



Speciation of Vanadium, Titanium, Manganese and Iron from contaminated site in the residential suburb of Port-Harcourt, Rivers State, Nigeria

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Abstract

This study concerns the investigation of the distribution of heavy metals Vanadium (V), titanium (Ti), manganese (Mn), and Iron (Fe) from soils around Eleme Port-Harcourt in Rivers State, Nigeria. The soil samples were collected systemically in the range of top soil, 0 m, 100 m, 200 m, 300 m, 400 m, and 500 m distance. The samples were analyzed following a five-stage sequential chemical extraction procedure using flame atomic absorption spectrophotometry. The concentration of V was found to be below the acceptable limit with the average mean of 11.27 $\mu\text{g/g}$, Ti was detected similar to V with average mean of 10.86 $\mu\text{g/g}$. Manganese and Fe decreased in concentration with average mean of 1.18 $\mu\text{g/g}$ and 5.27 $\mu\text{g/g}$ respectively. It was observed that the sediment samples contain more of V and Ti compared to Mn and Fe in their distribution. The analysis showed that V, Ti, Mn, and Fe concentrations have not exceeded the maximum allowable concentration for soil quality guidelines for environmental health prescribed by CCME and USEPA. Thus, the soil under study can conveniently be used for agricultural activities.

Keywords: Heavy metals, Petrochemicals, Sequential extraction, Speciation, FAAS, USEPA

Introduction

In recent years, there has been an increasing ecological and global public health concern associated with environmental contamination by heavy metals. Human exposure has equally risen dramatically as a result of an exponential increase of their use in several industrial, agricultural, domestic effluents, and atmospheric sources [1]. Environmental pollution is very prominent in point source areas such as mining, foundries and smelters, and other metal based industrial operations [2].

Although heavy metals are naturally occurring elements that are formed throughout the earth's crust, most environmental contamination and human exposure result from anthropogenic activities such as mining and smelting operations, industrial production and use, and metal-containing compounds [1]. Environmental contamination can also occur through metal corrosion, atmospheric deposition, soil erosion of metal ions and leaching of heavy metals, sediment re-suspension and metal evaporation from water resources to soil and ground water [3]. Natural phenomena such as

weathering and volcanic eruptions have also been reported to significantly contribute to heavy metal pollution [4]. Industrial sources include metal processing ion refineries, coal burning in power plants, petroleum combustion, nuclear power stations and high tension lines, plastics, textiles, microelectronics, wood preservation and paper processing plants [5]. It has been reported that metals such as Cobalt (Co), copper (Cu), manganese (Mn), iron (Fe) etc are essential nutrients that are required for various biochemical and physiological functions [6].

Soils may become contaminated by the accumulation of heavy metals and metalloids through emissions from the rapidly expanding industrial areas, mine tailings, disposal of high metal wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, wastewater, irrigation, coal combustion, residues, spillage of petrochemicals, and atmospheric deposition [7]. Soils are the major sink for heavy metals released into the environment by the aforementioned anthropogenic activities, and unlike organic contaminants that are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation [8]. Their total concentration in soils persists for a long time after their introduction [9].

Soil may contain appreciable amounts of Fe and Mn, which under conditions of water excess, activate redox process of soils. Gotoh and Patrick [10], studied the distribution of different forms of Fe and Mn in water logged soil over a wide range of closely controlled potential and pH conditions.

Reports indicate that increases in water-soluble and exchangeable iron were favoured by the decrease in both redox potential and pH. Moreover, they found that at pH 5 almost all of the spoil Mn was converted from reducible into water-soluble plus exchangeable [11].

The aim of this work is to determine the distribution of vanadium, titanium, manganese and iron speciation in soils from point of discharge of effluents from petroleum and product marketing company.

Materials and Methods

The materials and reagents used for this work are Flame Atomic Absorption Spectrometer (FAAS-Buck Scientific 210 GVP USA), pH Meter (Hanna Instruments, Poland), weighing balance (Mettler Toledo), Auger soil sampler, sediment samples, beakers, conical flasks 100 cm³, measuring cylinder, sand bath, stirring rods, polyethylene containers, conc. HF acid, conc. HNO₃ acid, conc. HClO₄ acid, 30% (v/v) HClO₄, 10% (v/v) HNO₃ acid, 1M CH₃COONH₄, volumetric flask 100 cm³, 0.02M HNO₃, 0.01M HNO₃, 0.1M NH₂OH.HCl, 1M CH₃COONa, buffer.

