

## Speciation of Some Heavy Metals in Soils around A Cement Factory In Gombe State, Nigeria

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### -----ABSTRACT-----

*The chemical forms of some heavy metals in soils around a cement factory was studied by determining soil Cu, Ni, and Co species using standard solvent extraction and Atomic Absorption Spectrophotometric techniques. The Chemical pools of the metals indicated that the metals were distributed into six fractions with most of the metals residing in the non-residual fractions, suggesting how readily the metals are released into the environment. Considering that the metals mostly occur in the most available forms, it is most likely that the metals must have been derived from anthropogenic source.*

**KEY WORDS:** Metal species, Heavy metals, Farmlands, Cement dust.

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### I. INTRODUCTION

Industrial processes have been implicated, among many other anthropogenic processes, as a possible source of hazardous metals in the environment. Industrial processes produce particulate emissions (Fennelly, 1975) even though measures have now been put in place to control these emissions so that there is relatively little dust escaping from closed processing plants in most of such industries. Nevertheless, quarrying, cement manufacture, coal processing, etc. have regularly caused serious problems as dust suppression could be very difficult. With the increasing construction demands, mineral extraction has also increased in many countries (Harris, 1975; Starton, 1989) such that emissions of particulate matter to the environment from crushing of limestone and during the manufacture of cement have been of environmental concern. The Dust, because of its fine particle size, travels over long distances and the total suspended particulate matter in the atmosphere is thus increased. The deposition of the dust particles may affect the state of the ecosystem as finer particles which contain various toxic elements (Fox, 1985) are deposited as the dust is transported away from emission source. The physical and chemical impacts of dust on the environment have been reviewed by Farmer (1993). The chemical effects on either the soil or directly on plant surface may be more important than any physical effects. The chemistry of dust may vary depending on their chemical effects. Some dusts are relatively inert while others are alkaline. The hard acidic rock quarries are inert (Farmer, 1993), but limestone quarry, cement dust and many road dusts are alkaline (Everet, 1980).

The presence of particulate matter in the atmosphere affects visibility and may add significantly to air pollution (Aidid, 1988; Ward, 1990). Tijani et al. (2005) showed that the activities of the West African Portland Cement Company (WAPCO PLC) in its two plants at Sagamu and Ewekoro constitute a source of environmental pollutants as dust and noise, thus subjecting the inhabitants to suffer from dust laden air, cracking of walls of structures as well as soil and water polluted by dust. The chemical and mineralogical characteristics of dry deposition in the surrounding of a cement factory in Jordan showed that lead and copper were statistically significant in the northwest sector of the city which was attributed to the heavy traffic of trucks carrying raw materials and cement in and out of the cement factory (Zaidat et al., 2006). Similarly, Cd, Al, Fe, Zn, Mn, Ni, Mo and Cr concentrations were high in all sampled areas and these were representative of the current cement industry operations which dominate the air quality of Fuhais city of Jordan. Changes in chlorophyll and carotenoid content were investigated in Norway spruce needles exposed to alkaline dust by Lepedus et al. (2003).

They reported that all measured pigments were reduced in dust exposed needles compared to needles harvested from areas not polluted by cement dust and that these could be due to deceleration of biosynthetic processes rather than degradation of pigments. Recently, Parn (2006) studied the radial growth of conifers in regions of different cement dust loads and report that cement dusts have a negative effect on the radial growth of pines. In another study, Kloseiko and Tilk (2006) reported the influence of cement clinker dust on carbohydrates in needles of Scots pines and show that soil pH and photosynthetic parameters were not increased by the clinker dust treatment. The potential of metals as pollutants has been attributed to their non-degradability, accumulation in the ecosystem and toxic effects can last long periods of time. Milford and Davidson (1985) have noted that many metals occur as small particulates and may form an important part of the smaller fractions of dust particles. Toxic compounds such as fluoride, magnesium, lead, zinc, copper, beryllium, sulphuric acid and hydrochloric acid were found to be emitted by a cement manufacturing plant (Andrej, 1987). Traces of toxic metals such as chromium and copper are common in some varieties of Portland cement and are harmful to human beings and other living systems (Omar and Jasim, 1990). Exposure to heavy metals can therefore provoke serious health effect.

