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Chemical and Process Engineering Research
ISSN 2224-7467 (Paper) ISSN 2225-0913 (Online)
Vol.26, 2014
www.iiste.org

Levels of Cobalt in Some Tree Barks and Soils from Yobe State Nigeria

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Abstract
Two different species of trees (*Ficus thoningi,* and *Adansonia digitata*) from Yobe State, north east, Nigeria were used in the investigations. The barks and the soils around these trees were analysed for their cobalt concentrations using atomic absorption spectrophotometry. The results of the analysis indicate various concentration levels obtained from soil solution through mineral uptake by plants. The mean values of Co range between 0.44 - 3.01μgg^{-1} in the bark and 0.26 - 2.68μgg^{-1} in the soil. All the values obtained correlate well with the anthropogenic activities in the study area and are below the recommended safe limits for heavy metals by WHO, FAO, EU, and NESREA guidelines. However, there is need for constant monitoring since the inhabitants depends on some of these plants for their primary health care. The statistical comparison of the values between the bark and soil shows correlation at $P < 0.01$ and significant difference at $P < 0.05$. The study further demonstrates the suitability of some of the trees as a good bioindicator.
Keywords: Cobalt, Tree back, Soil, Yobe State.

1.0 Introduction

Pollution is a problem in many parts of the world, particularly in developing countries (Smodis and Bleise, 2000). The significant contribution of soil pollution to the diminished health status of the exposed human populations, forest decline, loss of agricultural productivity, and so on, has been a cause of increasing public concern throughout the world. Therefore, pollution is a topic of intense scientific, governmental, and industrial interest.
Environmental pollution is a major hazard facing the world today and there is the increasing awareness that a clean environment is necessary for living and for the health of human beings. Industrial activities have a profound influence on the society and environment not only in terms of benefits but in risks and hazards. The adverse impact on the environment due to indiscriminate and unregulated exploitation of both renewable, unrenewable resources and abuse of the environment as a sink for dumping the waste products of development activities is on the increase. Therefore, environment is under constant threat from the human activities. The increasing population, industrialization, urbanization, intensive agriculture, and natural disasters have caused damages to our environment. Man's ignorance of the laws of nature and his overexploitation of natural resources have further aggravated the problem (Bhatia, 2006).

Cobalt is a component of super alloys used in making critical parts of jet engines, gas turbines and other machines operating under stress at high temperatures.

Cobalt compounds are useful catalysts for the synthesis of fuels, alcohols and aldehydes. They are used in petroleum refining and oxidation of organic compounds (Gerhard *et al.,* 1991).

The natural transport of cobalt is not affected by mining activities and industrial uses of the metal. Cobalt inhibits cellular respiration and enzymes of the citric acid cycle and thus generates a type of systematic hypoxia against which the organism responds with increased erythropoietin biosynthesis (Gerhard *et al.,* 1991). Workers exposed to cobalt containing dusts develop progressive pulmonary fibrosis and other forms of chronic lung damage (Taylor and Hawkins, 1987). Cobalt toxicity is relatively independent of its chemical form. Thus toxic effects are elicited by the oxides as well as the metal, they are not masked by alloying. Tungstein and titanium carbide dusts are toxic on inhalation due to their cobalt contents (Coates and Watson, 1971; Kerfoot *et al.,* 1975). Cobalt carbonyl Co $(CO)_5$ vapour causes headaches, weakness, irritability and changes in electrical activity of the brain in workers exposed to it (Herdon *et al.,* 1980). Threshold air concentration of cobalt and cobalt oxide of 0.01 mg/m^3 in air is adopted in Belgium (NIOSH, 1982). Therefore this research aimed to investigate the uptake from the soil of Co in an arid environment on the basis of its concentration in tree barks in the study area, and to compare the suitability of different tree barks as bioindicators of cobalt and determine a good choice of tree for planting if contamination with this metal is observed.

2.0 Materials and Methods

In the preparation of reagents, chemicals of analytical grade purity and deionized water were used. All glass wares were socked in (1:4) HNO_3 solution and were rinsed with tap and deionized water before drying in the oven at 105^0C. All weighings were on Toledo AB54 analytical balance. Pipette filler was used in pipetting all solutions.