Sampling

Using auger soil sampler, six samples of sediments were collected from six different locations at the point of discharge of effluents from petroleum and products marketing company (Port-Harcourt Refinery Company), Eleme, Rivers State. The six sediment samples were taken at varying distances ranging from 0 m, 100 m, 200 m, 300 m,

400 m and 500 m respectively from point of discharge from the refinery industry. The samples are placed in polyethylene containers, preserved with ice and labeled accordingly.

Quality control

All glass wares, crucible, and plastic containers were washed with liquid soap, rinsed with distilled water and soaked in 10% HNO₃ for 24 hours, cleaned with distilled water and in such a manner that no contamination occurred. All chemicals used in this study are all analytical grade reagent chemicals.

Sediment sample preparation

Sediment samples for metal analysis were allowed to defrost and then air-dried. Dry sediment samples were ground into powdered and homogenized using a clean mortar and pestle. The dry sediment samples were sieved with 200 nm sieve to obtain the fine particles. They were then stored in desiccators to obtain constant weight. Precautions were taken to avoid contamination during drying, grinding, sieving, and storage.

One gramme (1 g) of the dry sediment samples were weighed each using weighing balance. The weighed samples were subjected into sequential extraction separately. A five-step sequential extraction technique by Tessier et al [12] was used in the extraction. This scheme facilitates the distinction between exchangeable fractions, carbonate fraction, easily exchangeable fraction and residual fraction.

Procedure of sequential extraction by Tessier et al. [12]

Step 1: Exchangeable phase fraction

One gramme of sediment sample was placed into 500 cm³ conical flask and shaken with 25 cm³ ammonium acetate for 15 minutes, and allowed to stand at room temperature for 4 hours. This was then filtered using Whatman filter paper into 500 cm³ volumetric flask to give the exchangeable cation fraction at pH of 7.

Step 2: Carbonate bound fraction

The residue was shaken with 15 cm³ sodium acetate (1M at pH 5) for 15 minutes and allowed to stand for 5 hours at room temperature. The mixture was filtered to give carbonate fraction.

Step 3: Easily reducible fraction (Fe-Mn oxide phase)

The residue was shaken with 20 cm³ of 0.1 M of hydroxyl amine hydrochloride and 0.01 M nitric acid for 15 minutes, and allowed to stand for 5 hours at room temperature. The mixture was filtered to give easily reducible fraction.

Step 4: Oxidizable fraction (bound to organic matter)

A 5 cm³ of 30% (v/v) perchloric acid and 3 cm³ of 0.02 M nitric acid were added to the residue and shaken for 15 minutes, and allowed to stand at room temperature for 3 hours. The mixture was extracted using 1 m ammonium acetate for 24 hours at room temperature and filtered into 500 cm³ volumetric flask to give organic fraction.

Step 5: Residual fraction

A 8 cm³ of conc. HNO₃/HF acid were added to the residue and allowed to stand overnight

for initial reaction and 10 cm³ of conc. HClO₄ was added to the mixture. The mixture was tightly stoppered to reflux the vapour of acid and heated on a sand bath at 200 °C to 25 °C for at least 6 hours until complete evaporation to dryness of semi-dryness. The residue was diluted with 30 cm³ distilled water and filtered into 100 cm³ volumetric flask. The filter paper was washed with 10% (v/v) HNO₃. The resulting solution was diluted into 100 cm³ volumetric flask. The V, Ti, Mn and Fe concentrations in these fractions were determined using Flame Atomic Absorption Spectrometer (Buck Scientific 210 GVP, USA).

Geo-accumulation Index (I_{geo})

Enrichment of metal concentration above baseline concentrations was calculated using the method proposed by Muller [13] termed the geo-accumulation index (I_{geo}). It is expressed as $I_{geo} = \text{Log}_2 [C_m \text{ sample} / (1.5 \times C_m \text{ background})]$ [14].