Metals are diverse in their chemical and physical forms which change with perturbation of the system. As such, these metals are distributed among the solid and liquid phases of the soils, which determine their bioavailability. Much of the micronutrients associated with the solid phase are not available for plant uptake. In fact, <10% generally are in soluble and exchangeable forms (Lake *et al.*, 1984). However, the redistribution among forms is brought about by changes in soil properties due to natural and anthropogenic causes (Shuman 1991). The forms are classified as ion exchangeable, adsorbed, organic bound, hydrous oxide segment and lattice component micronutrients (Pickering, 1981). The fate of metals added to a soil is controlled by a number of physical and biological processes acting within the soil (de Haan and Zwerman, 1978). Their initial mobility after addition to soil will largely depend on the form in which the metals are added, which in turn depends on their sources. The deposition of cement dust on top soil may have potential impacts on human and animal health, vegetation and soil chemistry. Plants depend so much on soil micronutrient metals for the essential function of their organs. However, the levels and forms of the metals in the soil can be critical to the plants; this may in turn affect crop yield and contaminate the food chain. This research is aimed at determining metals redistribution among extractable fractions caused by changes in soil properties as a result of cement dust depositions on cultivated lands around a cement factory.

### **Study Area**

The study area is located in Jalingo village of Bajoga, Funakaye Local Government Area North of Gombe, Gombe State, Nigeria and lies between latitudes 10°45'N and 11°00'N and longitudes 11°15'E - 11°30'E. The company was established in 1976 to meet the needs of construction works in the North-Eastern part of Nigeria. It has an installed capacity of 500,000 MT per annum (NSE, 2004). The company produced huge amount of dust and gaseous pollutants to the environment in time past. These constituted serious hazards to humankind, farmlands and vegetations. However, recently the emissions have been reduced tremendously with the installation of dust bag filters but, the effects of past deposition may last a long time.

### **Experimental**

In the preparation of reagents, chemicals of analytical grade and de-ionized distilled water were used, unless otherwise stated.

### **Sampling and Sample Pre-treatment**

Soil samples were collected in polythene bags using auger from cultivated soils around Ashaka Cement Factory in Funakaye Local Government Area of Gombe State. Samples were taken randomly round the factory starting from the fence and proceeding away from the factory at 2km intervals in every direction of the cardinal points until 6km radius was covered round the factory. Soils from depths of 0-15cm and 15-30cm were taken at each sampling point. A total of 62 soil samples were brought to the laboratory for analysis. Soil samples were air-dried in the laboratory before being crushed in a ceramic mortar and sieved in a 2mm screen plastic sieve.

### **Metal Speciation**

Metals were fractionated using liquid extraction according to the method of Elsokkary *et al.* (1995). The metal species were extracted into six fractions according to the following methods:

#### **Determination of Exchangeable metal**

1g of the soil sample was weighed into a 250cm<sup>3</sup> conical flask and 10cm<sup>3</sup> of 1M sodium acetate adjusted to pH 8.7 with acetic acid was added. The mixture was shaken for 2 hours using the Edmund Bahler Swip mechanical shaker before being filtered into a 100cm<sup>3</sup> volumetric flask using a Whatman filter No. 1. The filtrate was made up to mark with distilled water from where the metals were determined using AAS. The residue was reserved for further fractionation

#### **Determination of Carbonate bound metals**

The residue from the exchangeable metal was leached for 3 hours with each of the sodium acetate adjusted to pH 5.0 with acetic acid. The leachate was transferred to a 100cm<sup>3</sup> volumetric flask and made up to mark with water. The leachate was then analysed for metals using AAS and the residue reserved for further analysis.

#### **Determination of Manganese oxide bound metals**

The residue from carbonate bound soil was leached with 10cm<sup>3</sup> 0.1M hydroxylamine hydrochloride and 0.01M nitric acid (adjusted to pH 2.0 with acetic acid) after shaking for 3 hours using an Edmund Bahler Swip mechanical shaker. The leachate was transferred quantitatively to 100cm<sup>3</sup> volumetric flask and made up to mark with distilled water. The leachate was then analysed for metals using AAS and the residue reserved for the next analysis.

#### **Determination of Iron-Manganese oxide bound metals**

The residue from the manganese oxide bound soil was extracted with 10cm<sup>3</sup> oxalate buffer of pH 3.0 after shaking for 12 hours at 90°C in a water bath. The extract was filtered into a 100cm<sup>3</sup> volumetric flask and water added to mark. The extract was then analysed for metals using AAS and the residue reserved for another analysis.

