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Determination of the Concentration and Soil-To-Plant Transfer Factor of Heavy Metals within Some Petrol Stations in Warri Metropolis, Delta State, Nigeria

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Abstract

This study investigates the contamination of soils and plants within the vicinity of petroleum products dispensing stations, otherwise known as petrol stations. Most products sold at these stations are premium motor spirit (PMS) also known as petrol and automotive gas oil Diesel). The essence is to determine the extent of contamination due to careless discharge of these products in the vicinity since it can result in health risk. The study was conducted within Warri metropolis of Delta State. Eight heavy metals of concern; namely copper (Cu), chromium (Cr), cadmium (Cd), lead (Pb), zinc (Zn), nickel (Ni), manganese (Mn) and cobalt (Co) were studied. From each site, bitter leaf plant (*Vernonia amygdalina*) samples and composite soil samples were collected for processing. Samples were treated and digested in accordance with USEPA Method 3050B. Filtrate from digested samples were diluted as required and the heavy metal concentrations from each of the samples were determined using atomic absorption spectrophotometer. The transfer factor for these heavy metals was then determined statistically. The result shows that apart from Cd, Cr and Pb that had zero value, the values for others are generally high. Cu, Co, Mn, Ni and Zn at most stations had values above one. This shows elevated values in these plants and a pointer to future disaster. Hence the need for surveillance, discourage planting edible plants around fuel dispensing stations and stricter government regulations. There is also the need for some safety measures and putting in place what ensures healthy environment.

Keywords: Heavy metals, Transfer factor, contamination.

Introduction

Heavy metals are essential minerals found in very small quantities in humans, and other living organisms. They are vital for some of their functions and survival. They are usually present in micrograms. However, they become harmful to the system when present in high quantities; especially when it persist. This is why in recent, the accumulation of heavy metals in most bodies such as soils, water, vegetables and other consumables have become issue of concern since they accumulate as either free radicals or complexes to become toxic in the body [6, 8, 28].

In very small quantities, they promote growth, disease prevention, and other important factors which are advantageous to human beings,

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animals and plants. Heavy metals are generally released into the environments in different forms and accumulation of these metals is dependent on the concentration of the metal and the exposure period. This can be in different processes and dimension [1, 2, 16].

Soil pollution by heavy metals constitute a threat to the environment due to the fast growth of industry and agriculture, and the disruption of natural eco-systems by anthropogenic pressure linked to the growth of human populations. [15, 17]. Environmental pollution and human exposure associated with heavy metals are attributed to different anthropogenic activities that include petroleum processing and discharge of processed products, mining, industrial activities; the use of metal containing compounds in domestic and agricultural settings, etc [4, 5, 10].

Vast majority of heavy metals are present naturally in the environment. However, most emanate from industrial effluents, mining, smelting, combustion of fossil fuels, waste and biomass burning, manufacturing, use and disposal of electronic gadgets, and a host of other human initiated processes [13, 14]. Studies have shown that the level of these heavy metals which have become toxic in some products due to accumulation or above permissible limit in some products such as canned water, beverages and some brands of canned beers in Nigeria need to be addressed [11]. This is because the outcome shows the need for the scientific community to be proactive and be more conscious of some of these heavy metals, especially chromium, nickel, cobalt, aluminum, copper, and zinc [17, 21].

Pollution is an undesirable change in the physical, chemical or biological characteristics of air, water and soil that may harmfully affect life in one way or the other to create potential health hazard to any living components and in particular undesirable for man, affecting adversely the industrial process, cultural and natural assets or general environment of living society [7, 24, 26]. Although, environmental pollution can be created by natural events such as forest fire and active volcanoes, the word pollution generally implies the contaminants have an anthropogenic source which is source created by human activities. The fact that ancient human settlements are recognised by their wastes accumulation shows that pollution has become part of human creation nowadays, especially due to nucleated settlement, urbanization and industrialization. [9, 12, 13, 21].

