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Chemical speciation of some heavy metals in sediments in the vicinity of Ashaka Cement Factory, Gombe State, Nigeria

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A speciation study has been carried out to determine the distribution of heavy metals in sediments in the vicinity of Ashaka cement factory. Samples from eight sediment locations in the vicinity of the factory were screened, for the heavy metals Pb, Mn, Cu and Zn, by fractionation followed by analyses of fractions using Atomic Absorption Spectroscopy. Metal concentration within the the individual metal fractions of the sequential extractions were obtained as (Exchange, Carbonate, Fe/Mn, Organic and Residual) fractions. In all the locations, carbonate fractions were high because of high concentration of CaCO₃ within the vicinity of the factory. In the sequential extraction scheme used in the present study, it is reasonable to envisage the mobility and bioavailability decreasing in the extraction procedure which is; Exchange> Carbonate>Fe/Mn>Organic. The metals Pb, Zn and Mn are predominantly in the Fe/Mn fractions and occur in this order in every sediment. Overall results of the present study suggest that the mobility and bioavailability decline in the following order: Mn> Pb= Zn > Cu. All the levels of the elements in the various sediments however do not cause threat to plants because their concentrations were generally low.

Keywords: Sediments, cement, concentrations, sequential, bioavailability, heavy metals.

INTRODUCTION

In environmental trace element research, the determination of the total concentration of an element is often only an initial step. If the pathways, mobility, bioavailability and potential toxicity of the elements to humans and animals are to be elucidated, it is necessary to obtain information on the different chemical forms of the elements in the soil, sediment and water. This is usually referred to as speciation Tessier *et al.*, (1979).

The forms and impact of dust pollution load on soil, sediment, water and plants is the major area of focus for evaluation of dust emitting industries such as cement factories. The study is necessary in view of the health effects of dust forms on plants, animals and human around the factories Tessier *et al.*, (1979).

A speciation study has been carried out by a number

of workers including Tessier *et al.*, (1979) and Florence *et al.*, (1992). An initial study of dust, sediment and soil is the fractionation process including a sequential extraction scheme deviced by Tessier *et al.*, (1979).This scheme would extract metal forms into classes; soluble, exchangeable, carbonate phase, Fe-Mn oxide phase, organic phase and residual phase. The various fractions obtained is then analysed for the various metal components under study. The results when interpreted would explain the bioavailable forms of elements which regulates plant intake.

Florence *et al.*, (1992) have defined speciation as the determination of the concentrations of the different physico-chemical form of the element which together make up its total concentration in the samples. The individual physico-chemical forms may include particulate and dissolved forms such as simple inorganic species, different oxidation states of the elements, organic complexes and the elements adsorbed on a variety of colloidal particles.

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Figure 1. Map showing sediment sample location around Ashaka Cement factory

In view of the importance of speciation studies in the environment, Pickering, (1981); Lund, (1990); Tack and Verloo, (1997); have carried out sequential extraction for solid phase associated trace elements in soil and sediment. For example, the chemical associations of Pb, Cd, Cu and Zn in street dust and road side soils have been investigated by Harrison *et al.*, (1981), by sequential extraction procedure similar to that of Tessier, (1979). The results of these extractions have been interpreted in terms of the, mobility, bioavailability and toxicity levels in plants.

The study area is a cement factory with several sediment locations. These locations include quarry reservoir, ponds, effluent discharge points and stream sediments. These sediments are formed and polluted by aerial particulate deposition and factory effluent discharges.

MATERIALS AND METHODS

Sampling and sample preparation

Sampling areas are indicated on Figure 1. There were seven sampling areas which included quarry pond sediment (QPS), Jalingo pond sediment (JPS), Factory effluent sediment (FES), Feshingo river sediment (FRS), sewage effluent sediment (SES), Maza river sediment (MRS) Juggol river sediment (JRS) and precipitator dust sediment (PDS). As indicated on the map, quarry pond sediment is located at about 1/2km west of the factory. The Jalingo pond is about 1/2km south of the factory and it is just at the edge of northern part of Jalingo village. Factory effluent sediment is located at the main factory effluent discharge point south-west of the factory. Feshingo sediment is located at the edge of north-west of



Feshingo village. Feshingo village is at the edge of western part of Jalingo village. The sediment here is

almost a continuation of factory discharge into the stream of the Maza river. Maza river sediment is at the

confluence of the Maza river entering river Gongola at Ashaka village. The Juggol river sediment is at the entrance of Juggol river into the Gongola river at the north-east of the factory. The sewage effluent sediment is about 2km south-east of the factory.