2.1 Study Site
Yobe State Nigeria is in the Sahel eco-climatic zone and was chosen as the study site. It is within the latitude 13.3^0N and longitude of 12.3^0E (Fig. 1). It is predominantly an agricultural state (YBSG, 2009). The climate of the region is the Sahel savannah type with low humidity and temperature variation.

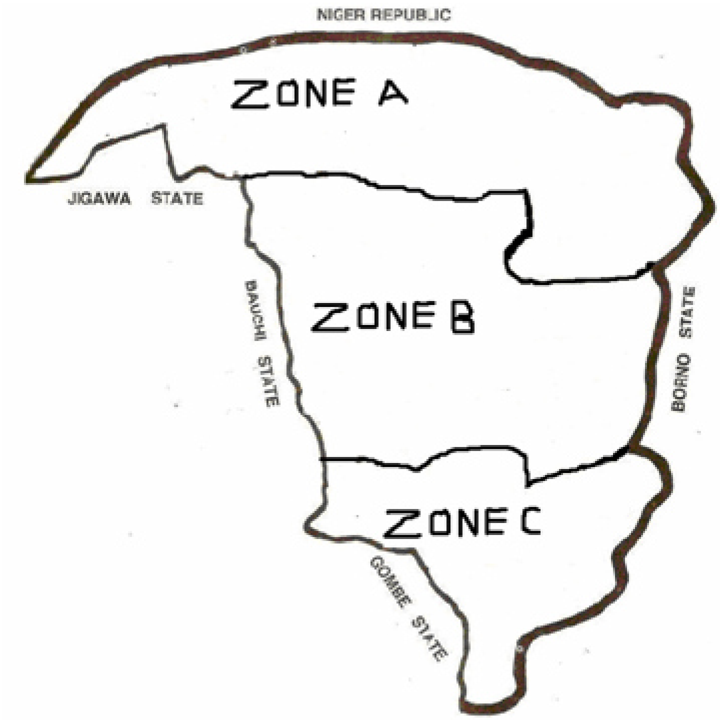

Fig. 1 Yobe State showing sampling sites

2.2 Sampling
Samples were collected from seven hundred and fifty (750) sampling sites between October and May 2008 – 2010 during the dry seasons. Representative of these matured samples of *Ficus thoningi,* and *Adansonia digitata,* were collected from the wild in the State. Several samples of each plant were collected from these locations. All samples were authenticated by the Department of Biological Sciences, and by comparison with Herbarium samples of Bayero University Botanical garden in Kano.

Similarly, surface soil samples were taken from the top to 10cm, at the base of trees used for bark collection with the help of stainless steel trowel to avoid contamination and were transferred to the laboratory in paper bags (Yilmaz *et al.,* 2006).

2.3 Sample Treatment
A clean stainless cutlass was used to remove the bark after it was etched with hard brush to remove lichens, mosses and dust (Grodzinska, 1982). The chips of the barks of the samples were collected from different sites during dry season. The number of sites from the sampling area was ten samples with twenty-five of each. The locations were carefully chosen to reflect the entire State. The trees used for sampling were matured and healthy plants. The barks were carefully removed using a cutlass to a depth of approximately 1cm (Tye *et al.,* 2006) at an average height of about1.5m above the ground level along the prevailing direction of the wind (Ayodele *et al.,* 2000). Samples were taken from the rough bark of trees not infected by insects. The knife was further washed after each sampling with 10% HNO_3 to avoid cross contamination. The samples were kept in paper envelopes and then placed in polyethylene bags before taken to the laboratory. The samples were then air dried in the laboratory. The dried samples were then pulverised with a laboratory mill (mortar and pestle). The mill was thoroughly cleaned with 10% HNO_3, distilled water and dried after each grinding to avoid cross contamination.

2.4 Sample Preparation
Soil and tree back samples were collected from the Zones and treated as discussed below:
2.4.1 Soil Sample.
The soil sample was ground and sieved to uniform size through a 2mm mesh and stored in a labelled plastic container. $20cm^3$ of concentrated Nitric acid was carefully added to 1g of soil sample in a $250cm^3$ beaker. The

mixture was allowed to cool for 1 hour. 15cm^3 of concentrated perchloric acid was added. The mixture was digested on a sandbath till the appearance of white fumes.

