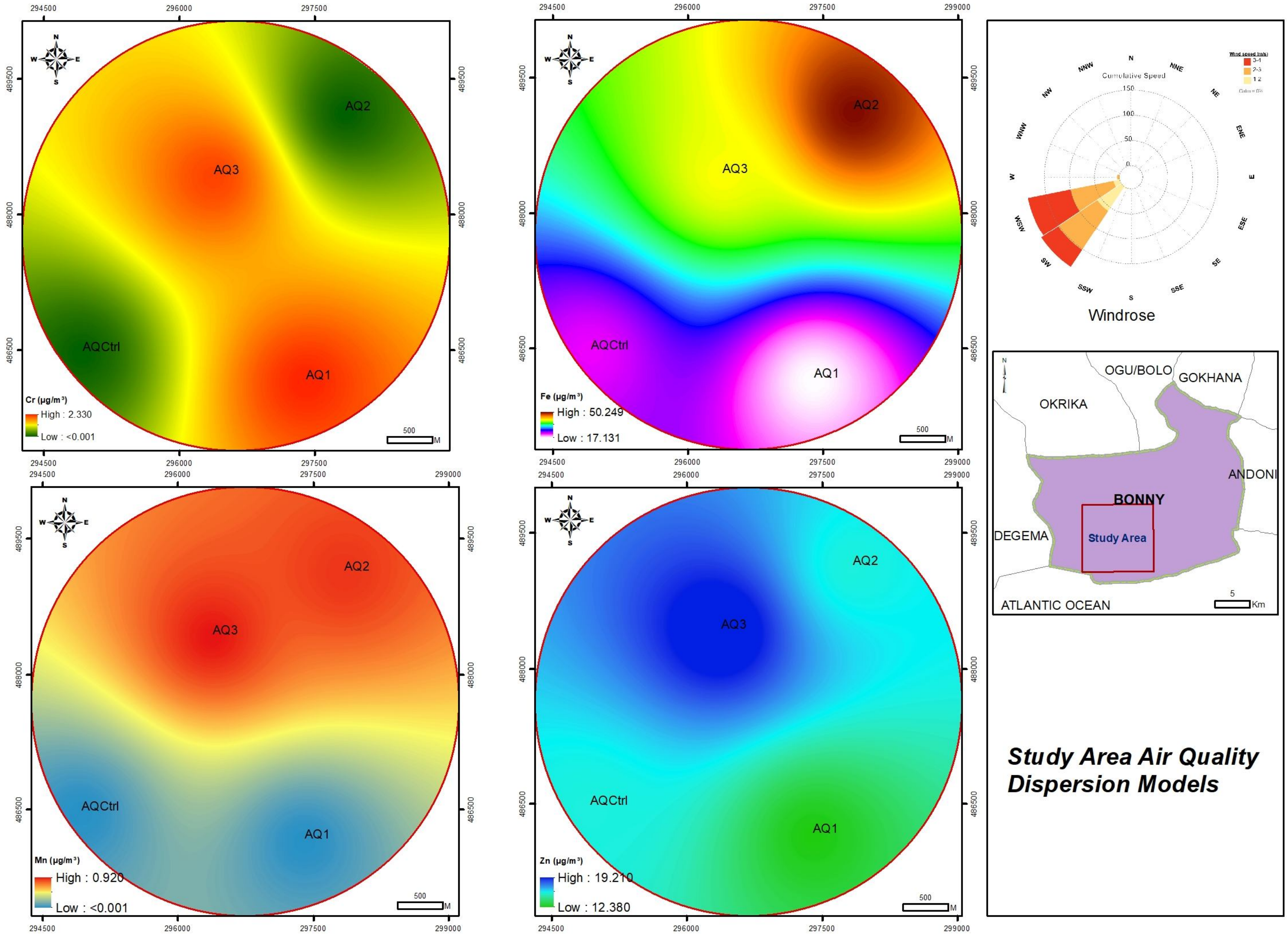

Fig. 2: Study Area Elemental Concentration Model

3.1.2 The Enrichment Factor of Heavy Metals in the Study Area

The enrichment factor of the heavy metals investigated in the study area is presented in Table 4.0.