Where $C_m \text{ sample}$ is the measured concentration of element in the soil sample and $C_m \text{ background}$ is the geochemical background value (world surface rock average given by Marthins and Meybeck [15]). The 1.5 is introduced to include possible variation of the background values due to lithogenic effect. Muller [13] proposed seven

grades or classes of the I_{geo}. These classes are given in Table 2 below.

The overall total I_{geo} (I_{tot}) is defined as the sum of I_{geo} for all trace elements obtained from the site [16]. The number of toxic elements determined in a soil sample and their respective I_{geo} value would influence the I_{tot}.

Muller's Classification for Geo-accumulation index (I_{geo}) is shown as follows:
 Class 0 = I_{geo} ≤ 0 (Unpolluted); Class 1 = I_{geo} 0-1 (Unpolluted to moderately polluted); Class 2 = I_{geo} 1-2 (Moderately polluted); Class 3 = I_{geo} 2-3 (Moderately to strongly polluted); Class 4 = I_{geo} 3-4 (Strongly polluted); Class 5 = I_{geo} 4-5 (strongly polluted to extremely polluted); Class 6 = I_{geo} >6 (Extremely polluted)

Results and Discussion

The results of the speciation of V, Ti, Mn and Fe are shown on Tables 1-5. Table 1 is the result of the pH measurement for the soil samples while Tables 2-5 are the results of the speciation studies of the soil samples from six different locations at t of effluents from the point of discharge of a petroleum refinery.

Table 1: pH measurements of aqueous soil extract

Distance (m)	pH	Temp. (°C)	Buffer calibration
0	4.30	31.0	3.674
100	4.42	31.0	3.60
200	4.30	31.0	3.69
300	5.01	31.0	3.73
400	5.66	31.0	4.18
500	4.15	30.9	3.80
Control soil sample	6.69	30.87	3.86

Table 2: Speciation of Vanadium from contaminated soil samples from residential suburb of Eleme ($\mu\text{g/g}$)

Distance (m)	Exchangeable cation fraction	Carbonate bound fraction	Easily reducible fraction	Organic fraction	Residual fraction	Total
0	1.26	0.65	0.89	12.69	0.74	16.23
100	2.03	4.94	3.58	1.75	0.73	13.03
200	1.40	4.46	0.92	1.23	0.77	8.78
300	2.01	2.67	3.09	1.28	0.76	9.81
400	1.77	2.79	5.89	1.23	1.44	13.12
500	1.15	1.64	1.87	1.15	0.82	6.63
Mean	1.60	2.86	2.71	3.22	0.88	11.27

Table 3: Speciation of Titanium from contaminated soil samples from residential suburb of Eleme ($\mu\text{g/g}$)

Distance (m)	Exchangeable cation fraction	Carbonate bound fraction	Easily reducible fraction	Organic fraction	Residual fraction	Total
0	1.12	4.01	1.01	12.47	0.67	19.28
100	1.79	4.27	3.46	1.56	0.67	11.75
200	1.26	3.19	0.84	1.10	0.69	7.08
300	1.76	2.35	2.89	1.15	0.96	9.11
400	1.51	2.45	5.42	1.08	1.39	11.85
500	1.02	1.45	1.78	1.05	0.79	6.09
Mean	1.41	2.95	2.57	3.07	0.86	10.86

Table 4: Speciation of Manganese from contaminated soil samples from residential suburb of Eleme ($\mu\text{g/g}$)

Distance (m)	Exchangeable cation fraction	Carbonate bound fraction	Easily reducible fraction	Organic fraction	Residual fraction	Total
0	0.01	0.07	0.04	0.52	0.01	0.65
100	0.02	0.11	3.04	0.47	0.06	3.70
200	0.01	0.07	0.05	0.47	0.10	0.70
300	0.25	0.04	0.01	0.48	0.33	1.11
400	0.03	0.02	0.03	0.40	0.04	0.52
500	0.20	0.04	0.01	0.07	0.08	0.40
Mean	0.09	0.06	0.53	0.40	0.10	1.18

Table 5: Speciation of Iron from contaminated soil samples from residential suburb of Eleme ($\mu\text{g/g}$)