Sample collection and preparation were done in line with procedure described by James and Wells, (1990). Leaves, grasses and logs were removed from the surface before sampling. A polyvinyl chloride (PVC) cylinder of about 12cm in diameter with a height of about 40 cm lengths was used. The corer tube was hammered into each sample point to obtain the desired sample. For each sampling area, three samples were obtained at random and later mixed to give a gross sample of about 1kg.

The samples were air dried, crushed, mixed and ground in agate mortar to give a representative sample. A final sample weighing about 200 g was obtained after passing material through a 90 micron sieve. This was stored in polypropylene bottles with cover.

Sequential Extraction Process

Speciation studies on sediments including precipitator dust was carried out, using the sequential extraction procedure. The procedure was based on the scheme developed by Tessier *et al.*, (1979). The flow diagram for the experimental studies is indicated in Figure 2.

Extractions were performed on duplicate samples of 1g. A similar extraction procedure was performed on standard clay.

The results were cross-checked using standard solution prepared from the standard clay sample, SCY/1/76, in accordance with BSS – 140, (1980) analyses procedure for calibration purpose. Extractions were performed in a 50ml polypropylene centrifuge tubes with a mechanical shaker to mix the solutions as necessary. Following each extraction the mixture was centrifuged at 3000rpm for 30min. The supernatant was removed by the use of syringe and transferred into polythene bottles, acidified to pH<2 and stored for analyses. Acid digestions were pre-cleaned by soaking in 10% HNO₃, and all chemicals were of Analar grades.

Metal analyses were carried out by atomic absorption spectrometry (SP9 Pye-Unicum). Results were easily calculated using the results of standard samples, whose concentration were already known.

RESULTS AND DISCUSSION

Speciation Studies of Sediments

Metal concentration within the individual metals fractions of the sequential extraction analysis are presented in Tables 1-4 for lead, manganese, copper and zinc respectively. A summary of the percentage range of elements in samples in different phases of sequential fractionation are displayed in Table 5. The mean and standard deviation of results of four tests and the percentage of elements in the extractants are given for the study sites.

The results are described in terms of the distribution within each fraction. The speciation patterns show broad agreement between the samples collected from the wide range of the factory sites. There were perhaps insufficient samples, however, to judge whether the small difference that do occur between the sites result from different site characteristics or merely within site variations which may be quite considerable.

The relatively high concentration of $CaCO_3$ in sediments in the vicinity of cement factories is reflected in a greater proportion of metals in the carbonate phase (Shaheen, 1995) in these samples studied.

It is considered useful however to examine the elements separately as follows:

Lead

The lead in the sediments is strongly associated with the carbonate and Fe-Mn oxide phases with only a slight amount in the residual, and a negligible proportion in the exchangeable phase (Tables 1). The predominance of the carbonate and Fe-Mn oxide phases is in broad agreement with the results for some river sediments (Shaheen, 1995). Trends in the sediments indicate that the carbonate fraction were more significant in precipitator dust and quarry sediments. The high value in precipitator dust is in agreement with the high carbonate content of sediment around cement plants.

The results obtained are in agreement with the Glasgow and Lancaster partitioning data in identifying the environmentally important fractions for lead as iron and manganese oxide (Gibson and Farmer, 1986; Harrison and Laxen, 1981). Other authors (Fergusson and Kim, 1991) confirmed from several studies that most of the lead is tied up with the carbonate and amorphous iron/manganese hydrous oxide phases.

Generally, the data obtained indicates that the chemical forms of lead decreased in the following order of abundance in the sediments studied:

Carbonate > Fe-Mn oxide > residual > organic > exchangeable.