Table 4.0: Enrichment Factor of Heavy Metals in the Study Area

Heavy Metal	AQ1	AQ2	AQ3
Cd	1.306	0.4454	0.5492
Cr	3044.1	0.4454	1213.7
Cu	1.306	0.4454	0.5492
Fe	1	1	1
Mn	1.306	389.7	505.4
Pb	1.306	0.4454	0.5492
Zn	1.069	0.4454	0.6973
As	1.306	0.4454	0.5492

3.2. Discussion

3.2.1 Heavy Metals Concentrations in the Study Area

The comparisons made in this study were based on results obtained at the control station (reference) and air quality guidelines of the Federal Ministry of Environment (Nigeria), Environmental Guidelines and Standards for the Petroleum Industry in Nigeria (EGASPIN) (2018 revised) and the World Health Organization (WHO). Generally, the order of distribution of the metals investigated in this study is Fe>Zn>Cr>Mn>Cd≥Pb≥Cu≥As (Fig. 3).

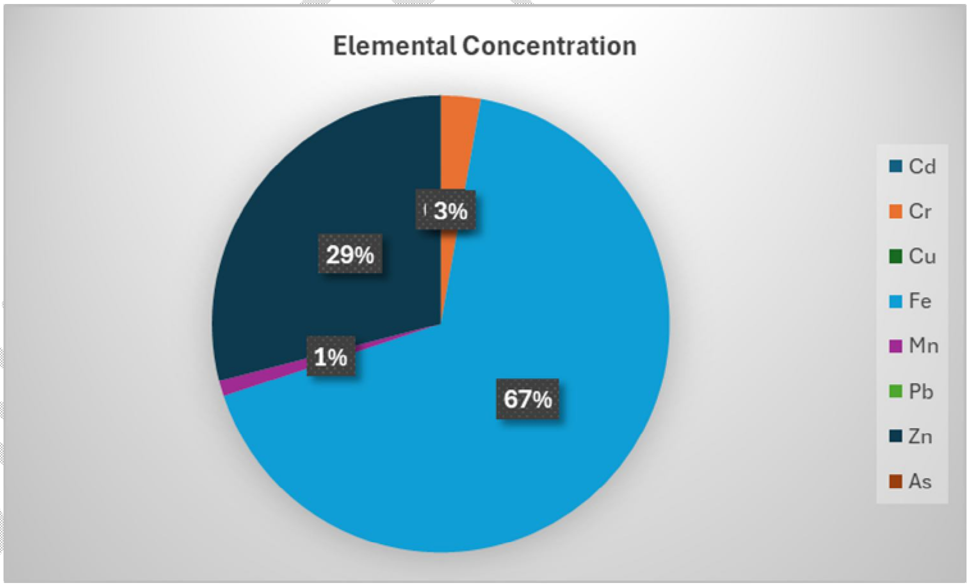

Fig. 3: Distribution of Heavy Metals in the Study Area

The iron (Fe) concentration obtained in this study ranged from 17.13 µg/m^3 to 50.25 µg/m^3 with mean of 36.04 µg/m^3 while 22.38 µg/m^3 was obtained at the control station (AQC). The highest concentration of Fe (50.25 µg/m^3) was obtained at AQ2 (Wilbros Junction). This station had high vehicular density with other activities such as welding and fabrication works, vehicle repairs workshops, etc., which could have contributed to the concentration of Fe obtained in the study area. Besides being one of the most abundant elements in the earth crust, Fe could be released in the environment through wear from brake components, both pads and rotors as well as wear to engine (Liati *et al*., 2015). On the other hand, the Fe concentration obtained could have been influenced by the meteorological conditions of the area. During the study, wind direction was observed in the southwest (Fig. 2) which implied that particulate and heavy metals would have been transported to the north and north-eastern direction where AQ2 station was. Wind speed is another major meteorological parameter that determines the distance in which pollutants including heavy metals and particulates are transported and dispersed. The average wind speed recorded in the study was 2.48 m/s which is below those previously recorded in Bonny Island during the wet season (WWO, 2024). According to the findings of Edokpa and Ede (2013), high concentrations of pollutants were observed within 0 to 8 km for wind speed of 1-3m/s while at high wind speed, concentration of pollutants decreased with increased distance. The concentration of Fe obtained in this study is higher than 0.416 µg/m^3 reported by Yaman and Erel (2013) in Turkey and 8.233 µg/m^3 reported by Uzoekwe *et al*., (2021) in Bayelsa, Nigeria, who investigated heavy metals in particulate matter suspended around industrial areas. Nevertheless, Azham *et al.* (2024), reported higher concentration of Fe (54.200 µg/m^3) in the atmosphere of Indonesia. Serious health problems such as vomiting, upper abdominal pain, pallor, cyanosis, diarrhea, dizziness, shock, heamochromatosis, diabetes, liver, lungs and kidney diseases, haepatoma and cardinomyopathy can be attributed to excessive exposure to Fe (Ebong *et al*., 2009).

