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Metal Distribution along the Major Roads of Trans-Amadi Industrial Complex Port Harcourt, Nigeria

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Authors' contributions

This work was carried out in collaboration between all authors. Author PEO designed the study and wrote the protocol. Author HOA preformed the statistical analysis, managed the literature search and author SCE wrote the first draft of the manuscript with assistance from author UCU. All authors read and approved the final manuscript.

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Original Research Article

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ABSTRACT

Topsoil samples were collected along six major roads within Trans-amadi industrial complex within the period of April to May. The pH of the soil had a range of 7.2 to 8.1, while moisture content had a range of 0.3% to 0.9%. Fe was seen to have higher concentration in all the soil samples with the highest concentration (0.231 mg/kg) which was found in Slaughter road. Cd recorded the least concentration (0.002 mg/kg) in Ahiramakara road. Fe > Mg > Zn > Cr > Ni > Pb > Cd, Fe > Mg > Zn > Cd > Cr > Pb >Ni, Fe > Mg > Cr > Pb=Cd > Ni, Fe > Mg > Zn > Cd > Ni > Cr > Pb, Fe > Mg > Zn > Ni > Pb > Cr > Cd > Pb, Fe > Mg > Zn > Cr > Cd > Pb > Ni were the observed trend in the total metal concentration for Ahiramakara, Nkpogu, Elekahia, Peter Odili, Slaughter and Incar roads respectively. Mg was discovered to be the most Bioavailable metal (65.61%), while the least bioavailable metal was Pb (29.00%). There was no significant difference in the result at 95% confidence interval in almost all the fractions. Most of the metals in the soil samples were distributed within the residual, Carbonate and reducible fraction except for Fe which was mostly distributed in the water soluble fraction.

Keywords: Speciation; discharge; channels; soil; fractions; digestion.

1. INTRODUCTION

Contamination of soils by heavy metals is the most serious environmental problem and has significant implication for human health process [1,2]. Sources such as atmospheric deposition, waste disposal, fertilizer application and waste water in agricultural land constitute the major anthropogenic input. Generally the distribution of heavy metals is influenced by nature of parent materials, climate conditions, and their relative mobility depending on soil parameters, such as mineralogy, texture and classification of soil [3]. Global industrialization and environmental pollution from technology have started to affect human health. Speciation helps in the identifications and quantification of the defined geochemical fractions, forms or phases in which an element exists in the environment [4,5]. Speciation in sediment compartment is a significant step to understand the potential environmental risk, distribution, mobility and bioavailability of pollutants. Determining the total content of heavy metals in the sediments may be useful for the characterization of pollution intensity, however, speciation of heavy metals with selective extracting agents gives further information about the fundamental reactions that govern the behaviour of metals in sediment and helps to assess the environmental impact of contaminated soil and sediment [6-8]. Sequential extraction procedure is used to partition heavy metals in soil and sediments in order to assess the forms of heavy metals in contaminated soils and sediments. It provides information on potential mobility as well as bioavailability and plant uptake of heavy metals [9,10]. It also determines the bioavailability of the metal in soil and sediment to other biota within the aquatic ecosystem. Metals dissolved in soil solution, surface and interstitial waters and those adsorbed on the sediment by cation exchange processes are usually readily available to aquatic and benthic organisms as well as to plants. Metals strongly bound to the sediments and complexes with other chemical compounds are of less concern as they most likely unavailable to the biota [11]. Sediments contaminated with metals may act as a secondary pollution source for aquatic ecosystem, and study of metal concentration in sediment is useful for the estimation of pollution trends [8]. The major objective of the study is to assess the distribution of the selected heavy metals in trans-amadi

industrial complex so as to ascertain their bioavailability.

1.1 Justification and Objective of the Study

Because of the anthropogenic activities going on in Trans-amadi, we considered it essential to assess the heavy metal distribution in the area. The major objective of the study is to assess the distribution of the selected heavy metals in transamadi industrial complex so as to ascertain their bioavailability.

