https://chemclassjournal.com/
ChemClass Journal Vol. 9 Issue 2 (2025); 298-309
e-ISSN:3092-8214 p-ISSN:3092-8206
DOI: https://doi.org/10.33003/chemclas-2025-0901/159

Speciation of Lead, Cadmium and Nickel in Soils Around an Effluent Discharge From an Oil Processing Factory in Port-Harcourt South-South Nigeria

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Abstract

Speciation study to investigate the concentration of Pb, Cd and Ni in various fractions of soils around an effluent discharge from an oil processing factory in Port-Harcourt using sequential extraction procedure and Atomic Absorption Spectrometry (AAS) respectively was carried out. Results obtained indicated a mean concentration of these metals in the order of Ni > Pb > Cd. The total observed concentration with reference to the distance ranged from 0.80 -1.90 µg/g for Pb; 0.16 - 0.29 µg/g for Cd and 2.53 – 7.20 µg/g for Ni. The I_{geo} values of ≤ 0 which showed that these two metals were below the world surface average. Consequently, a negative I_{geo} was observed for Pb except for few chemical specie with I_{geo} values below 1, which was an indication that the soil quality was unpolluted to moderately polluted. The exchangeable cation fractions were all below the lowest effect level and are therefore not detrimental to human health.

Keywords: Atomic absorption spectrometer, Effluent discharge, Heavy metals, Oil factory, Speciation, Pollution

Introduction

Soil is the building block of basic materials that constitute the earth's environment and it also provides a basis for the survival and development of living organisms, both plants and animals, including human beings. Heavy metals are released into the environment by both natural and anthropogenic sources, especially mining and industrial activities, as well as automobile exhausts (for lead) [1]. They leach into underground waters, moving along water pathways and eventually depositing in the aquifer, or are washed away by runoff into surface waters thereby resulting in water and subsequently soil pollution [2]. Soil can also be a source of heavy metals migration into animal and human food chains and can affect plant growth and have negative impacts on environmental conditions [3].

Heavy metals like, cadmium (Cd), lead (Pb) and nickel (Ni) are not essential for plant growth; they are readily taken up and accumulated by plants in toxic forms. Ingestion of vegetables

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irrigated with waste water and grown in soils contaminated with heavy metals pose a possible risk to human health and wildlife [4]. However, some heavy metals have bio-importance as trace elements but, the biotoxic effects of many of them in human biochemistry are of great concern [5]. These heavy metals are not biodegradable and may be absorbed by the body through inhalation, dermal contact, ingestion from minor amounts in food and hand -to- mouth activity [6].

There is, therefore the need for proper understanding of the conditions, such as the concentrations and oxidation states, which make them harmful, and how biotoxicity occurs. It is also important to know their sources, leaching processes, chemical conversions and their modes of deposition to pollute the environment, which essentially supports lives [3].

Researches carried out over the years have shown that, although heavy metals occur naturally, human activities have increased its levels in the biosphere. Effluent water which is the collection of polluted water obtained from industries can contribute to increased occurrence of heavy metals in the biosphere [7][8]. These metals from a range of sources reach humans via air, dust, food, soil and water. Once in the body they circulate in the blood, while most are excreted, some can remain in the tissues, organs and bones. It is therefore important to ensure that these heavy metals are kept within the international limit for pollution control while preventing threat to life and damage to the environment.

Heavy metals are those metallic compounds with relative high density and are toxic to the human system in low concentration. They have great ecological significance due to their toxicity and accumulative behaviour. Examples are arsenic, chromium, mercury, nickel, cadmium, lead etc.

The poisoning effects of these metals are due to their interference with the normal body biochemistry in the normal metabolic processes. Poisoning and toxicity occur frequently through exchange and co-ordination mechanisms. When ingested, in the acid medium of the stomach, they are converted to their stable oxidation states (Zn^{2+}, Pb^{2+}, Cd^{2+}, As^{2+}, As^{3+}, Hg^{2+} and Ag^{+}) and combine with the body's biomolecules such as proteins and enzymes to form strong and stable biotoxic compounds, thereby mutilating their structures and hindering them from the bioreactions of their functions [9].

Among heavy metals, lead (Pb) is a potential pollutant that readily accumulates in soils and sediments [10]. Significant increase in the Pb content of cultivated soils has been observed near industrial areas. It exerts adverse effects in humans due to sufficient exposure and accumulation in the body. The neurological, reproductive, renal, and haematological systems are known to be susceptible to its effects [11].