The digest was dissolved in 0.1M Hydrochloric acid, filtered into a 100cm^3 volumetric flask and made to mark (Arnold *et al.,* 2005).

2.4.2 Bark Sample

The bark sample was air dried in the laboratory at room temperature. The dried samples were pulverised to uniform size with a laboratory mill (mortar and pestle), sieved through a 2mm aperture and stored in a labelled plastic container (Mansor and Afif, 2011).

2g of the bark sample was taken into porcelain crucible and ashed at 500^{0}C in a muffle furnace to constant weight. Upon cooling overnight, the samples were then digested using 10% HNO_3 (Odukoya *et al.,* 2000), filtered in to 50ml volumetric flask and diluted to volume.

2.5 Elemental Analysis

The Co was determined using an atomic absorption spectrophotometer model VGB 210 SYSTEM, Buck Scientific. The result of each sample was the average of three sequential readings. Deionized water used as blank was treated using the same procedure.

3.0 Statistical treatment

All statistical computations were carried out with the aid of Microsoft Excel 2007 version obtained from Microsoft Corporation, USA; and Statistical Package for Social Sciences. One way analysis of variance (ANOVA) in randomized complete block design was performed to check the variability of data and validity of the results with SAS software system (SAS, 2002).

4.0 Results and Discussion

The concentrations of Co in the bark and soil vary among the two trees and in the state thus a number of samples from a population were analysed and the results treated statistically for a meaningful correlation**.**

The frequency distribution pattern for cobalt (Co) concentrations for the two plants samples in the State is as shown in (Figs. 2 and 3). The distribution pattern for Co in the bark of *Ficus thoningi* is shown in (Fig. 3).The distribution is bimodal and is skewed towards low concentrations of low frequencies with a mean and standard deviation of 2.39± 0.62µgg^{-1}. The distribution pattern for Co in the soil around *Ficus thoningi* is as shown in (Fig. 3). The distribution is multimodal and is skewed towards high concentrations of low frequencies with a mean and standard deviation of 0.85 ± 0.50µgg^{-1}. Co is not classified as an essential element for plants, however, it is usually described as beneficial. Co can be a contaminant in the soil through agricultural additives or metal refinery activities (Nies, 1999). Co is known to cause irreversible damage to a number of vital metabolic constituents in plant cells and root cell membrane (Neis, 1999). Comparing the Co concentration in the bark and soil a significant correlation is indicated ($P < 0.01$) to exist between them (Table. 1). Similarly, a significant difference was observed ($P < 0.05$) in both soil and bark when the mean Co concentrations in *F. thoningi* was compared with its concentration in other trees from the state.

The distribution pattern for Co in the bark of *Adansonia digitata* is as shown in (Fig. 3). The distribution is multimodal with a mean and standard deviation of 2.27± 0.68 µgg^{-1}. Contamination of the soil in mining areas, spills of toxic metals into rivers and eventual contamination of water, among other possible events, have been responsible for the deterioration of the environment and have affected people's lives in several ways. Also, heavy metals have adverse effect on plants and their productivity even though some metals are essential for plant growth in small quantities (Webber, 1981). The distribution pattern for Co in the soil around *Adansonia digitata* is as shown in (Fig. 3). The distribution is multimodal and is skewed towards high concentrations of low frequencies with a mean and standard deviation of 0.64±0.26 µgg^{-1}. Heavy metals may enter the plant system, accumulate and later enter the food chain and cause harm to humans and animals (Jayakumar *et al*., 2008). The photosynthetic pigments such as chlorophyll – a, b and total chlorophyll contents of a plant may decrease with increasing cobalt level in the soil. Comparing the Co concentration in the bark and soil a significant correlation is indicated ($P < 0.01$) to exist between them (Table. 2). Similarly, a significant difference was observed ($P < 0.05$) in both soil and bark when the mean Co concentrations in *A. digitata* was compared with its concentration in other tree from the state.