2. MATERIALS AND METHODS

2.1 Apparatus Used

In the course of the research the following apparatus was used: water Bath, Fume Cupboard, Funnels, Whatmann grade 4 filter papers, 50 ml sample bottles, Cetrifuge, Oven, 250 ml beakers, Jenway pH Meter, Jenway weighing balance (Jenwey 3505) and FAAS (Analyst 200).

2.2 List of Reagents

1 M Magnesium chloride (MgCl₂), Aqua Ragia $(HCl: HNO₃$ in 3:1), Deionized water, 1M sodium acetate (CH₃COONa) adjusted to pH 5 with acetic acid, 0.04M Hydroxylamine hydrochloride $(NH₂OH-HCl)$ in 25% (v/v) acetic acid, 0.02 M Nitric acid (HNO₃), 30% Hydrogen Peroxide $(H₂O₂)$ adjusted to pH 2 with $HNO₃$, 3.2M Ammonium acetate (CH_3COONH_4) in 20%(v/v) $HNO₃$, Hydroflouric acid (HF)

2.3 Sampling and Pre-Treatment of Sample

Soil samples were collected in the vicinity of TRANS-AMADI Industrial layout between April and May. The sampling site was six major roads, Ahiramakara road (road 1), Nkpogu road (road 2), Elekahia road (road 3), Peter Odili road (road 4), Slaugther road (road 5) and Incar road (road 6) as shown in Fig. 1. In all, 6 samples were collected from each road and merged to form one sample, representing each road. This was done using a plastic scoop into a polythene bag well labeled. The sampling site is surrounded by manufacturing industries, a residential estate -

Bozgomero Estate and Golden Valley Housing Estate. The samples were dried at room temperature and sieved through a 200 mesh before analysis. The soil sediments drying at higher temperature were avoided to ensure that organic matter content and the metal binding properties of the sediments remained unaltered. All chemicals and acids used were of Analytical Reagent Grade (ARG), and were used without further purification.

2.4 Methods for Moisture Content Determination

The moisture content of the samples was determined using the weight-difference method. First the weight of the Watch glass (W_1) was taken and about 20 g of the soil sample was weighed into the Watch glass $(W₂)$. The Watch glass containing the sample was placed in an Oven at 105°C for 24 hours. Thereafter, it was transferred into a Dessicator and allowed to cool [12]. It was removed and the weight of the residue and the Watch glass taken (W_3) . Finally, the moisture content was calculated as

Moisture content = $(W_1 + W_2) - W_3$.

2.5 Methods for pH Determination

2 g of the soil sample was weighed into 250 ml Beaker and 20 ml of deionized water added. It was centrifuge for 20 minutes and allowed to settle. Finally, a standardized pH meter was used to read the pH of the mixture [12].

2.6 Methods for Determination of Total Metal Content

2 g of the soil sample was weighed into and 5 ml of Hydrofluoric acid (HF) was added. 10 ml Aqua Ragia was also added and the mixture heated over water bath for about an hour, 30 minutes. Then, it was allowed to cool. The process was repeated again. Thereafter, the solution was filtered and made-up to 50 ml with deionized water [12]. Finally, analysis of the extracts was carried out by Flame Atomic Absorption Spectrometry (Analyst 200).

Location of sampling station

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Fig. 1. Map of the location

2.7 Sequential Extraction

Modified form of Tessier et al. [13] were used to establish the distribution of the total concentration of the metals in the soil samples with their contents in the water soluble. exchangeable, carbonate, Fe/Mn oxide, oxidisable and residual fraction. Below are the procedure taken in establishing the various metal concentrations:

2.7.1 Water soluble fraction

2 g soil sample was weighed into the centrifuge. A plastic tube and 8 ml of deionized water measured into it. Then, it was centrifuged for 1hour and filtered into the sample bottle. Finally, it was made up to 50 ml and using FAAS the metal concentration in the extract.