Toxic pollution affects more than 200 million people worldwide. In some of the world worst polluted areas, babies are born with birth defects, and children have lost 30 to 40 IQ points. It also drastically reduces life expectancy in some countries [26, 27]. In Nigeria, the overall average is 54.6 years to 54.9 years; which is considered to be one of the lowest in the world. It is higher in females compare to males. In males it is approximately 54.3 years, while in females it is approximately 54.9 years. While in India, it is approximately 72.49 years; which is far higher

than Nigeria [27]. This is due series of sickness which are pollution induced, some of which are diseases like stroke, heart diseases, cancer and respiratory illnesses. In recent times, the society is more concerned than ever before because pollution of all kinds can have negative effects which usually result in devastating consequences [5, 10].

Generally, metals are discharged into the air, soil and water from a wide range of natural and anthropogenic sources. This makes it possible for one to distinguish the sources from which metals pollute the environment. Based on this, six different sources were identified [7, 12, 28].

Materials and Methods

Sample Collection

Samples were collected from ten (10) different petroleum dispensing stations within Warri metropolis. Collected were soil and fresh leaf samples. The leaf of bitter leaf plant (*Vernonia amygdalina*) was chosen for this research since it was found to have been grown in all the petrol station sampled. They were collected into a clean polythene bags. While the soil samples were collected at three different one foot equidistance points at each station. They were then mixed together as composite samples and kept in clean polythene bag. The samples were kept in an isolated clean place under room temperature to avoid degradation and contamination. The coordinates of the ten (10) prime motor spirit stations sampled were:

Table 1: Coordinates of the ten (10) prime motor spirit stations sampled

SN	CODE	COORDINATE
1	PDSA	Lat. 5°44477'N; Long. 5°32304'"E
2	PDSB	Lat. 5°45267'N; Long. 5°30579'E
3	PDSC	Lat. 5°44471'N; Long. 5°32298'E
4	PDSD	Lat. 5°45267'N; Long. 5°30579'E
5	PDSE	Lat. 5°54361'N; Long. 5°32439'E
6	PDSF	Lat. 5°45214'N; Long. 5°31108'E
7	PDSG	Lat. 5°30266'N; Long. 5°31108'E
8	PDSH	Lat. 5°377'N; Long. 5°570'E
9	PDSI	Lat. 5°56907'N; Long. 5°79787'E
10	PDSJ	Lat. 5°56907'N; Long. 5°79787'E

They are all located within Warri metropolis and are all strategically located in such a way that motorist find it hard to avoid them when wanting to refill their fuel tanks.

Sample Preparation

Samples were prepared in accordance with USEPA Method 3050B (USEPA 1996) and method adopted by Radojevic & Bashkin (1999) for the digestion of leaf and soil samples [15, 20]. While wearing hand gloves to avoid contamination, the leaf samples were neatly plucked from their stems, dirt removed and carefully placed in the oven at $100^{O}C$ for about six hours to ensure that they are completely dry and turned to ash [20, 25].

To digest the leaf samples, 5 gm of each sample was placed in a clean 250 ml flat bottom conical flask. This was made wet with distilled water; and to it was added 5ml of 10% trioxonitrate (V) acid (HNO_3) and 1ml of

perchloric acid ($HClO_4$). This was heated at $90^{O}C$ to almost dryness and to it was added 10 ml of 4M hydrochloric acid (HCl). This was further heated for about 10 minutes to ensure complete digestion of the sample and homogeneity. The digested samples were then filtered using Whatman medium filter paper (Whatman 42). The filtrates were then transferred into 100 ml standard flask; and filled to the 100 ml mark with deionised water. After which it was poured into clean sample bottle and kept inside a refrigerator to prevent decomposition. The concentration of heavy metals in these samples were determined using atomic absorption spectrophotometric (AAS) method [4].