The concentration of Chromium obtained in this study ranged from 0.001 µg/m^3 to 2.33 µg/m^3 with mean of 1.51 µg/m^3 whereas the value obtained at the control station was less than 0.001 µg/m^3 (Table 3.0). The highest concentration of chromium was obtained at AQ1 sampling station (Finima roundabout) followed by AQ3 (Industrial complex). Finima roundabout (AQ1) is the economic hub of Bonny Island with high vehicular density while the major activities observed at the industrial complex (AQ3) were construction activities ranging from welding, steel erection, pipe grinding, vehicular movements and industrial gas flares from plant operations in the area. Although chromium (Cr) is a naturally occurring element present in the earth's crust, with oxidation states ranging from chromium (II) to chromium (VI), the anthropogenic activities at AQ1 and AQ3 could have contributed to the concentrations obtained in this study. According to Tchounwou *et al*. (2012), chromium enters various environmental matrices (air, water, and soil) from a wide variety of natural and anthropogenic sources with the largest release coming from industrial activities. Abbey *et al*. (2024) reported very high concentration of Cr in Bonny metropolis and suggested that activities of localized industries within sampled sites might be responsible. The mean value of chromium obtained in this study is higher than the concentration of 1.30 µg/m^3 reported by Uzoekwe *et al.* (2021) in their study of determination of heavy metals in particulate matter suspended around a gas flaring facility in Bayelsa State but lower than 11.88 µg/m^3 reported by Rauf *et al.* (2021) who determined potentially toxic element levels in air around industrial area of Maros, Indonesia. When compared with WHO (2016) guidelines for ambient air, the mean value obtained for chromium in this study exceeded the 8 – hour time weighted average (TWA) (Table 2.0). Multiorgan toxicity, including kidney and liver damage, allergy, asthma and respiratory tract cancer in humans, pulmonary congestion, edema, skin irritation and tooth erosion and discolouration have been linked to occupational and environmental exposure to high concentration of chromium and chromium containing compounds (Iyebor *et al*., 2020; Tchounwou *et al*., 2012). Moreover, chromium is classified as a member of group 1 metal by the International Agency for Research on Cancer (IARC) and is defined as proven carcinogens to human (Suvarapu and Back, 2016).

The concentration of manganese (Mn) obtained ranged from 0.001 µg/m^3 (at AQ1) to 0.92 µg/m^3 (at AQ3) with mean of 0.60 µg/m^3. Whereas at the control station, the concentration obtained was less than 0.001 µg/m^3. Mn is found in rocks, soil, foods and soil. However, industrial and other anthropogenic activities can release Mn into the air. Therefore, the concentration of 0.92 µg/m^3 obtained at sampling station AQ3 could be attributed to the construction activities ranging from welding, steel erection, pipe grinding to industrial gas flares from plant operations in the area. Moreover, the Mn concentration obtained could have been influenced by the meteorological conditions of the area. During the study, wind direction was observed in the southwest where AQ1 and AQC sampling stations were (Fig. 2). This implied that particulate and heavy metals would have dispersed to the north and north-eastern direction where AQ2 and AQ3 sampling stations were (Fig. 2). Furthermore, the average wind speed recorded in the study was 2.48 m/s which is below those previously recorded in Bonny Island during the wet season (WWO, 2024). The concentration of Mn obtained at sampling stations AQ2 and AQ3 were consistent with 0.88 µg/m^3 reported by Michelle *et al.*, 2015 in the atmosphere of Ohio, US however, exceeded the annual average limit of 0.15 µg/m^3 stipulated by the WHO, 2016. According to Michigan Department of Environmental Quality, Air Quality Division (2012), occupational studies have found that workers exposed to very high concentrations of manganese can develop Parkinson-like neurological syndrome known as manganism.