2.7.2 Exchangeable metal fraction

About 2 g of soil sample was weighed into the centrifuge tube and 8 ml of 1 m MgCl₂ solution added to it then it was agitated for 1 hour. It was also centrifuged, decanted and 4 ml of Aqua Ragia added and the residue washed with deionized water into the sample bottle in which it was made up to 50 ml.

2.7.3 Carbonate-bound fraction

8 ml of 1 m sodium acetate solution which has been adjusted to pH 5.0 with acetic acid was added to the residue of the previous leach. The mixture agitated periodically at room temperature for two hours (2 hrs). Then, it was centrifuged, decanted and 4 ml aqua ragia added. Finally, it was filtered and washed with de-ionized water and FAAS was used to ascertain the metal concentration in the extract.

2.7.4 Fe-Mn oxide fraction

20 ml 0.04 M NH₂OH.HCl in 25% (v/v) acetic acid was added to the previous leach, agitated periodically in boiling water bath for 1 hour 30 minutes, centrifuged, decanted and 4 ml Aqua Ragia was added. The residue was then washed with de-ionized water and made up to 50 ml.

2.7.5 Oxidisable metal fraction

The extraction of oxidisable metal fraction was done in the following order:

- 3 ml of 0.02 M HNO₃ and 5 ml of 30% H₂O₂ which was adjusted to $pH 2$ with $HNO₃$ was added to the previous leach.
- The mixture was agitated periodically at 85℃ for 1 hours.
- 3 ml of H_2O_2 (pH 2) was added and it was agitated periodically at 85℃ 1 hours.
- It was cooled to room temperature.
- 5 ml of 3.2 m ammonium acetate in 20% (v/v) HNO₃ was added and the mixture agitated periodically at room temperature for 30 minutes.
- Thereafter, it was centrifuged, decanted and 4 ml Aqua Ragia added.

Finally it was filtered and the residue was washed with deionized water and it was made up to 50 ml. FAAS was used to determine the metal concentration in the extract.

2.7.6 Residual metal fraction

10 ml hydrofluoric acid and 16 ml Aqua Ragia was added to the previous leach. Then the mixture was heated over water bath for 1 hour. It was washed with deionized water and made up to 50 ml.

3. RESULTS AND DISCUSSION

Presented in Table 4 are the moisture contents and the pH of the various soil samples collected from the six major roads. The pH of the soil affects the mineral mobility in the soil. The soil pH of the soil samples ranged from 7.2 to 8.1 in water indicative of alkalinity to neutrality. The moisture contents ranged from 0.3% to 0.9%. The low moisture content can be attributed to the dry season in which the analysis was carried out. The pH of the analysis data obtained shows that sample 5 (slaughter road) 8.1 is more basic followed by sample 6 (Incar road) 8.0 and others sample 2 (Nkpor Road) 7.8, sample 3 (Elekehia road) 7.8 sample 4 (Peter Odili road) 7.8 and sample 1 (Ahiramakara road) 7.2 has a close rage of pH value of $7.2 - 7.8$.

Percent moisture content was found to be higher in sample 2, next to sample 1 and 6 while sample 3 and 4 had the same value content but sample 5 had the least of it all.

Presented in Table 2 and Fig. 2, is the total metal concentration on roads. The result outlined that Fe was high (0.231 mg/kg) in the sample Rod5. This may be as a result of motor spare parts and

other anthropogenic activities going on in the area. Cd had the least concentration (0.002 mg/kg) as found in sample Rod1. For Rod1 it was $Fe > Mg > Zn > Cr > Ni > Pb > Cd$, while for Rod2 it was Fe > Mg > Zn > Cd > Cr > Pb >Ni. The trend $Fe > Mg > Cr > Pb = Cd > Ni$, was $Fe > Mg > Zn > Cd > Ni > Cr > Pb$, $Fe > Mg$ > Zn > Ni > Pb > Cr > Cd > Pb, Fe > Mg > Zn > $Cr > Cd > Pb > Ni$ were the observed trends for the heavy metal concentration for Rod3, Rod4, Rod5 and Rod6 samples respectively.