Cadmium (Cd) is toxic at extremely low levels and is generally present in the environment at very low levels. However, human activity has greatly increased its level and it can travel long distances from the source of emission by

atmospheric transport [12]. In humans, long term exposure results in renal dysfunction, characterized by tubular proteinuria. It is readily accumulated in many organisms, notably molluscs and crustaceans. Lower concentrations are found in vegetables, cereals and starchy roots. Human exposure occurs mainly from consumption of contaminated food, active and passive inhalation of tobacco smoke and inhalation by workers in the non-ferrous metal industry [12]. National, regional and global actions are needed to decrease global environmental cadmium pollution, occupational and environmental exposure.

Nickel (Ni) is a natural constituent of soil; its level varies widely depending on local geology and anthropogenic input. The typical concentrations of nickel reported in soil range from 4 to 80 ppm. Nickel may be transported into streams and waterways from the natural weathering of soil as well as from anthropogenic discharges and runoff. Occupational exposure to nickel may occur by dermal contact or by inhalation of aerosols, dusts and fumes. Nickel is released into the atmosphere mainly in the form of aerosols that cover a broad spectrum of sizes.

The aim of this research work was to determine the chemical species of Pb, Cd and Ni cum their concentrations around an effluent discharge from an oil processing factory in Port-Harcourt, South-south Nigeria.

Materials and Methods

Study area

This research was carried out around an effluent run-off of an oil processing factory in Port-Harcourt. The area is a host to the Port-Harcourt Refining Company (PHRC), and Pipeline Product Marketing Company (PPMC) all subsidiaries of the Nigerian National Petroleum Corporation (NNPC). This research work covers the speciation and investigation of the concentration of Pb, Cd and Ni in contaminated soils. It is limited to the analysis of soil samples obtained at various distances along the effluent discharge of an oil processing factory in Port-Harcourt. Figures 1- 6 below indicates the various sampling points from the point of discharge.

Materials

The materials used were as follows: Atomic absorption spectrometer (Buck scientific 210 GVP, USA), Weighing balance (Hanna, Poland), pH meter (Mettler Toledo), Ceramic mortar and pestle, Whatman filter paper (No. 20), Soil sample, Polyethylene containers.

Reagents

Concentrated nitric acid (HNO_3), concentrated hydrofluoric acid (HF), Concentrated perchloric acid ($HClO_4$), 30% (v/v) perchloric acid ($HClO_4$), 10% (v/v) nitric acid (HNO_3), 1 M ammonium acetate (CH_3COONH_4), 1 M sodium acetate (CH_3COONa), 0.02 M nitric acid (HNO_3), 0.1 M hydroxyl ammonium hydrochloride

($NH_2OH.HCl$), distilled water. All reagents used were of analytical grade.

Sample collection

Soil samples were collected from an industrial site in Port-Harcourt metropolis at the effluent discharge point. Six different samples were collected from various distances of a 100 m interval ranging from 0 m (source) to 500 m away from the source. The samples obtained were placed in polyethylene containers and transported to the laboratory.

Sample preparation

Soil samples obtained from different distances were air-dried under clean conditions, homogenized using a ceramic mortar/pestle and impurities (small stones, plant debris etc.) were removed using a 2mm mesh. The fine powder samples were placed separately in polythene bags and labelled accordingly ready for sequential extraction.

Sequential extraction procedure for soil analysis

Sequential extraction procedure was used to extract the metals from the soil into various fractions [13]. A summary of the sequential extraction steps as used are shown in Table 1 below.

Table 1: Sequential extraction steps

Steps	Extraction Condition	Target phase
1.	9 cm^3 of $MgCl_2$ at pH 7, T=20 ^oC	Exchangeable (water soluble)
2.	Residue + 8 cm^3 distilled water, CH_3COONa; CH_3COOH. T=20 ^oC	Bound to carbonate (acid soluble)
3.	20 cm^3, 0.04 $NH_4OH.HCl$ in 25% CH_3COOH T= 96 ^oC	Bound to (Fe-Mn) oxides (Reducible)
4.	9 cm^3, O.02 M of HNO_3, 5 cm^3 of H_2O_2(30%), T=85% for 2 h, 3 cm^3 H_2O_2, CH_3COONH_4	Bound to organic matter (oxidation)
5.	Oven dried at 105 ^oC, 5 cm^3 HNO_3, 10 cm^3 HF and 10 cm^3 $HC1O_4$	Residual fraction.

pH Determination

The pH of soil samples was determined using a pH meter. The instrument was calibrated using appropriate buffer and the pH of samples were run and recorded accordingly.