The concentration of Zinc (Zn) obtained ranged from 12.38 µg/m^3 to 19.21 µg/m^3 with mean of 15.57 µg/m^3, which compared favourably with 15.13 µg/m^3 obtained at the control station (AQC). Although Zn concentrations were obtained across the sampling stations (AQ1, AQ2 and AQ3) including control (AQC), the highest concentration was obtained at AQ1 sampling station (Finima roundabout), the economic hub of Bonny Island with high vehicular density and other anthropogenic activities. Besides natural occurrence, Zn can enter the environment through mining, steel production, coal burning and incineration of waste. According to Abdullah (2015); Sloof (1999), Zn from anthropogenic activities could originate from its use in lubricating oil and vehicular tyre wear. The concentration of Zn obtained in this study is lower than 44.7 µg/m^3 reported by Ogundele *et al.* (2017) in their study of heavy metals in air around an industrial area in Ile-Ife, Nigeria but higher than 1.7 µg/m^3 reported by Abdullah (2015) in his study of sources of metal pollution in the urban atmosphere of Tuzla, Istabul. Long time exposure to zinc exceeding its threshold has been reported to cause headache, nausea, vomiting, diarrhea, abdominal discomfort, metabolic imbalance, impaired immune function, decreased levels of high-density lipoprotein (HDL) and increased levels of low-density lipoprotein (LDL) (Schoofs *et al.*, 2024; Rim *et al.*, 2010; Barceloux 1999).

The concentration of Cd, Pb, As and Cu obtained in this study was 0.001 mg/kg across the three sampling stations (Table 3.0). Similar results were also recorded at the control station suggesting natural origin of the elements in the study area. According to the European Commission (2001), cadmium is a relatively rare element in the earth crust, which probably explains the very low concentrations obtained in this study. No mining and smelting activities were observed in the study area which might be the reason Pb concentration was very minute. Cadmium compounds are released into the atmosphere from production processes of zinc, copper and lead, combustion processes (coal and oil), refuse incineration, and iron and steel production (Erik, 2001). Cadmium and lead are metals with unknown essential functions in higher plants (Erik, 2001) and animals (Iyebor *et al.*, 2020). Long term exposure to Cd either through inhalation or ingestion has been reported to be highly toxic to humans especially kidney and bones and with the potential to cause cancer of the lungs (Iyebor *et al.*, 2020). Cd build up in the body over time also affects vitamin D metabolism, disturbing the calcium balance within the body which may lead to a decrease in the mineral content within the bones, resulting in Osteoporosis and Osteomalacia (Iyebor *et al.*, 2020). Lead is undesirable to humans because of its health hazards. A notable serious health effect of lead toxicity is its tetratogenicity (Fern, 2001). Lead poisoning also causes inhibition of the synthesis of haemoglobin, dysfunctions in kidney, joints and damage to the central nervous system (Fern, 2001). Arsenic has been reported to cause cancer of the skin, lung, bladder, kidney, cardiovascular disease and neurological effects (De and Roy, 2023). Copper is considered an essential element for the human body, however, exposure to large doses can cause serious health effects including upper respiratory irritation, nasal and pharyngeal congestion, metal fume fever, gastric pain, nausea, kidney damage and anemia (CEPA, 2004).

3.2.2 Enrichment Factor of Heavy Metals in the Study Area

The enrichment factor (EF) of each metal investigated in this study is presented in Table 4 and Figs. 4 – 10.