Much of the iron was associated with water soluble fractions with a mean value of 0.195 mg/kg (Table 3) indicating that it is readily available. $F1 > F5 > F4 > F3 > F6 > F2$ and Rod1 > Rod3 > Rod4 > Rod5 > Rod6 >Rod2, Were the observed trend in the range of iron concentration and percentage bioavailability respectively.

The highest fraction of Fe was found in sample R5 (0.246 mg/kg) in the water soluble fraction (F1), and this contributed to the high value of the %BAF of Fe (49.07%) in the sample.

Table 1. Percent moisture content and pH of soil samples

Table 2. Heavy metal concentrations in the samples (mg/kg)

Fig. 2. Total metal concentration in the sample

F1, F2, F3, F4, F5 and F6 equals Water soluble Fraction, exchangeable metal fraction, carbonate fractions, reducible Fractions, oxidizable and residual fractions respectively. ND equals not detected

Table 4 presents the fractional concentration of Pb in the sample. Great quantity of the Pb was predominant in the residual fraction with a mean of 0.029 mg/kg and lead concentration in Rod2 was found to be more bioavailable (53.85%) than its counterparts. The least bioavailable Pb was found in Rod 3 with percentage BAF of 29.00%.

This is also shown by the observed trend of the various fractions of $Pb - F6 > F5 > F3 > F2 > F1$ > F4. Pb was detected in all the samples. The observed trend in the percentage bioavailable fractions of the samples was Rod2 > Rod1 > Rod4 > Rod6 > Rod3> Rod5 (Table 4). Much of the Pb was associated with the residual bound fraction and is potentially bioavailable in most of the studied area, most especially for sample 2 (Rod2) were the %BAF was above 50% in the residual bound fraction, but lower in the reducible fraction.

Presented in Table 5 is the fractional concentration of Zn in the samples. Zn is mostly found in the residual fractions. 0.067 mg/kg was the mean concentration at the residual fraction and the %BAF of Zn in the samples was below 50% and so led to a mean %BAF of 40.850%.

Rod3 > Rod4 > Rod1 > Rod5 > Rod2 >Rod6 was the observed trend in the percentage Bioavailable fraction. The trend for the mean fractional concentration was F6 > F4 > F5 > F3 > $F2 > F1$.

Fig. 3. Fractional concentration of Fe in mg/kg

Sample	F1	F ₂	F3	F4	F5	F6	Total	Mean	BAF	$%$ BAF
Rod1	0.002	0.004	0.017	0.006	0.006	0.027	0.062	0.010	0.023	37.10
Rod ₂	0.012	0.012	0.011	0.002	0.013	0.015	0.065	0.011	0.035	53.85
Rod3	0.009	0.002	0.018	0.011	0.027	0.033	0.100	0.017	0.029	29.00
Rod4	0.008	0.009	0.006	0.004	0.017	0.019	0.063	0.011	0.023	36.51
Rod ₅	0.003	0.005	0.009	0.005	0.009	0.042	0.073	0.012	0.017	23.29
Rod6	0.005	0.008	0.014	0.001	0.018	0.035	0.081	0.014	0.027	33.33
Total	0.039	0.04	0.075	0.029	0.09	0.171	0.444	0.074	0.154	34.68
Mean	0.007	0.007	0.013	0.005	0.015	0.029	0.074	0.012	0.027	36.49

Table 4. Fractional concentration of lead in mg/kg

Fig. 4. Fractional concentration of Pb in mg/kg

Fig. 5 pictorially presents the distribution pattern of Zn in the fractions of the samples and it showed that the residual fraction had the highest occurrences at the Rod 5.

It can be deduced (Table 6) that the mean %BAF of Mg is 59.67% which is above 50% and so Mg is readily bioavailable in the studied area. This is also supported by the observed trend in the concentration of Mg in the various fractions – F3 $>$ F1 $>$ F2 $>$ F4 $>$ F6 $>$ F5. The trend in the percentage bioavailability of Mg in the samples is Rod6 > Rod5 > Rod3 > Rod2 > Rod1 > Rod4. Much of the Mg fractions were distributed in the carbonate bound fraction (F3) with mean value of 0.076 mg/kg.