Distance (m)	Exchangeable cation fraction	Carbonate bound fraction	Easily reducible fraction	Organic fraction	Residual fraction	Total
0	0.14	0.17	0.27	0.86	5.17	6.61
100	0.20	0.10	0.18	0.52	4.94	5.94
200	0.41	0.22	0.44	5.05	3.84	9.96
300	0.24	0.17	0.23	0.26	1.33	2.23
400	0.19	0.05	0.26	0.13	3.04	3.67
500	0.20	0.17	0.18	0.07	2.53	3.15
Mean	0.23	0.15	0.26	1.15	3.48	5.27

Table 6. Geo-accumulation analysis of the selected heavy metals

Distance (m)	V	Ti	Mn	Fe
0	-3.48	-8.51	-13.96	-13.90
100	-3.80	-9.23	-11.45	-14.05
200	-4.37	-9.96	-13.86	-13.30
300	-4.21	-9.60	-13.19	-15.47
400	-3.79	-9.22	-14.29	-14.75
500	-4.78	-10.18	-14.67	-14.97
Mean	-4.01	-9.34	-13.10	-14.22

Vanadium speciation

The results from Table 2 indicates the concentrations of vanadium in the various fractions. The V in the exchangeable fraction ranged from 1.15-2.03 $\mu\text{g/g}$, while that of the carbonate bound fraction ranged from 0.65-4.94 $\mu\text{g/g}$. that of the easily reducible and organic fractions ranged from 0.89-5.89 $\mu\text{g/g}$ and 1.15-12.69 $\mu\text{g/g}$ respectively. The residual fraction ranged from 0.73-1.44 $\mu\text{g/g}$. the total vanadium composition in then sediment ranged from 6.63-16.23 $\mu\text{g/g}$. the mean of V in the exchangeable, carbonate bound, easily reducible, organic and residual fractions are 1.60 $\mu\text{g/g}$, 2.86 $\mu\text{g/g}$, 2.71 $\mu\text{g/g}$, 3.22 $\mu\text{g/g}$ and 0.88 $\mu\text{g/g}$ respectively.

The variation in the values of V in the exchangeable and carbonate bound fractions may be attributed to pH and leaching/runoff. The soils are generally low in recorded pH as indicated on Table 1, and therefore the low pH increases the mobility of V in the soil [17].

Vanadium had a lower concentration at 0 m distance (point source discharge), which increased at 100 m with a value of 1.26-2.03 $\mu\text{g/g}$, and decreased at 200 m from 2.03-1.40 $\mu\text{g/g}$. there was

an increase at 300 m distance from 1.40-2.01 $\mu\text{g/g}$. this afterwards decreased from 300m to 500 m with the following values 2.01 $\mu\text{g/g}$, 1.77 $\mu\text{g/g}$ and 1.15 $\mu\text{g/g}$. this decrease could be as a result of leaching/runoff. The 300 m distance is ascribed as a zone of transition.

The carbonate bound fraction showed similar trend with that of exchangeable fraction. The V also had a low concentration at 0 m distance (point source discharge) which increased at 100 m with the following values 0.65 $\mu\text{g/g}$ and 4.94 $\mu\text{g/g}$ respectively. Afterwards, there was a decrease in the V concentration at this fraction from 200 m to 300 m distance with values of 4.46 $\mu\text{g/g}$ and 2.67 $\mu\text{g/g}$ respectively.

However, an increase in V in the carbonate fraction was recorded at 400 m with a value of 2.79 $\mu\text{g/g}$, which later decreased at 500 m to 1.64 $\mu\text{g/g}$. This variation could also be as a result of leaching/runoff and the pH level of the soil could be a contributing factor. In the easily reducible fraction, V displayed an irregular variation at 0-500 m with concentrations of 0.89 $\mu\text{g/g}$, 3.58 $\mu\text{g/g}$, 0.92 $\mu\text{g/g}$, 3.09 $\mu\text{g/g}$, 5.89 $\mu\text{g/g}$, and 1.87 $\mu\text{g/g}$ respectively. The concentration of V increased and

decreased at an interval which can be ascribed to leaching/runoff.