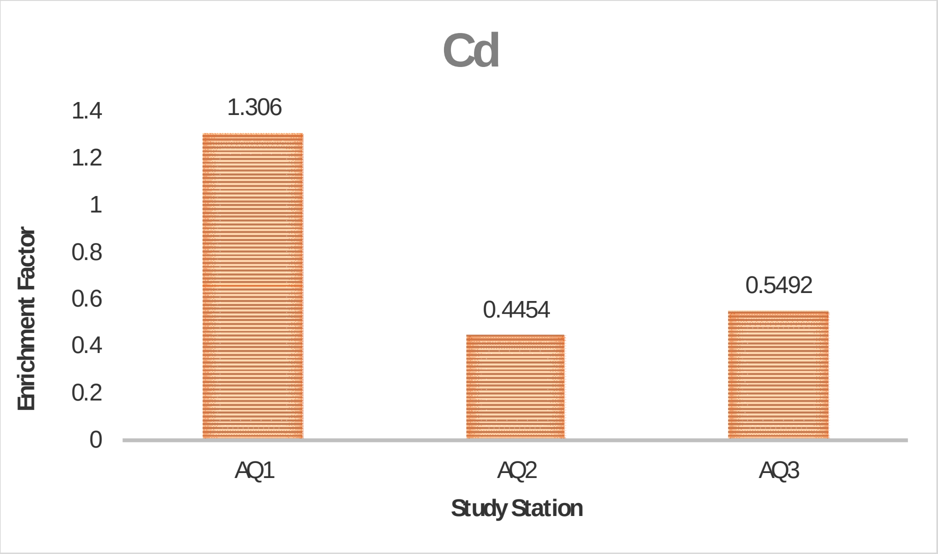

Fig. 4: Enrichment factor of Cd across the Study Station

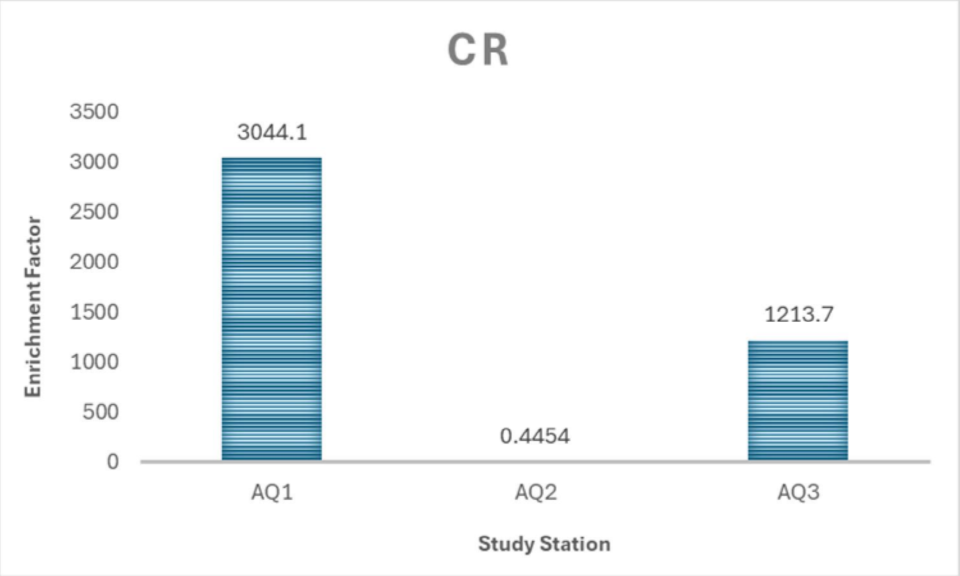

Fig. 5: Enrichment factor of Cr across the Study Station

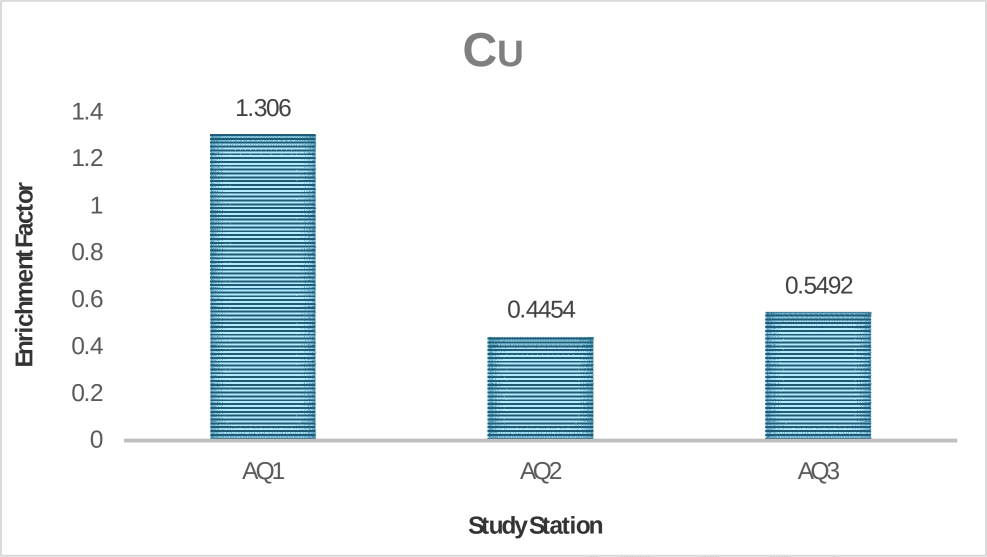

Fig. 6: Enrichment factor of Cu across the Study Station

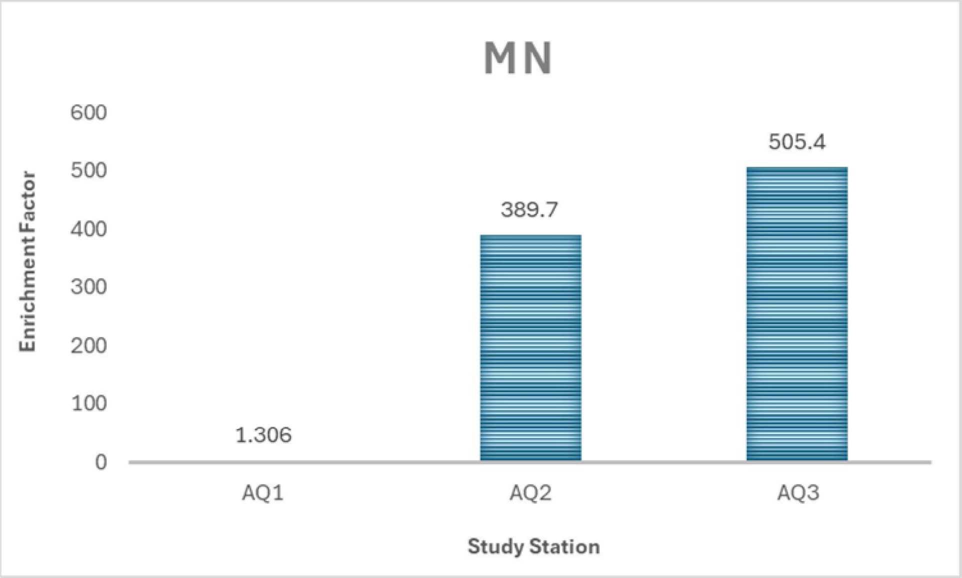

Fig. 7: Enrichment factor of Mn across the Study Station

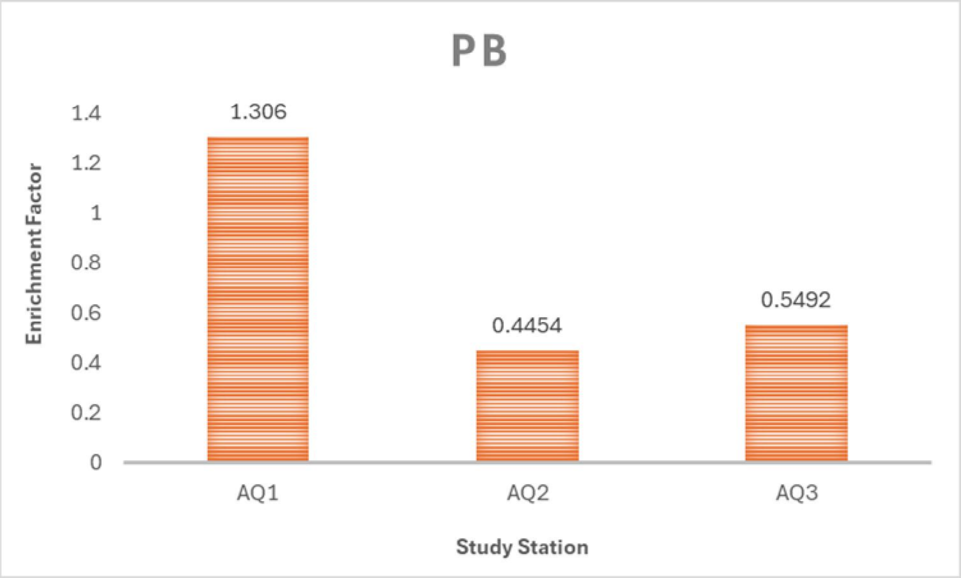

Fig. 8: Enrichment factor of Pb across the Study Station

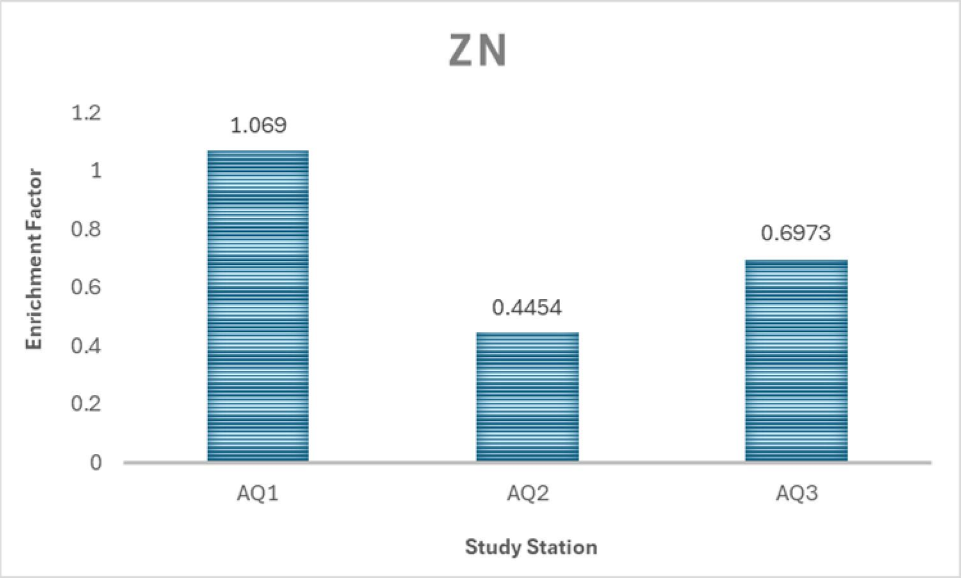

Fig. 9: Enrichment factor of Zn across the Study Station

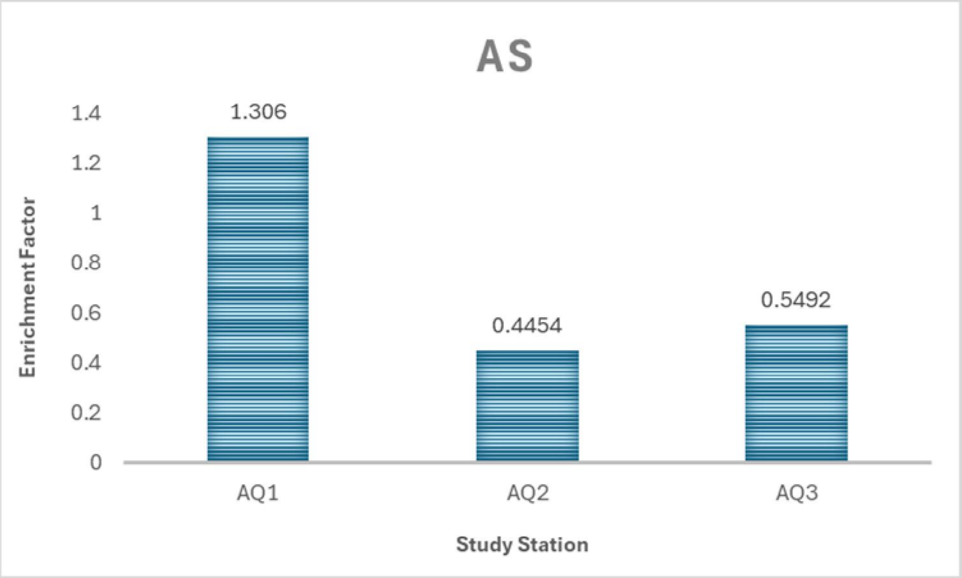

Fig. 10: Enrichment factor of As across the Study Station

The enrichment factor (EF) of all the elements investigated in this study was generally higher at AQ1 except Mn (Figs. 4 – 10, Table 4.0). Cd, Cu, Pb, Zn and As had EF of <1 at AQ2 and AQ3 whereas at AQ1, the EF obtained was >1 but <10 (Table 4.0, Figs. 4, 6, 8, 9 and 10). This finding indicated no enrichment as well as minimal enrichment implying that sources of Cd, Cu, Pb, Zn, and As across the study stations could have resulted from natural origin especially at AQ2 and AQ3 while anthropogenic activities might have influenced the minute concentrations obtained at AQ1 (Liu *et al.