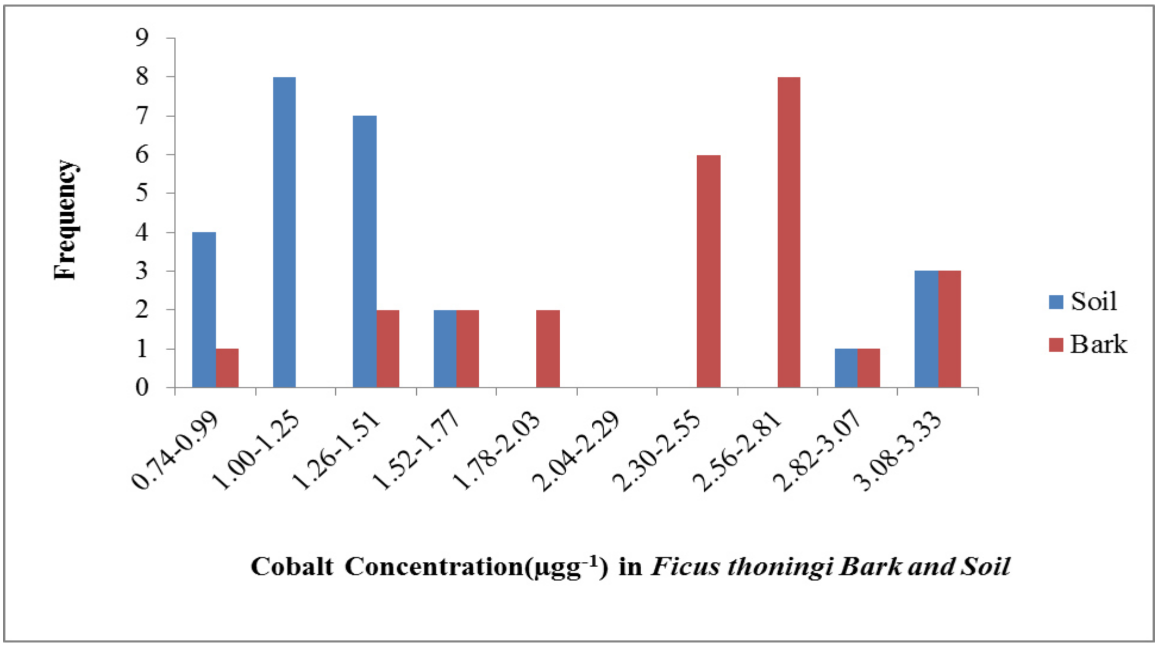

Fig 2: Frequency Distribution pattern for Cobalt in *Ficus Thoningi*

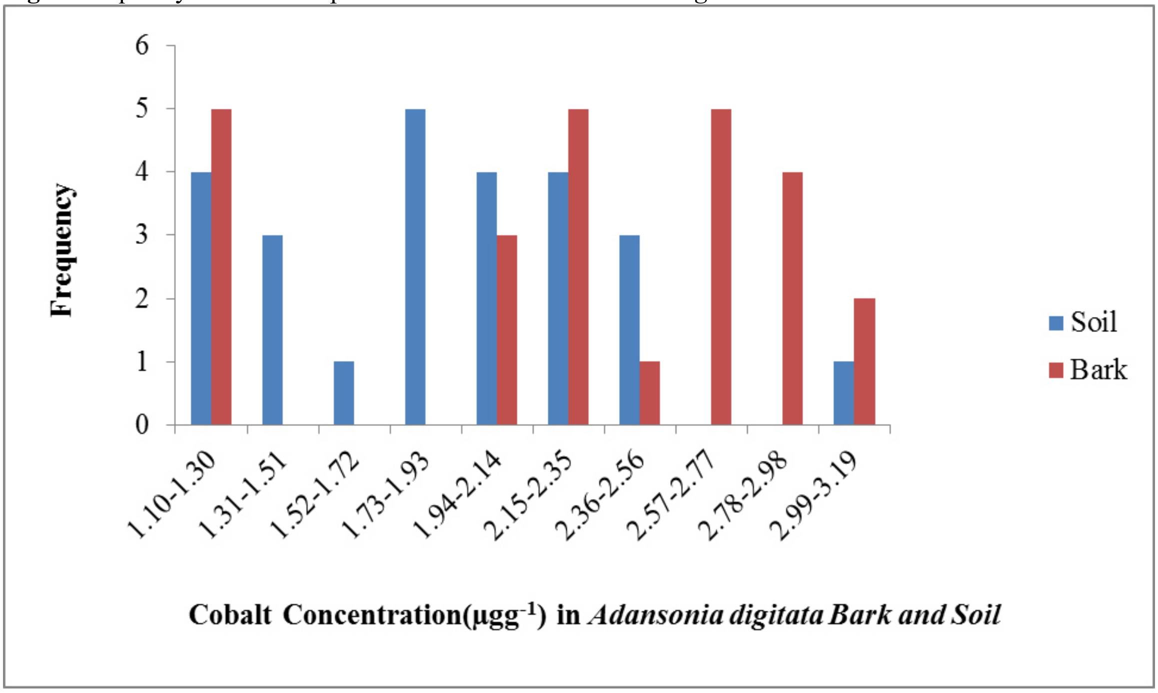

Fig 3: Frequency Distribution pattern for Cobalt in *Adansonia digitata*

CORRELATION TABLES FOR COBALT

Table 1: Correlation of Co levels between Bark and Soil for *Ficus thoningi*

Correlations1			
		Cobark	**Cosoil**
Cobark	**Pearson Correlation**	1	.765(**)
	Sig. (2-tailed)		.000
	N	25	25
Cosoil	**Pearson Correlation**	.765(**)	1
	Sig. (2-tailed)	.000	
	N	25	25
** Correlation is significant at the 0.01 level (2-tailed).			

Table 2: Correlation of Co levels between Bark and Soil for *Adansonia digitata*

Correlations2			
		Cobark	**Cosoil**
Cobark	**Pearson Correlation**	1	.935(**)
	Sig. (2-tailed)		.000
	N	25	25
Cosoil	**Pearson Correlation**	.935(**)	1
	Sig. (2-tailed)	.000	
	N	25	25
** Correlation is significant at the 0.01 level (2-tailed).			

Cobalt occurs naturally in the earth's crust in the soil at low levels. Elevated levels of Cobalt in soil may result from anthropogenic activities such as vehicular emission, mining and process of cobalt bearing ores, the application of cobalt containing sludge or phosphate fertilizer to soil, the disposal of cobalt containing wastes and atmospheric deposition from activities such as the burning of fossil fuels, smelting, refining of metals, and windblown soils (Smith and Carson, 1981).

Co may be taken up from soil by plants, the translocation from roots to above-ground parts of plants is not significant in most soils, the transfer coefficient (concentration in plant/concentration in soil) for cobalt is generally low 0.01 – 0.3 (Smith and Carson, 1981; Mermut *et al.,* 1996). However, in highly acidic soil, pH = 3.3, and in some higher plants significant higher transfer has been observed (Watabe *et al.,* 1984).