In the organic phase, V was detected at a higher concentration at the point source (0 m) with a value of 12.69 $\mu\text{g/g}$, and decreasing down to 200 m distance with concentrations of 12.69 $\mu\text{g/g}$, 1.75 $\mu\text{g/g}$ and 1.23 $\mu\text{g/g}$ respectively. A slight increase was observed at 300 m which decreased at 500 m with concentration values of 1.28 $\mu\text{g/g}$, 1.23 $\mu\text{g/g}$ and 1.15 $\mu\text{g/g}$. this could be as a result of leaching/runoff and pH level of the soil. In the residual fraction, V was detected at a decreased value at 0 m and 100 m with concentrations of 0.74 $\mu\text{g/g}$ and 0.73 $\mu\text{g/g}$ respectively. There was a further increase at 200 m from 0.73 $\mu\text{g/g}$ to 0.77 $\mu\text{g/g}$. This showed clearly an irregular mobility of V from 300 m to 500 m with concentrations of 0.76 $\mu\text{g/g}$, 1.44 $\mu\text{g/g}$ and 0.82 $\mu\text{g/g}$ respectively. This variation in the mobility of V could also be ascribed to variation in pH and leaching.

The total concentration of V in the whole fractions were found to be below the recommended value for soil by the Canadian Council of Minister of Environment [18]. The recommended value for V in the soil according to CCME is 130 $\mu\text{g/g}$. this implies that the level of V in the soil sediment of industrial effluents in Port Harcourt is below the prescribed limit and therefore may not pose any immediate harm to the environment. However, bioaccumulation in plants may lead to the inherent side effects in the ecology. Soil organic matter can equally adsorb V [19]. Redox potential is an important factor that affect the aqueous free electron activities of trace elements. This is evident

in the values observed in the exchangeable fraction [20].

Titanium speciation

The speciation results of Ti in the sediment samples are indicated on Table 3. The exchangeable fraction ranged from 1.02- $\mu\text{g/g}$ to 1.79 $\mu\text{g/g}$, while the carbonate bound and easily reducible fractions ranged from 1.45-4.27 $\mu\text{g/g}$ and 0.84-5.42 $\mu\text{g/g}$ respectively. The organic and residual fractions ranged from 1.05-12.47 $\mu\text{g/g}$, and 0.67-1.39 $\mu\text{g/g}$ respectively. The total Ti composition ranged from 6.09-19.23 $\mu\text{g/g}$. The mean of Ti in the whole fractions are 1.41 $\mu\text{g/g}$, 2.95 $\mu\text{g/g}$, 2.57 $\mu\text{g/g}$, 3.07 $\mu\text{g/g}$ and 0.86 $\mu\text{g/g}$ respectively.

The variations in the values of Ti is similar to that of V, however, the values of Ti observed in each sample in the exchangeable fraction increases at 0-500 m distance, but the variation is an irregular type because at 0 m to 100 m, the concentration of Ti increased sequentially with the concentration values of 1.12 $\mu\text{g/g}$ and 1.79 $\mu\text{g/g}$ respectively. This value then decreased at 200 m and 300 m distances with concentrations of 1.26 $\mu\text{g/g}$ and 1.76 $\mu\text{g/g}$ respectively. Another sequential slight decrease was recorded from 400 m to 500 m distance with detected Ti values of 1.51 $\mu\text{g/g}$ and 1.02 $\mu\text{g/g}$ respectively. This variations could best be ascribed to existence of different oxidation states of Ti. Leaching may also play an important role in the erratic mobility of Ti in the study area.

In the carbonate bound fraction, Ti was detected at a concentration value of 4.01 $\mu\text{g/g}$ (0 m), which increased to 4.27 $\mu\text{g/g}$ (100 m). However, a

decrease in the concentration of Ti was recorded from 200 m to 300 m distances with values of 3.19 $\mu\text{g/g}$ and 2.35 $\mu\text{g/g}$ respectively. This value increased at 500 m to 2.45 $\mu\text{g/g}$.

In the easily reducible fraction, Ti had a concentration value of 1.01 $\mu\text{g/g}$ (0 m), which increased to 3.46 $\mu\text{g/g}$ (100 m), and decreased to 0.84 $\mu\text{g/g}$ (200 m). a slight increase was also recorded at 300 m to 400 m with Ti concentration values of 2.89 $\mu\text{g/g}$ and 5.42 $\mu\text{g/g}$ respectively. The decrease in the value of Ti at 500 m (1.78 $\mu\text{g/g}$) could be as a result of leaching and pH variation in the soil matrix. This also is an irregular variation.