*, 2018). On the other hand, the EF of Cr was >1000 at AQ1 and AQ3 (Fig. 5), indicating extremely high enrichment which could be attributed to human activities at the respective study stations. Although chromium (Cr) is a naturally occurring element present in the earth's crust, with oxidation states ranging from chromium (II) to chromium (VI), Tchounwou *et al*, (2012), averred that chromium enters various environmental matrices (air, water, and soil) from a wide variety of natural and anthropogenic sources with the largest release coming from industrial activities, such as stainless steel welding, power plant combustion, refining, leather tanning, etc (CEPA, 2004). For this reason, anthropogenic activities at AQ1 and AQ3 such as high vehicular movements, welding and fabrication, pipe grinding, steel structure erection, civil works, flaring of gases from nearby flare stacksat could have contributed to the concentration of Cr obtained in this study. The EF of Mn obtained at AQ2 and AQ3 was >100 but <1000 indicating significant enrichment (Liu *et al.*, 2018), which could be attributed to anthropogenic activities in the study area (Fig. 7, Table 1.0). Mn is a metal found in rocks, soil, foods and soil. However, industrial and other anthropogenic activities can release Mn into the air. Therefore, the EF obtained at AQ2 and AQ3 could be attributed to the construction activities (especially at AQ3) ranging from welding, steel erection, pipe grinding to industrial gas flares from plant operations in the area.

4.0 CONCLUSION

This study has revealed that industrial activities and vehicular traffic have the potential to increase the concentration of heavy metals in the atmosphere. The concentrations of Cr and Mn obtained in $PM_{2.5}$ exceeded the 8-hour time weighted average (TWA) exposure limit of 1.1 µg/m^3 and annual average limit of 0.15 µg/m^3 respectively by the World Health Organization. This implies that the residents of Bonny, especially those who live around the industrial area and vehicular traffic hotspots such as Finima roundabout, Wilbros Junction, etc, might be exposed to high concentrations of Cr and Mn. The main sources of the heavy metals detected were from construction works and other anthropogenic activities including welding, steel erection, pipe grinding, vehicular traffic and industrial gas flares from plant operations in the area. Long term exposure to these metals (especially Cr and Mn) through various channels such as air (inhalation) or food chain (ingestion) can lead to some health problems including manganism, kidney and liver damage, tooth erosion, cancer, etc. Hence, there is dire need for critical stakeholders such as the Rivers State Ministry of Environment, National Environmental Standards Regulations and Enforcement Agency (NESREA), Federal Ministry of Environment, Nigerian Upstream Petroleum Regulatory Commission (NUPRC), etc to intensify their enforcement effort towards regular monitoring of heavy metals around industrial areas for a healthy environment.

5.0 RECOMMENDATIONS

- Bonny Local Government Authority should develop and sustain a framework that allows “free flow” speeds of vehicles within the Island.
- Further research should be carried out into the health risk of heavy metals around industrial areas and vehicular traffic hotspots (like Wilbros Junction and Finima roundabout) in Bonny Island.

Disclaimer (Artificial intelligence)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

Acknowledgement

The authors would like to thank the management of GIMLAS Integrated Services Ltd for their support with field equipment and laboratory analysis.

Conflicts of interest

Authors declare no conflicts of interest as regards this research paper.

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