Geo-accumulation Index (I_{geo})

Enrichment of metal concentration above baseline concentrations was calculated using the method proposed by Muller [14] termed the geo-accumulation index (I_{geo}). It is expressed as

$$I_{geo} = log_2 \frac{C_{m\ sample}}{1.5\ x\ C_{m\ background}} \quad [15]$$

Where $C_{m\ sample}$ is the measured concentration of element in the soil sample and C_m

$_{background}$ is the geochemical background value (world surface rock average given by Marthins and Meybeck [16]. The 1.5 is introduced to include possible variation of the background values due to lithogenic effect. Muller [17] 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 [18]. The number of toxic elements determined in a soil sample and their respective I_{geo} value would influence the I_{tot}.

Table 2: Muller's Classification for Geo-accumulation index (I_{geo})

Igeo Value	Class	Sediment/soil quality
≤ 0	0	Unpolluted
0-1	1	From unpolluted to moderately polluted
1-2	2	Moderately polluted
2-3	3	From moderately to strongly polluted
3-4	4	Strongly polluted
4-5	5	From strongly polluted to extremely polluted
>6	6	Extremely

Results

The results of the speciation of Pb, Cd and Ni in soils around an effluent discharge from an oil processing factory in Port-Harcourt South-south Nigeria are indicated in Tables 3 – 5, the geo-accumulation index (I_{geo}) for the three metals from the study area are indicated in Tables 6 – 8 while Table 9 contains the result of pH measurement at various sampling points.

Table 3**:** Speciation of Pb in µg/g

Distance (m)	Exchangeable cation fraction	Carbonate bound fraction	Easily reducible fraction	Organic fraction	Residual fraction	Total
0	0.40	0.80	0.20	0.10	0.40	1.90
100	0.40	0.40	0.20	0.10	0.50	1.60
200	0.20	0.30	0.10	0.40	0.40	1.40
300	0.20	0.20	0.30	0.20	0.10	1.00
400	0.60	0.10	0.10	0.10	0.10	1.00
500	0.10	0.20	0.10	0.30	0.10	0.80
Mean	0.32	0.33	0.17	0.20	0.27	1.28

Lowest effect level (LEL) = 31.0 µg/g

Table 4: Results of the speciation of Cd (µg/g)

Distance (m)	Exchangeable cation fraction	Carbonate bound fraction	Easily reducible fraction	Organic fraction	Residual fraction	Total
0	0.03	0.02	0.04	0.06	0.11	0.26
100	0.03	0.02	0.07	0.02	0.09	0.23
200	0.02	0.09	0.01	0.02	0.02	0.16
300	0.02	0.10	0.04	0.02	0.02	0.20
400	0.09	0.10	0.06	0.01	0.03	0.29
500	0.03	0.01	0.01	0.04	0.06	0.15
Mean	0.04	0.06	0.04	0.03	0.06	0.22

Lowest effect level (LEL) = 0.6 µg/g

Table 5**:** Results of the speciation of Ni (µg/g)

Distance (m)	Exchangeable cation fraction	Carbonate bound fraction	Easily reducible fraction	Organic fraction	Residual fraction	Total
0	1.80	1.62	1.17	2.19	0.42	7.20
100	0.35	0.90	0.27	0.69	0.32	2.53
200	1.10	0.81	0.22	1.75	0.38	4.26
300	0.25	2.94	1.17	0.53	0.13	5.02
400	1.79	0.55	1.38	0.37	2.48	6.57
500	2.02	1.09	0.28	0.50	0.87	4.76
Mean	1.22	1.32	0.75	1.01	0.39	5.06

Lowest effect level (LEL) = 16.0 µg/g

Table 6: Results of the Geo-accumulation index of Pb in soil obtained from Port-Harcourt

Distance (m)	Exchangeable cation fraction	Carbonate bound fraction	Easily reducible fraction	Organic fraction	Residual fraction	Total
0	-5.7028	-4.7027	-6.7040	0.0159	-5.7028	-22.7964
100	-5.7028	-5.7028	-6.7040	0.0159	-5.3820	-23.4757
200	-6.7040	-6.1190	0.0159	-5.7028	-5.7028	-23.5379
300	-6.7040	-6.7040	-6.1190	-6.7040	0.0159	-25.5511
400	-5.1190	0.0159	0.0159	0.0159	0.0159	-5.0554
500	0.0159	-6.7040	0.0159	-6.1190	0.0159	-12.7753
Mean	-4.9861	-4.9861	-3.2466	-3.0797	-2.7810	-18.8653

Table 7: Results of the Geo-accumulation index of Cd in soil obtained from Port-Harcourt