To prepare the soil samples, the three samples from each station were mixed to form a composite sample. They were then cleaned by removing dirt and pebbles. About 20 gm of each composite sample was placed in a clean petri dish after all debris, roots and stones have been removed from the soil and dried in oven at 105ºC for six (6) hours. After drying, the samples were grinded with a clean ceramic mortar and pestle into powdery form. To digest the sample, 1gm of soil sample was measured into 250 ml flat bottom conical flask. This was made wet with deionised water; and to it was added 10 ml of tetraoxosulphate (VI) acid (H_2SO_4), 5 ml of trioxonitrate (V) acid (HNO_3) and 1ml of perchloric acid ($HClO_4$). The mixture was heated on a hot plate to digest the soil content. The process was carried out for all the ten samples. Where the digestion is not fully achieved, the process of adding these acids is repeated until clear solution, which indicate proper digestion is attained. To the almost dry digested samples were added 10 ml of 4M hydrochloric acid (HCl) and further heated to ensure homogeneity.

The digested samples were then filtered using Whatman medium filter paper (Whatman 42). The filtrates were then transferred into 100 ml standard flask; and deionised water added to the 100 ml mark. After which it was poured into clean sample bottle and kept inside a refrigerator to prevent decomposition. These samples were later sent for atomic absorption spectrophotometric (AAS) analyses [3].

Results and Discussion

Table 2: Concentration of Total Heavy Metals in Soil Samples of Some Petrol Stations in Warri Metropolis (mg/kg)

SN	Sample Code	Cd	Cr	Cu	Co	Pb	Zn	Mn	Ni
1	NESREA/ WHO/FAO	3	10,000	36	10,000	167	300,000	10,000	10,000
2	PDSA	<0.001	<0.001	5.599	3.007	<0.001	30.005	12.836	0.429
3	PDSB	<0.001	<0.001	2.054	3.357	<0.001	21.822	10.301	0.485
4	PDSC	<0.001	<0.001	2.375	4.319	<0.001	22.752	12.066	0.44
5	PDSD	<0.001	<0.001	2.76	4.162	<0.001	13.799	6.258	0.58
6	PDSE	<0.001	<0.001	1.38	4.297	<0.001	14.505	9.242	0.559
7	PDSF	<0.001	<0.001	5.038	5.59	<0.001	10.87	14.505	0.585
8	PDSG	<0.001	<0.001	2.701	4.12	<0.001	2.92	10.87	2.701
9	PDSH	<0.001	<0.001	6.217	5.227	<0.001	32.106	10.753	3.453
10	PDSI	<0.001	<0.001	6.445	5.975	<0.001	35.224	12.778	2.722
11	PDSJ	<0.001	<0.001	8.357	6.358	<0.001	37.054	19.575	5.557

Table 2, which is the concentration of total heavy metals in the soil samples reveals that the concentrations of Zn (2.92 – 37.054mg/kg) and Mn (6.258 – 19.575 mg/kg) are alarming; while Ni (.44 – 5.557 mg/kg), Cu (1.38 – 8.357 mg/kg) and Co (3.007 – 6.358 mg/kg) also are of high concentrations, but not comparable to the first two heavy metals. However, all of them are within NESREA and WHO/FAO permissible limit. The result is consistent with the findings of some researchers [18, 19, 21].

Table 3: Concentration of Total Heavy Metals in Leaf Samples of Some Petrol Stations in Warri Metropolis (mg/kg)

SN	Sample Code	Cd	Cr	Cu	Co	Pb	Zn	Mn	Ni
1	PDSA	<0.001	<0.001	1.957	1.897	<0.001	34.868	3.015	0.321
2	PDSB	<0.001	<0.001	3.24	3.965	<0.001	33.713	3.368	1.091
3	PDSC	<0.001	<0.001	0.642	2.415	<0.001	6.8	11.443	2.085
4	PDSD	<0.001	<0.001	0.321	2.608	<0.001	3.978	10.257	3.368
5	PDSE	<0.001	<0.001	0.449	3.089	<0.001	2.566	10.609	0.064
6	PDSF	<0.001	<0.001	0.289	2.303	<0.001	6.576	8.545	1.411
7	PDSG	<0.001	<0.001	3.477	7.734	<0.001	4.347	12.543	4.542
8	PDSH	<0.001	<0.001	8.542	7.779	<0.001	35.557	13.548	5.558
9	PDSI	<0.001	<0.001	8.967	8.378	<0.001	39.385	15.575	3.786
10	PDSJ	<0.001	<0.001	11.694	8.695	<0.001	40.335	22.549	7.976