#### **Determination of Organic matter/sulphide bound metals**

The residue from the iron-manganese oxide bound soil was extracted by shaking with 10cm<sup>3</sup> 30% hydrogen peroxide that has been adjusted to pH 2.0 with drops of nitric acid for 6 hours at 90°C in a water bath. It was then re-extracted at room temperature with 10cm<sup>3</sup> 1M ammonium acetate that has been adjusted to pH 2.0, after shaking for 3 hours, into the first extract in a 100cm<sup>3</sup> volumetric flask and made to mark with water. The extract was then analysed for metals using AAS and the residue reserved for the final analysis.

#### **Determination of Residual metals**

The residue from the organic and sulphide bound extraction was digested with 10cm<sup>3</sup> aqua regia by heating in a digestion tube at a digester temperature of 250°C. The clear digest was removed and allowed to cool before transferring quantitatively into a 100cm<sup>3</sup> volumetric flasks. It was made up to mark with water and the solution analysed for the metals.

#### **Elemental Analysis and Instrumentation**

The concentration of Cu<sup>(λ=324.8nm)</sup>, Ni<sup>(λ=232.0nm)</sup>, and Co<sup>(λ=240.7nm)</sup> was determined from the soil extracts using a BUCK SCIENTIFIC Atomic Absorption Spectrophotometer Model 210 VGP. The spectrophotometer was calibrated by aspirating standard solutions of Cu, Co and Ni nitrates at their various wavelengths and Acetylene-air mixtures in the ratio of 6:8 was used. Measurements were made after calibration, instrument settings optimized and blue flame obtained.

## **II. RESULT AND DISCUSSION**

Results of Cu, Ni and Co fractions expressed as percentage of the sum of individual fractions for the overall (0-30cm) soils revealed principally the partitioning of these metals among six fractions, F1 – F6, (Exchangeable, F1; Carbonate bound, F2; Manganese oxide bound, F3; Iron-Manganese oxides bound, F4; Organic Matter and Sulphide bound, F5; Residual Fractions, F6). The distribution of the metals varies greatly among fractions. On average, the order of partitioning for the metals are shown in figures 1 – 9.