Distance (m)	Exchangeable cation fraction	Carbonate bound fraction	Easily reducible fraction	Organic fraction	Residual fraction	Total
0	-2.7004	-3.3854	-2.2854	-1.7004	-0.8259	-10.7975
100	-2.7004	-3.3854	-1.4780	-3.3854	-1.1154	-11.8646
200	-3.2854	-1.1154	-4.2854	-3.3854	-3.3854	-15.2570
300	-3.3854	-0.9635	-2.2854	-3.3854	-3.3854	-13.5343
400	-1.1154	-0.9635	-1.7004	-4.2854	-2.7004	-10.7651
500	-2.7004	-4.2854	-4.2854	-2.2854	-1.7004	-15.2570
Mean	-2.6312	-2.3164	-2.7200	-3.0212	-2.1522	-12.9126

Table 8: Results of the Geo-accumulation index of Ni in soil obtained from Port-Harcourt

Distance (m)	Exchangeable cation fraction	Carbonate bound fraction	Easily reducible fraction	Organic fraction	Residual fraction	Total
1	-6.0786	-6.3206	-6.7000	-5.7957	-8.1779	-33.0728
100	-8.4412	-7.0786	-8.8159	-7.4619	-8.5707	-40.3683
200	-6.7891	-7.2307	-9.1114	-6.1192	-8.3224	-37.5728
300	-8.9266	-5.3708	-6.7000	-7.8424	-9.8695	-38.7093
400	-6.0867	-7.7891	-6.4619	-8.3608	-5.6163	-34.3148
500	-5.9122	-6.8023	-8.7629	-7.9266	-7.1274	-36.5314
Mean	-7.0391	-6.7654	-7.7587	-7.2511	-7.9474	-36.7616

Table 9: Results of the determination of soil pH

Distance (m)	pH	Temp. (^{O}C)
0	4.43	28.7
100	4.74	28.8
200	4.74	28.9
300	5.37	29.0
400	5.43	29.1
500	5.04	29.3

From the results in Table 3, the exchangeable cation fraction for lead (Pb) ranged from 0.1 – 0.6 µg/g, the carbonate bound fraction ranged from 0.1 – 0.8 µg/g, easily reducible

fraction ranged from 0.1 – 0.3 μg/g, while the organic and residual fractions ranged from 0.1 – 0.4 μg/g and 0.1 – 0.5 μg/g respectively. The total metal concentration with reference to distance ranged from 0.80 – 1.90 μg/g.

For cadmium (Cd) speciation, the observed exchangeable cation fractions ranged from 0.02 – 0.09 μg/g; carbonate bound fraction (0.01 – 0.10 μg/g); easily reducible fraction (0.01 – 0.07 μg/g); while the organic and residual fractions ranged from 0.01 – 0.06 μg/g and 0.02 – 0.11 μg/g respectively. The total observed Cd concentration in the soil as a function of distance ranged from 0.15 – 0.29 μg/g.

For nickel (Ni) speciation, the observed concentration for the exchangeable cation fraction ranged from 0.25 – 2.02 μg/g; carbonate bound fraction (0.55 – 2.94 μg/g); easily reducible fraction (0.22 – 1.38 μg/g); while the organic and residual fractions ranged from 0.37 – 2.19 μg/g and 0.13 – 2.48 μg/g respectively. The total observed Ni concentration in the soil as a function of distance ranged from 2.53 – 7.20 μg/g.

Discussion

From the results, the observed concentration of Pb (Table 3) in the exchangeable cation fraction decreased from 0.40 μg/g at 0m to 0.20 μg/g at 300 m distance. At 400 m it recorded a Pb concentration of 0.60 μg/g which reduced drastically to 0.10 μg/g at 500 m from the point of discharge. Thus, the decrease from 0 m to 300 m could be attributed to the metal soil interaction as the metals migrate along its pathway [6].

The carbonate bound fraction showed the same trend of mobility with that exhibited by the exchangeable cation fraction with the reduction of the concentration of Pb as the distance from the point of discharge is increased. The observed trend of decreased from 0.80 μg/g at 0 m to 0.10 μg/g at 400 m. The easily reducible fraction equally exhibited the same trend while the organic fraction increased from the point source to 200 m and decreased at 400 m with slight increment at 500 m.

The high increase of the organic fraction at 200 m may be attributed to the formation of soluble metal complexes [19]. The residual fraction equally had a similar trend and decreased from 100 m to 500 m as the distance from the source is increased. Previous studies indicates that pH is the main variable controlling the solubility, mobility and transports of trace elements as it controls metal hydroxide, carbonate and phosphate solubility. From the results in Table 3, the total concentration of Pb decreased as the pH increased. Thus, the pH affects the solubility of Pb [6][12][20].