Presented in Table 7 and Fig. 7 is the fractions of Cd. The trend in the mean concentration of Cd was found to be $F5 = F3 > F4 > F1 > F6 > F2$. It distributed more in the oxidizable fraction and carbonate fraction. Even though the %BAF of Cd was below average with a mean of 47.06%, it was above average in Rod6 and Rod1 suggesting that Cd is potentially bioavailable in the studied area.

Presented in Table 8 is the fractions of Ni in the samples. Residual faction recorded the highest concentration of Ni in the samples with a value 0.017 mg/kg (Rod1) and the least was found on sample Rod1 as seen in the oxidizable fraction (0.001 mg/kg). Rod4 > Rod2 > Rod6 > Rod1 > $Rod5 > Rod3$ and $F6 > F1 > F4 > F3 = F2 > F5$ are the observed trends in the %BAF and the mean concentration of the samples in the fractions respectively. The bioavailable fraction of Ni is generally low but the mean %BAF was above 50% indicating that it is readily bioavailable.

Fig. 5. Fractional Concentration of Zn in mg/kg

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Fig. 6. Fractional concentration of Mn in the soil samples (mg/kg)

Sample	F1	F ₂	F3	F4	F5	F6	Total	Mean	BAF	%BAF
Rod1	0.012	0.002	0.011	0.005	0.005	0.011	0.046	0.008	0.025	54.35
Rod ₂	0.008	0.006	0.007	0.007	0.018	0.006	0.052	0.009	0.021	40.38
Rod3	0.011	0.017	0.004	0.014	0.024	0.002	0.072	0.012	0.032	44.44
Rod4	0.009	0.001	0.023	0.019	0.007	0.015	0.074	0.012	0.033	44.59
Rod5	0.013	0.014	0.016	0.022	0.019	0.017	0.101	0.017	0.043	42.57
Rod6	0.005	0.009	0.020	0.012	0.011	0.003	0.06	0.01	0.034	56.67
Total	0.058	0.049	0.081	0.079	0.084	0.054	0.405	0.068	0.188	46.42
Mean	0.01	0.008	0.014	0.013	0.014	0.009	0.068	0.011	0.032	47.06

Table 7. Fractional concentration of cadmium in mg/kg

Table 9 presents the Fractional Concentration of Chromium in the Sample. The mean concentration (0.011 mg/kg) was found in the reducible fraction and the least mean concentration was found in the exchangeable fraction. Carbonate fraction and oxidizable fraction had the same mean value of 0.006 mg/kg.

The observed trend in %BAF was R6 > R2 > R4 >R3 >R5 >R1. Cr in all the samples was generally low with a mean 43.18% except for R6.

From study it could be inferred that Mg is the most bioavailable metal for organism's uptake in the studied area having had the highest %BAF in the soil samples. This is in line with the observation by Erwin, 2006. for Rod1 it was Mg > Cd > Fe > Ni > Zn > Pb > Cr and for Rod2, it was $Mg > Ni > Pb > Cr > Fe > Cd > Zn$, for Rod3, it was $Mg > Fe > Zn > Cd > Ni > Cr > Pb$, were the trends in the percentage bioavailability of the various heavy metals respectively, while for Rod4 it was $Ni > Mg > Fe > Cr > Cd > Cr >$ Zn > Pb, Rod5 $Mg > Fe > Cd > Ni > Zn > Cr >$ Pb and Rod6 $Mg > Cr > Cd > Ni > Fe > Zn > Pb$ respectively.

It can be observed from the trends that Pb had the least bioavailable fractions in most of the soil surface samples. Mg recorded the highest ground mean concentration (60.15%) and the least was found in lead (35.51%). The trend of the ground mean percentage bioavailability for the various heavy metals was $Mq > Ni > Fe > Cd$ $> Cr > Zn > Pb$.