The amount in the exchangeable is relatively very small and negligible. This is very important because from previous reports (Evans et al., 1992; Tessier *et al.*, 1979; Xingfu and Shokohifard, 1989) it seems likely that solid sediments and dust samples which contain high amount of lead in the exchangeable and carbonate fraction poses threat to both plants and humans. The threat is that the exchangeable, and to a lesser extent, the carbonate phase, contains the bio-available lead.

| | | | Concentration (mg/Kg) | | | | |
|--------------|------|----------|-----------------------|-------|---------|----------|--------|
| Sample Site | | Exchange | Carbonate | Fe/Mn | Organic | Residual | Total |
| Quarry Pond | MEAN | 1.75 | 112 | 46.60 | 8.92 | 10.60 | 179.87 |
| | S.D | 0.16 | 4.50 | 1.97 | 0.37 | 0.85 | 7.85 |
| | % | 0.97 | 62.27 | 25.91 | 4.96 | 5.89 | 100 |
| Jalingo Pond | MEAN | 1.19 | 82.30 | 66.90 | 8.00 | 24.60 | 182.99 |
| | S.D | 0.04 | 7.47 | 6.79 | 0.78 | 2.35 | 17.43 |
| | % | 0.65 | 44.97 | 36.56 | 4.37 | 13.44 | 100 |
| Maza River | MEAN | 3.96 | 29.1 | 24.2 | 6.65 | 8.80 | 72.71 |
| | S.D | 0.13 | 0.48 | 1.48 | 0.33 | 0.66 | 3.08 |
| | % | 5.45 | 40.02 | 33.28 | 9.15 | 12.10 | 100 |
| Juggol River | MEAN | 4.90 | 49.9 | 31.60 | 5.11 | 9.10 | 100.61 |
| | S.D | 0.37 | 1.29 | 1.77 | 0.55 | 0.54 | 4.52 |
| | % | 4.87 | 49.60 | 34.40 | 5.08 | 9.04 | 100 |
| Sewage | MEAN | 3.70 | 8.19 | 33.40 | 13.50 | 17.20 | 75.99 |
| Discharge | S.D | 0.31 | 0.29 | 0.94 | 0.97 | 0.55 | 3.06 |
| | % | 4.87 | 10.77 | 43.95 | 17.76 | 22.63 | 100 |
| Factory | MEAN | 1.25 | 66.50 | 32.20 | 5.56 | 12.20 | 117.71 |
| Effluent | S.D | 0.16 | 1.98 | 1.45 | 0.37 | 0.97 | 4.94 |
| | % | 1.06 | 56.49 | 27.35 | 4.72 | 10.36 | 100 |
| Feshingo | MEAN | 0.55 | 43.90 | 15.60 | 3.88 | 9.36 | 73.29 |
| River | S.D | 0.07 | 1.55 | 1.03 | 0.29 | 0.52 | 3.46 |
| | % | 0.75 | 59.89 | 21.28 | 5.29 | 12.77 | 100 |
| Precip Dust | MEAN | 0.54 | 76.50 | 21.70 | 1.37 | 2.67 | 102.78 |
| | S.D | 0.12 | 1.08 | 0.56 | 0.09 | 0.79 | 2.65 |
| | % | 0.53 | 74.43 | 21.11 | 1.33 | 2.59 | 100 |