For Cd (Table 4) speciation, the exchangeable cation fraction which is the lethal fraction was observed more at 400 m from the point of discharge. The same trend was observed in the carbonate bound fraction where the concentration increased with increase in distance from the point of discharge to 0.10 μg/g at 400 m. Consequently, the easily reducible fraction exhibited the same trend with a progressive increase from 200 m to 400 m and an observed concentration of 0.01 – 0.06 μg/g. Thus, 400 m for

these fractions could be described as a zone of transition for Cd mobility [21]. It is equally important to know that Cd is transported mostly in the clay fraction of the soil and therefore the mobility of this metal increased as distance from the source increased [22].

The organic fraction component of Cd indicated a different trend from the first three fractions with a progressive decrease from the point of discharge as the distance increased. Previous studies have reported that, Cd can move readily in sandy-loam soils but organic matter in the surface layer will act as a sink for Cd and will reduce the rate of its migration [23]. It was reported that the presence of Pb did significantly reduce the adsorption maximum of Cd in soils. The residual fraction equally exhibited the same trend as observed with the organic fraction. Thus, the residual Cd decreased as the distance from the point of discharge is increased. The variation in the total concentration of Cd may also be linked to the variations in solubility as a result of variations in pH at the sampling stations [24]. Sulayman [25] observed that Cd sorption doubled for each 0.5 increase in pH from 3.8 to 4.9.

For Ni speciation (Table 5), the exchangeable cation fraction is inconsistent with increase in the distance from 0 m to 200 m. However, at 300 m the concentration of the exchangeable cation fraction increased progressively from 0.25 to 2.02 μg/g
(500 m from point of discharge).

The exchangeable fraction here is particularly worrisome because of the high values observed, more so that this fraction has the higher toxic effect in the environment [26]. The carbonate bound fraction reduced from 0 m (1.62 μg/g) to 200 m (0.81 μg/g). A higher concentration of 2.94 μg/g was observed at 300 m from the point of discharge. The easily reducible fraction decreased from the point source (1.17 μg/g) to 200 m (0.22 μg/g).

However, there was a slight increase at 300 m (1.17 μg/g) to 400 m (1.38 μg/g). Variations in the distribution of the carbonate bound, easily reducible and exchangeable cation fractions may be due to competing ions. Competing ions can have a marked effect on ions sorption by soils and that there is a positive correlation which exists between Mn and Ni, Ni and Cu, Ni and Fe, Pb and Cu, Pb and Fe, Pb and Mn in soils [27].

The organic fraction component of Ni had the highest observed concentration at the point of discharge of 2.19 μg/g, while at 500 m the observed concentration is 0.50 μg/g. The variation in the distribution of organic Ni as the distance increased may be attributed to leaching and runoff. The probability of movement of transition metals also increases with their concentration. Migration of transition metals may take place when their concentrations exceed the capacity of the soil to retain them that is, especially in stabilized soils [28]. The metal loss from application sites is usually low but varies significantly among elements.

The residual fraction of Ni indicated a high concentration at 400 m (2.48 μg/g). Previous studies have shown that the amount of metals

absorbed increases with increasing ionic strength for minerals with permanent surface charge density [29]. The influence of pH on Ni solubility in the soil as observed in this study agreed with previous studies [30]. The total Ni concentration was observed to be far higher than that of Cd and Pb.

The I_{geo} of the various fractions of Cd from the soil at different distances were generally found to be negative. Consequently, the same result was observed for Ni where the I_{geo} were all negative at different distance away from the point of discharge. The I_{geo} obtained suggests that the concentration mean of these two metals in the soil are lower than the world surface rock average. A negative I_{geo} was observed for Pb except for few chemical species at various distances with I_{geo} values below 1 and therefore, falls within the I_{geo} value of 0 – 1 which is an indication that the soil quality is unpolluted to moderately polluted.

Conclusion

The speciation of Pb, Cd and Ni from Port-Harcourt, South-south Nigeria showed a mean concentration in the following order; Ni > Pb > Cd. High values of Ni was ascribed to anthropogenic factor as a result of the effluent discharge from the crude oil refining industry.

The exchangeable cation fractions in the soil are all below the lowest effect levels for soil/sediment quality guidelines for metals and nutrients and therefore, are not inimical to humans. However, bioaccumulation and over-exposure of biological systems as a result of the continuous discharge of this effluent without recourse to bioremediation may lead to bioaccumulation in biological systems.

Conflicting Interests

The authors declare that no conflicting interest exist.

Authors Contributions

The authors received no specific funding for this work.

Acknowledgement

The authors wish to acknowledge the Department of Science Laboratory Technology, The Federal Polytechnic Idah, Kogi State Nigeria for giving us access to the AAS machine for the heavy metals analysis.

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