Table 3 shows the same trend in the leaf samples with Zn and Mn having higher concentrations; while Ni, Cu and Co also are having lower values for total heavy metals concentrations. The Zn value ranged from 2.566 – 40.335 mg/kg; Mn ranged from 3.015 – 22.549 mg/kg; Ni ranged from .064 – 7.976 mg.kg; Cu ranged from .289 – 11.694 and Co ranged from 1.897 – 8.695 mg/kg. These values are also high but are within the NESREA and WHO/FAO permissible limits. In both leaf and soil samples, values obtained for Cd, Cr and Pb were all below detectable limits, which agrees with some researchers findings [2, 9, 10, 22]. This also makes them safer for consumption by humans and animals.

To calculate the transfer factors (TF), which is the ratio of concentration of substance (heavy metal) in the plant (which is the leaf samples) to that of the concentration of substance in the soil sample; were determined.

$$TF = \frac{C_{plant}}{C_{soil}}$$

Where: C_{plant} is the concentration of a heavy metal in the plant and C_{soil} is the concentration of heavy metal in the soil

Table 4: Transfer Factors Obtained for Soil-To-Plant of Total Heavy Metals Concentrations in the Areas under Study in Warri Metropolis

SN	Sample Code	Cd	Cr	Cu	Co	Pb	Zn	Mn	Ni
1	PDSA	0	0	0.350	0.631	0	1.162	0.235	0.748
2	PDSB	0	0	1.577	1.181	0	1.545	0.327	2.249
3	PDSC	0	0	0.270	0.559	0	0.299	0.948	4.739
4	PDSD	0	0	0.116	0.627	0	0.288	1.639	5.807
5	PDSE	0	0	0.325	0.719	0	0.177	1.148	0.114
6	PDSF	0	0	0.057	0.412	0	0.605	0.589	2.412
7	PDSG	0	0	1.287	1.877	0	1.489	1.154	1.682
8	PDSH	0	0	1.374	1.488	0	1.107	1.260	1.610
9	PDSI	0	0	1.391	1.402	0	1.118	1.219	1.391
10	PDSJ	0	0	1.399	1.368	0	1.089	1.152	1.435

Table 5: Summary of Heavy Metals with Transfer Factors Greater Than One

Soil-to-Plant Range	Number of Petrol Stations
Cu: 1.287 - 1.577	Five Petrol Stations
Co: 1.368 - 1.877	Five Petrol Stations
Mn: 1.152 - 1.639	Four Petrol Stations
Ni: 1.391 - 5.807	Four Petrol Stations
Zn: 1.089 - 1.545	Six Petrol Stations

Table 5 is extracted from Table 4 and it shows the heavy metals with transfer factor greater than one. This shows the vulnerability of the vegetables from these areas to the heavy metals from soils.

Conclusion

From the results obtained, the heavy metals concentration in the soil samples were in the order Zn > Mn >Co > Cu > Ni; while that of the leaf

samples were also of the same pattern. This shows the same pattern of transfer from the soil at the various filling stations to the plant leaves. This is in agreement with some findings that are related to this type of research [1, 13, 16, 17]. The values obtained for the transfer factors based on this formula as in Table 3 and extractions as in Table 4 revealed that values less than one indicated less movement of heavy metals from soil into the vegetables and this affected the entire analyses of Cd, Cr and Pb. While five same stations had values less than one for Cu and Co; while four of these stations also had values less than one for Zn. All these stations are located in areas with less vehicular activities, hence less purchasing of petroleum products at these stations. Four other stations had values less than one at different dispensing stations; while two had values less than one for Ni. When the value is greater than one, implies high uptake of heavy metals from soil into the vegetables or plants. Table 4 summarizes the soil-to-plant transfer factor with higher uptake as shown for most stations for Cu, Co Mn, Ni and Zn. From this findings, it can be concluded that the stations with transfer factors greater than one needs attention so that eating these edible plants may not result into disaster in the future. These plants may need to be cleared from these stations so that unsuspected individuals may not become victims of poisonous edible plants. Hence the need for strict regulations from the authorities saddled with protection of human life.

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