Table 1. Results of Sequential Extraction of Lead

Table 2. Results of Sequential Extraction of Manganese

| | | Concentration (mg/Kg) | | | | | | |
|------------------|------|-----------------------|-----------|--------|---------|----------|--------|--|
| Sample Site | | Exchange | Carbonate | Fe/Mn | Organic | Residual | Total | |
| Quarry Pond | MEAN | 112.00 | 271.00 | 482.00 | 40.10 | 77.80 | 982.9 | |
| | S.D | 7.45 | 27.04 | 40.66 | 2.29 | 4.74 | 82.18 | |
| | % | 11.39 | 27.57 | 49.04 | 4.08 | 7.92 | 100.00 | |
| Jalingo Pond | MEAN | 60.20 | 120.00 | 191.00 | 23.00 | 36.50 | 430.70 | |
| | S.D | 2.17 | 9.73 | 11.80 | 1.45 | 0.78 | 25.93 | |
| | % | 13.98 | 27.86 | 44.35 | 5.34 | 8.47 | 100.00 | |
| Maza River | MEAN | 47.40 | 177.00 | 577.00 | 34.90 | 106.00 | 942.30 | |
| | S.D | 3.29 | 14.43 | 33.90 | 2.43 | 11.14 | 65.19 | |
| | % | 5.03 | 18.78 | 61.23 | 3.70 | 11.25 | 100.00 | |
| Juggol River | MEAN | 28.00 | 93.90 | 290.00 | 17.30 | 38.30 | 467.50 | |
| | S.D | 1.25 | 4.67 | 5.77 | 1.07 | 1.85 | 14.61 | |
| | % | 5.99 | 20.08 | 62.03 | 3.70 | 8.19 | 100.00 | |
| Sewage | MEAN | 90.70 | 228.00 | 402.00 | 37.20 | 39.90 | 797.80 | |
| Discharge | S.D | 3.80 | 15.54 | 26.06 | 1.40 | 1.57 | 48.37 | |
| | % | 11.36 | 28.58 | 50.39 | 4.66 | 5.00 | 100.00 | |
| Factory Effluent | MEAN | 45.60 | 141.00 | 249.00 | 22.60 | 38.80 | 497.00 | |
| | S.D | 1.76 | 5.36 | 14.12 | 2.12 | 1.44 | 24.80 | |
| | % | 9.18 | 28.37 | 50.10 | 4.55 | 7.81 | 100.00 | |
| Feshingo River | MEAN | 31.30 | 100.00 | 229.00 | 16.20 | 33.70 | 410.20 | |
| | S.D | 1.51 | 10.04 | 8.49 | 1.09 | 2.51 | 23.64 | |
| | % | 7.63 | 24.39 | 55.85 | 3.95 | 8.22 | 100.00 | |
| Precip Dust | MEAN | 64.80 | 462.00 | 275.00 | 15.90 | 27.70 | 845.40 | |
| | S.D | 1.69 | 20.93 | 7.92 | 1.22 | 0.69 | 32.46 | |
| | % | 7.66 | 54.65 | 32.53 | 1.88 | 3.28 | 100.00 | |

| | | Concentration (mg/Kg) | | | | | |
|------------------|------|-----------------------|-----------|-------|---------|----------|--------|
| Sample Site | | Exchange | Carbonate | Fe/Mn | Organic | Residual | Total |
| Quarry Pond | MEAN | 4.56 | 53.20 | 12.80 | 74.10 | 20.60 | 165.26 |
| | S.D | 0.16 | 1.16 | 0.90 | 2.64 | 2.15 | 7.10 |
| | % | 2.76 | 32.19 | 7.74 | 44.84 | 12.47 | 100.00 |
| Jalingo Pond | MEAN | 0.90 | 8.35 | 18.70 | 116.00 | 24.30 | 168.25 |
| | S.D | 0.14 | 0.77 | 2.20 | 7.23 | 0.59 | 10.93 |
| | % | 0.53 | 4.96 | 11.11 | 68.95 | 14.44 | 100.00 |
| Maza River | MEAN | 1.54 | 2.07 | 23.10 | 75.00 | 36.40 | 138.11 |
| | S.D | 0.21 | 0.27 | 0.95 | 4.59 | 1.09 | 7.11 |
| | % | 1.12 | 1.50 | 16.73 | 54.30 | 26.36 | 100.00 |
| Juggol River | MEAN | 2.30 | 2.48 | 24.10 | 62.10 | 33.00 | 123.98 |
| | S.D | 0.24 | 0.15 | 1.21 | 4.79 | 1.82 | 8.21 |
| | % | 1.86 | 2.00 | 19.44 | 50.09 | 26.62 | 100.00 |
| Sewage | MEAN | 4.49 | 7.57 | 39.10 | 96.30 | 16.60 | 164.06 |
| Discharge | S.D | 0.24 | 0.22 | 1.74 | 1.64 | 0.50 | 4.34 |
| | % | 2.74 | 4.61 | 23.83 | 58.70 | 10.12 | 100.00 |
| Factory Effluent | MEAN | 0.85 | 18.30 | 21.50 | 95.90 | 31.70 | 168.25 |
| | S.D | 0.16 | 0.99 | 1.54 | 4.18 | 1.73 | 8.60 |
| | % | 0.51 | 10.88 | 12.78 | 57.00 | 18.84 | 100.00 |
| Feshingo River | MEAN | 1.17 | 15.90 | 24.30 | 76.10 | 21.20 | 138.67 |
| | S.D | 0.12 | 1.14 | 1.91 | 3.29 | 1.45 | 7.91 |
| | % | 0.84 | 11.47 | 17.52 | 54.88 | 15.29 | 100.00 |
| Precip Dust | MEAN | 2.52 | 97.60 | 8.88 | 26.60 | 14.80 | 150.40 |
| | S.D | 0.12 | 0.79 | 0.19 | 0.83 | 0.25 | 2.18 |
| | % | 1.68 | 64.89 | 5.90 | 17.69 | 9.84 | 100.00 |