In the organic fraction, Ti was detected with increased values from 0-400 m distances. The recorded concentrations are 12.47 $\mu\text{g/g}$, 1.56 $\mu\text{g/g}$ and 1.10 $\mu\text{g/g}$ respectively. These value increased at 300 m (1.15 $\mu\text{g/g}$), and decreased from 400-500 m. The observed concentrations at these distances are 1.08 $\mu\text{g/g}$ (400 m) and 1.05 $\mu\text{g/g}$ (500 m). This could also be as a result of leaching and pH variation in the soil.

The detected results of Ti in the residual fraction indicated an increase in the value of Ti from 0-400 m distances, with concentrations of 0.67 $\mu\text{g/g}$ (0 m), 0.67 $\mu\text{g/g}$ (100 m), 0.69 $\mu\text{g/g}$ (200 m), 0.96 $\mu\text{g/g}$ (300 m) and 1.39 $\mu\text{g/g}$ (400 m). The Ti value decreased at 500 m to 0.79 $\mu\text{g/g}$. this variation at this fraction may be due to the different oxidation states of Ti.

The above variations in the residual and organic phases may be attributed to the variations in the redox potential and soil organic matter [21]. Mobilities of these metals is equally dependent on

pH and therefore with their low pH values, the trace element mobilities in the soil are enhanced.

Manganese speciation

The results for Mn speciation as indicated on Table 4 showed that its occurrence in the exchangeable, carbonate bound, easily reducible, organic and residual fractions ranged from 0.01-0.25 $\mu\text{g/g}$, 0.02-0.11 $\mu\text{g/g}$, 0.01-3.04 $\mu\text{g/g}$, 0.07-0.52 $\mu\text{g/g}$ and 0.01-0.33 $\mu\text{g/g}$ respectively. The total Mn composition ranged from 0.4-3.7 v. the mean of Mn in exchangeable, carbonate bound, easily reducible, organic and residual fractions are: 0.09 $\mu\text{g/g}$, 0.06 $\mu\text{g/g}$, 0.53 $\mu\text{g/g}$, 0.40 $\mu\text{g/g}$ and 0.10 $\mu\text{g/g}$ respectively.

The concentration of Mn in the exchangeable fraction indicated an irregular variation from 0 m to 500 m distances, therefore, at 0 m and 100 m distances there is an increase in the recorded value of Mn (0.01 $\mu\text{g/g}$ and 0.02 $\mu\text{g/g}$ respectively), but at 200 m, it decreased to 0.01 $\mu\text{g/g}$, while at 300 m it increased to 0.35 $\mu\text{g/g}$. At 400 m distance the observed Mn decreased (0.03 $\mu\text{g/g}$) while at 500 m an elevated concentration was observed (0.20 $\mu\text{g/g}$). In the carbonate bound fraction, Mn was detected at low concentration of 0.07 $\mu\text{g/g}$ (0 m) while a slight increase was detected at 100 m (0.11 $\mu\text{g/g}$).

In the easily reducible fraction, the Mn detected at the 0 m and 100 m distances indicated an elevated values of 0.04 $\mu\text{g/g}$ (0 m) and 3.04 $\mu\text{g/g}$ (100 m). This value decreased at 200 m (0.05 $\mu\text{g/g}$) and 300 m (0.01 $\mu\text{g/g}$). Manganese increased at 400 m (0.03 $\mu\text{g/g}$) while it decreased at 500 m (0.01

µg/g). Results for the detected Mn in the organic fraction indicated a decrease from 0 m to 200 m with values of 0.52 µg/g (0 m), 0.47 µg/g (100 m) and 0.47 µg/g (200 m). However, at 300 m, Mn indicated a slight elevation in the concentration with a value of 0.48 µg/g. This was followed with a decrease at 400 m (0.40 µg/g) and 500 m (0.07 µg/g) distances.