Sample code	F1	F ₂	F3	F4	F5	F6	Total	Mean	BAF	%BAF
Rod1	0.010	0.012	0.003	0.011	0.001	0.017	0.054	0.009	0.025	46.30
Rod ₂	0.008	0.005	0.006	0.007	0.003	0.005	0.034	0.006	0.019	55.88
Rod ₃	0.011	0.003	0.003	0.003	0.007	0.013	0.04	0.007	0.017	42.5
Rod4	0.009	0.006	0.008	0.005	0.001	0.010	0.039	0.007	0.023	58.97
Rod ₅	0.007	0.003	0.010	0.013	0.005	0.009	0.047	0.008	0.02	42.55
Rod ₆	0.006	0.007	0.004	0.003	0.009	0.003	0.032	0.005	0.017	53.13
Total	0.015	0.036	0.034	0.042	0.026	0.057	0.246	0.041	0.085	34.55
mean	0.009	0.006	0.006	0.007	0.004	0.010	0.041	0.007	0.021	51.22

Table 8. Fractional concentration of nickel in mg/kg

Fig. 8. Fractional concentration of Ni in mg/kg

Fig. 9. Fractional concentration of chromium in mg/kg

Sample	Fe	Pb	Zn	Mq	Cd	Ni	Сr
Rod1	53.88	37.10	40.83	58.93	54.34	46.30	31.11
Rod ₂	45.22	53.85	37.72	59.11	40.38	55.88	48.21
Rod3	53.21	29.00	49.66	60.07	44.44	42.50	39.13
Rod4	50.06	36.51	42.09	53.78	44.59	58.97	45.10
Rod ₅	49.07	23.29	39.09	63.42	42.57	42.55	33.33
Rod6	46.80	33.33	34.56	65.61	56.67	53.13	59.38
Ground Total	298.24	213.08	243.95	360.92	282.99	299.33	256.26
Ground Mean	49.71	35.51	40.67	60.15	47.17	49.89	42.71

Table 10. Summary of the percentage bioavailability of the heavy metals

Fig. 10. Percentage bioavailability of metal concentration in the topsoil

Analysis of variance (ANOVA) and correlation showed that there was no significance relation at a probability of $P > 0.05$ for Mg, Zn and Fe, but for Cd, Ni and Cr, there was a positive significant difference. In the case of Pb, it was a negative significant difference that was observed from the analysis of variance.

4. CONCLUSION

From the results, it is evident that among Fe Pb, Zn, Mg, Cr, Ni and Cd, the total mean metal concentration in the soil sample of the industrial layout indicates that Mg was highest. The speciation of Cr was different as the concentration was evenly distributed in all the fractions of the samples. In all the samples, Fe was observed to have had the highest concentration. Its highest concentration (0.231 mg/kg) was found in Slaughter road. Cd had the least concentration (0.002 mg/kg) and that was in Ahiramakara road. The observed trend in the concentration for total metal concentration was $Fe > Mg > Zn > Cr > Ni > Pb > Cd$, Fe $> Mg > Zn$ $> Cd > Cr > Pb > Ni$, Fe $> Mg > Cr > Pb = Cd > Ni$, $Fe > Mg > Zn > Cd > Ni > Cr > Pb$, $Fe > Mg >$ $Zn > Ni > Pb > Cr > Cd > Pb$, $Fe > Mg > Zn > Cr$ > Cd > Pb > Ni for Ahiramakara, Nkpogu, Elekahia, Peter Odili, Slaughter and Incar roads respectively. Mg was discovered to be the most Bioavailable metal (65.61%), while the least bioavalable metal was Pb (29.00%). There was no significant difference in the result at 95% confidence interval in almost all the fractions. Most of the metals in the soil samples were distributed within the residual, Carbonate and reducible fraction except for Fe which was mostly distributed in the water soluble fraction.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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