Table 3. Results of Sequential Extraction of Copper

Manganese

The results obtained in respect of manganese in the sequential extraction processes (Table 2) indicate that most of the manganese is tied up with the Fe/Mn oxide followed by the carbonate phase. The next fraction with significance is the exchangeable fraction followed by residual. The results are in agreement with partitioning data in identifying the environmentally important fractions for iron and manganese (Gibson and Farmer, 1986).

Copper

Copper association with the sediment is dominated by the organic phase (Table 3); with the carbonate and residual being of secondary importance. The preference of copper in the organic phase as well as the importance of the residual phase is often observed in aquatic sediments (Marrison and Vicky, 2000) as well as soils. The Jalingo Pond has the highest value for the organic fractions followed by sewage sediment. Maza river and factory effluent also have significant values.

Zinc

The speciation pattern for Zn is very similar to that of lead as shown in Tables 4. The predominance of the carbonate and Fe/Mn oxide phases is in agreement with the studies of Zn in river sediments (Morrison, and Vicky, 2000), estuarial and near shore sediments (Rauret et al, 1999). The precipitator dust has the highest carbonate phase again followed by sewage sediments as expected. For Fe/Mn fractions, the samples have comparable results except precipitator dust with very low value (23.42%). Exchangeable values are also low and are comparable. Zinc is an important element to both plants and animals. Its bioavailability defined by the exchangeable fraction is low because of the low results for the exchangeable fraction.

The sediment profile (Table 5) shows that for carbonate fraction, precipitator dust has the most significant value (54.65%) followed by factory effluent (28.37%). The other sediments have comparable results with. (20-28%)

In the proportion of Fe/Mn oxide fraction, Juggol river has the most significant value (62%) followed by Maza

| | | Concentration (mg/Kg) | | | | | |
|------------------|------|-----------------------|-----------|-------|---------|----------|--------|
| Sample Site | | Exchange | Carbonate | Fe/Mn | Organic | Residual | Total |
| Quarry Pond | MEAN | 2.04 | 32.20 | 43.90 | 2.50 | 0.56 | 81.20 |
| | S.D | 0.14 | 1.52 | 2.11 | 0.24 | 0.05 | 4.06 |
| | % | 2.51 | 39.66 | 54.06 | 3.08 | 0.69 | 100.00 |
| Jalingo Pond | MEAN | 1.26 | 24.70 | 37.80 | 4.55 | 2.87 | 71.18 |
| | S.D | 0.14 | 1.51 | 1.48 | 0.54 | 0.33 | 3.99 |
| | % | 1.77 | 34.70 | 53.10 | 6.39 | 4.03 | 100.00 |
| Maza River | MEAN | 1.75 | 18.60 | 28.90 | 4.46 | 3.11 | 56.82 |
| | S.D | 0.09 | 0.33 | 0.69 | 0.14 | 0.61 | 1.85 |
| | % | 3.08 | 32.73 | 50.86 | 7.85 | 5.47 | 100.00 |
| Juggol River | MEAN | 1.96 | 18.00 | 37.40 | 6.53 | 3.52 | 67.41 |
| | S.D | 0.16 | 0.91 | 1.17 | 0.31 | 0.23 | 3.32 |
| | % | 2.91 | 26.70 | 55.48 | 9.69 | 5.22 | 100.00 |
| Sewage | MEAN | 3.29 | 44.50 | 47.40 | 8.20 | 5.27 | 108.66 |
| Discharge | S.D | 0.29 | 0.56 | 1.25 | 0.29 | 0.39 | 2.78 |
| | % | 3.02 | 40.95 | 43.62 | 7.55 | 4.85 | 100.00 |
| Factory Effluent | MEAN | 0.72 | 30.20 | 41.70 | 3.83 | 2.20 | 78.65 |
| | S.D | 0.15 | 1093 | 2.80 | 0.25 | 0.18 | 5.30 |
| | % | 0.92 | 38.39 | 53.01 | 4.87 | 2.79 | 100.00 |
| Feshingo River | MEAN | 0.43 | 23.90 | 46.70 | 5.13 | 2.76 | 78.92 |
| | S.D | 0.07 | 1.19 | 3.15 | 0.47 | 0.17 | 5.05 |
| | % | 0.54 | 30.28 | 59.17 | 6.50 | 3.49 | 100.00 |
| Precip Dust | MEAN | 1.33 | 63.40 | 20.80 | 2.68 | 0.58 | 88.79 |
| | S.D | 0.08 | 0.98 | 0.79 | 0.09 | 0.09 | 2.03 |
| | % | 1.49 | 71.40 | 23.42 | 3.01 | 0.06 | 100.00 |