The observed concentration of Mn in the residual fraction showed a slight increase from 0 m (0.01 µg/g), 100 m (0.06 µg/g), 200 m (0.10 µg/g) and 300 m (0.33 µg/g) distances. A sudden decrease was noticed at 400 m (0.04 µg/g), while an increase was observed at 500 m (0.08 µg/g) distance. This variation may be attributed to redox processes as a result of the manifestation of different oxidation states of Mn in the environment. Manganese occurs in four valence states, Mn II, Mn III, Mn IV, and Mn VII. Mn II is unstable and easily oxidized to Mn III which is stable [22].

Manganese was also found to have a low concentration compared to the recommended value by the United States Environmental Protection Agency [23] in all the fractions. The recommended limit for Mn in the sediment by USEPA is 30 µg/g. This implies that the soil sample from industrials and product marketing company have low levels of Mn below the prescribed limit and therefore will pose no harm to the environment.

Iron speciation

The results of Fe speciation as shown on Table 5 indicates that the concentration in the exchangeable fraction increased in the following

order: 0.14 µg/g (0 m), 0.20 µg/g (100 m), 0.41 µg/g (200 m). A slight decrease was observed at 300 m (0.24 µg/g) and 400 m (0.19 µg/g). However, an elevated Fe concentration was observed at 500 m with a value of 0.20 µg/g. In the carbonate bound fraction, the concentration of Fe increased from 0 m (0.17 µg/g), 100 m (0.10 µg/g) and 200 m (0.22 µg/g) distances. A decrease was detected from 300 m (0.17 µg/g) to 400 m (0.50 µg/g), and 500 m (0.17 µg/g).

The recorded concentration of Fe in the easily reducible fraction showed an irregular variation in its concentration. Iron decreased in concentration at 0 m (0.27 µg/g) and 100 m (0.18 µg/g) distances. There was an increase from this point through 200 m (0.44 µg/g) and a slight decrease at 300 m (0.23 µg/g). With a further decrease at 400 m (0.26 µg/g) and 500 m (0.18 µg/g). Thus 200 m distance can be ascribed as a zone of transition.

In the organic fraction, the concentration of Fe displayed a decrease from 0 m (0.86 µg/g) to 100 m (0.52 µg/g). A higher concentration was recorded at 200 m (5.05 µg/g), while a slight decrease was observed at 300 m (0.26 µg/g), 400 m (0.13 µg/g) and 500 m (0.07 µg/g). For the residual fraction, Fe was detected at a high concentration which decreased from 0 m (5.17 µg/g), 100 m (4.94 µg/g), 200 m (3.84 µg/g) and 300 m (1.33 µg/g). This value was increased further at 400 m (3.04 µg/g) and subsequently decreased at 500 m (2.53 µg/g).

This speciation results of V, Ti Mn and Fe indicates that anthropogenic factor may partly be responsible for the occurrence of these metals in the

soil samples under investigation. Moreover, the total concentration of Fe in all the fractions was found to be below the recommended limit (30 µg/g) by the USEPA. This means that the soil sample from the industrial site and product marketing company have low level of Fe compared to the prescribed limit, and thus will not pose any harm to the environment.

Geoaccumulation index

The results obtained from the analysis of I_{geo} on Table indicates that all the values are below 0 and therefore are all unpolluted according to the classification. This clearly indicates that anthropogenic factors does nit have an influence over the heavy metal load in the samples under investigation.

Conclusion

From the results of the analysis of soil samples from contaminated areas of Eleme Port-Harcourt, the total metal concentrations evaluated are within the acceptable limits for the growth and development of different organisms, and pose no threat to the ecosystem. The concentration of V was found to be below the acceptable limit with the average mean of 11.27 µg/g, Ti was detected similar to V with average mean of 10.86 µg/g. both Mn and Fe decreased in their average mean with the values 1.18 µg/g and 5.27 µg/g respectively. However, bioaccumulation in plants overtime may lead to inherent side effects in human such as inhibition of some biochemical and physiological functions. This result also showed that the effluent from oil

refinery in Port-Harcourt contains appreciable low concentrations of V, Ti, Mn and Fe.

Conflicting interests

There is no conflicting interest in this work.

Authors contribution

The authors did not receive any funding for this work. The sponsorship of this research was borne by the authors.

Acknowledgements

The authors wish to acknowledge The Federal Polytechnic, Idah, Kogi State Nigeria for granting them access to their laboratory.

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