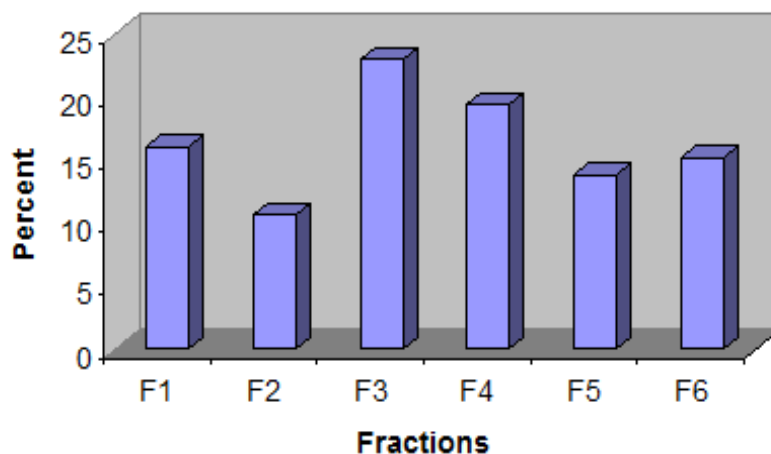


Fig.1: Relative distribution of copper among six fractions (F1-F6) of soil

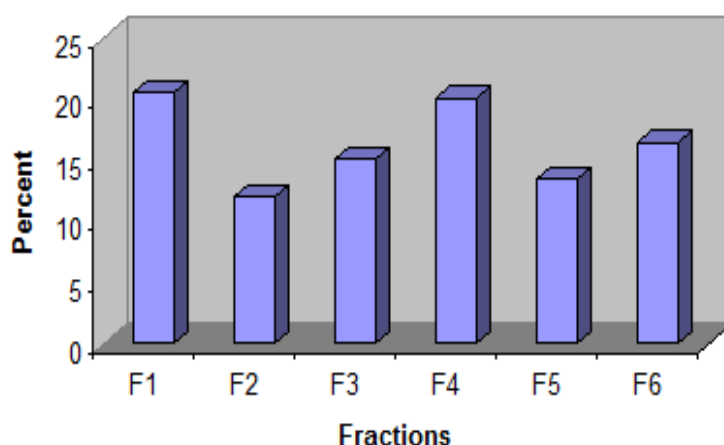


Fig.2: Relative distribution of nickel among six fractions (F1-F6) of soil

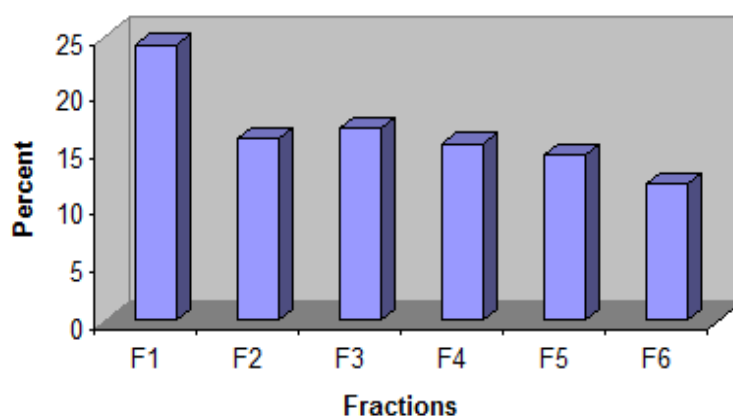


Fig.3: Relative distribution of cobalt among six fractions (F1-F6) of soil

Manganese oxide bound was the dominant fraction for copper while carbonate bound was the least dominant fraction (Fig.1) for the 0 – 30 cm depth soil. There is variation in the distribution of copper among the different fractions. Nevertheless, the non-residual form accounts for 84.74%. The low Cu in the carbonate fraction might be due to increased manganese oxide and Fe/Mn oxides activity in concentrating Cu, thereby reducing co-precipitation reactions with carbonates (Stone and Droppo, 1996). Earlier, Stone and Droppo (1996) had reported that there was strong association between Cu and Pb, and carbonates. The residual fraction

constitutes 15.26% thus suggesting that the Cu must have, to a great extent, been derived from anthropogenic sources. On average, the distribution of Cu among the chemical fractions occur in the following order,

F3>F4>F1>F6>F5>F2

The non-residual form binds 86.41% and this indicates the quantity of Cu that could readily be available. The anthropogenic source might be the cement dust that deposits on the soils around the factory and later gets leached down the soil gradient. The order of distribution in various chemical fractions is

F1>F3>F6>F5>F4>F2.

The dominant fraction for nickel in soils around the cement factory was the exchangeable phase (fig.2). This chemical form was closely followed by the Fe/Mn oxide phase. The partitioning of Ni varies among all the fractions. More than 80% of Ni was held in the non-residual form, which indicates the potential bioavailability of Ni. The stability of metals bound to sediments as inorganic compounds (metal oxides, hydroxides, carbonate and sulphides) is controlled primarily by the system pH (Poulton et al., 1988). The acidic nature of the soil must have influenced the high retention of Ni in the exchangeable phase. The order of the partitioning of Ni in the soils around the cement factory is

F1>F4>F6>F3>F5>F2

The pattern indicates the influence of anthropogenic Ni on the non-residual forms.

The partitioning of cobalt among the six chemical phases of the soil around the cement factory decreases from the exchangeable fractions down to the residual fractions (fig.3). The dominant form was found in the exchangeable phase. Greater than 80% of Co was held in the non-residual fraction. This indicates the potential bioavailability of Co. The source of the Co may be anthropogenic since the geochemical form (residual fraction) was about 12%. The order of the chemical partitioning of Co in the soils around the cement factory is

F1>F3>F2>F4>F5>F6

The chemical pools of the Heavy metals shows that they are distributed among six soil fractions. Nevertheless, most of the metals resided in the non-residual fraction, suggesting how readily the metals are released into the environment. Considering that the metals mostly occur in the most available forms, it might be assumed that the metals must have been derived from anthropogenic sources. This also buttresses the points that people living around the factory stand a risk of being exposed to high levels of micronutrient metals. The metals may be taken up by plants or leached into water bodies and their accumulation may have serious consequences, since their consumption from these sources forms the principal pathway by which metals enter the food chain.

### III. CONCLUSION

Fractionation of the metals species in soils around the cement factory shows higher percentages of the metals residing in the non-residual fractions. This suggests potential bioavailability of copper, nickel, and cobalt in the soils around the cement factory, indicative of their anthropogenic source. The knowledge of the chemical speciation of metals in the soil may assist in determining the behaviour of the metals since they occur in different forms in the soil, and may influence their mobility and bioavailability. The rapidly mobilizable metals in the soil indicate the potential health hazards of cultivated agricultural lands around the factory.

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