Table 4. Results of Sequential Extraction of Zinc

Table 5. Summary of percentage range of the elements in samples in different phases for sequential fractionation

| Element | Phase | (%) Range for Samples | | | |
|---------|--------------|-----------------------|--|--|--|
| Zn | Exchangeable | 0.54-3.08 | | | |
| | Carbonate | 26.70-71.40 | | | |
| | Fe/Mn Oxide | 23.42-59.17 | | | |
| | Organic | 3.01 - 9.69 | | | |
| | Residual | 0.06-5.47 | | | |
| Mn | Exchangeable | 5.03-13.98 | | | |
| | Carbonate | 18.78-54.65 | | | |
| | Fe/Mn Oxide | 32.53-62.03 | | | |
| | Organic | 1.88-5.34 | | | |
| | Residual | 3.28-11.25 | | | |
| Cu | Exchangeable | 0.51-2.76 | | | |
| | Carbonate | 1.50-64.89 | | | |
| | Fe/Mn Oxide | 5.90-23.83 | | | |
| | Organic | 17.69-68.95 | | | |
| | Residual | 9.84-26.62 | | | |
| Pb | Exchangeable | 0.53-5.45 | | | |
| | Carbonate | 10.77-74.43 | | | |
| | Fe/Mn Oxide | 21.11-43.95 | | | |
| | Organic | 1.33-17.76 | | | |
| | Residual | 2.59-22.63 | | | |

| Concentration (mgKg ⁻¹) | | | | | | | | | |
|-------------------------------------|--------------|------|------|------|------|------|------|------|------|
| Metal | Fraction | SES | FES | QPS | JPS | MRS | JRS | FRS | PDS |
| Pb | Exchangeable | 3.70 | 1.25 | 1.75 | 1.19 | 3.96 | 4.9 | 0.55 | 0.60 |
| | Carbonate | 48.9 | 66.5 | 112 | 82.3 | 29.1 | 49.9 | 43.9 | 76.5 |
| | Fe Mn oxide | 33.4 | 32.4 | 32.2 | 46.6 | 66.9 | 24.2 | 31.6 | 15.6 |
| | Organic | 3.5 | 55.6 | 8.92 | 8.00 | 6.65 | 51.1 | 3.88 | 1.37 |
| | Residual | 17.2 | 12.2 | 10.6 | 24.6 | 8.80 | 9.0 | 9.36 | 2.67 |
| Mn | Exchangeable | 90.7 | 45.6 | 11.2 | 60.2 | 47.4 | 28.0 | 31.3 | 64.8 |
| | Carbonate | 228 | 141 | 121 | 120 | 177 | 93.9 | 100 | 462 |
| | Fe-Mn oxide | 402 | 249 | 482 | 191 | 597 | 270 | 229 | 275 |
| | Organic | 37.2 | 22.6 | 40.1 | 25.0 | 34.9 | 17.3 | 16.2 | 15.9 |
| | Residual | 39.9 | 38.8 | 77.8 | 36.5 | 106 | 38.3 | 33.7 | 27.7 |
| Cu | Exchangeable | 4.49 | 0.85 | 4.56 | 0.90 | 1.54 | 2.30 | 1.17 | 2.52 |
| | Carbonate | 2.57 | 18.3 | 20.6 | 8.35 | 2.07 | 3.48 | 15.9 | 26.6 |
| | Fe-Mn oxide | 19.1 | 21.5 | 12.8 | 18.7 | 23.1 | 24.1 | 24.3 | 8.88 |
| | Organic | 96.3 | 95.9 | 74.1 | 116 | 75.0 | 62.1 | 76.1 | 97.6 |
| | Residual | 26.6 | 31.6 | 53.2 | 24.3 | 36.4 | 33.0 | 21.2 | 14.8 |
| Zn | Exchangeable | 3.29 | 0.72 | 2.04 | 1.26 | 1.75 | 1.96 | 0.43 | 1.33 |
| | Carbonate | 44.5 | 30.2 | 32.2 | 24.7 | 18.6 | 18.0 | 23.9 | 63.4 |
| | Fe-Mn oxide | 47.4 | 41.7 | 43.9 | 37.8 | 28.9 | 37.4 | 46.7 | 20.8 |
| | Organic | 8.20 | 3.83 | 2.50 | 4.55 | 4.46 | 6.53 | 5.13 | 2.68 |
| | Residual | 5.27 | 2.20 | 0.56 | 2.87 | 3.11 | 3.52 | 2.76 | 0.58 |

 Table 6. Summary of Sequential Extraction of Metals at different locations

river (61.23%) Sewage sediment (50.,39%, factory effluent (50.1%). Feshingo river has the most significant value (62%) followed by Maza river (61.23%). Sewage sediment (50.9%). Factory effluent (50.1%).

Exchangeable organic and residual are generally low in all the sediments and the results are all comparable.

The four metals examined are associated with various chemical fractions in the various sediments as distinguished by the sequential chemical extraction in summary Table 4. The carbonate and Fe-Mn oxides phases dominate for Pb, Zn and Mn whereas for Cu, the organic and residual phases are most important. The speciation patterns are broadly, similar for most of the sediments except for precipitator dust which has extraordinarily high values in the carbonate phases.

It should be borne in mind however that the samples examined cover only the pH range 7.5-10.2 and that somewhat different patterns of speciation may be found in the commonly encountered soils and sediment.

Mobility and Availability

In the sequential extraction scheme used in the present study it is reasonable to envasage the mobility and bioavailability decreasing approximately in the order of the extraction procedure from readily available to unavailable as described by Harison and Laxen, (1981). The portion of the metals extracted with MgCl₂ is the one that is presumed to be readily available and decreases down the extraction process. In this work almost all the metals do not have significant fractions to consider them bioavailable (Table 6) at almost all the locations.

However, Pb, Zn and Mn which predominantly occur in the carbonate and Fe-Mn oxide fractions can be considered as moderately available. But copper occurring largely in the organic and residual phases is of very limited availability

Overall, results of the present study suggest that the mobility and bioavaibility of the four metals decline in the following order: Mn > Pb = Zn > Cu.

CONCLUSION AND RECOMMENDATION

From the results in this study, the following conclusions can be summerized.

- (1) Deposition of carbonate materials has resulted to high carbonate fractions.
- (2) Most heavy metal levels were found in the Fe/Mn and carbonate fractions.
- (3) This work has also stressed the importance of determining metals speciation and its use in investigating the interactions between pollutant metals in sediments and their bioavailability. The results also showed that the heavy element forms of Zn, Mn and Pb are partially bioavailable while copper is not.

In view of the limitaion in research and screening facilities, more work is needed to establish the levels of some of the most toxic elements; Hg, Cd, Cr, Tl, Ni and As. It would also be necessary to study the speciation of soil profiles in the area to ascertain the validity of the results obtained in this study.

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