Alloway (1990) and Landon (1991) recommended 5 – 15μgg^{-1} Co concentrations in the soil. The result of these studies are below the recommended levels. Therefore the area under investigation are within the safe limit. Co is essential to plant growth and needed in small quantities, however, its excessive concentration in plant tissues may cause toxic symptoms (Malik *et al.,* 2010), Co concentration 20 to 30 μgg^{-1} dry matter could induce toxicity in plants and cause toxic effects in animals feeding on them (Annenkov, 1982).

This nutrient is vital physiologically and is an important constituent of enzymes thus critical for a number of plant functions and health (Malik *et al.,* 2010). Cobalt occurs in association with other metals such as Cu, Ni, Mn and As. Also, small amounts are found in rocks, soil surface and underground water (MOE, 2001). Natural sources of cobalt in the environment are soil, dust, seawater, volcanic eruptions and forest fires. It is also released to the environment from burning coal and oil, from car, truck and airplane exhausts, and from industrial processes that use the metal or its compounds (MOE, 2001).

Cobalt is essential in trace amounts for human life. It has been used as a treatment for anaemia because it causes red blood cells to be produced (MOE, 2001). However, exposure to very high levels of cobalt can cause health effects on lungs, asthma, pneumonia and wheezing which have been found in workers who breathed high levels of cobalt in air (MOE, 2001).

5.0 Conclusion

Co concentrations in the bark were generally found to correlate very well with the trace metal deposition in the soil. Levels of Co concentrations in the soil beneath the tree samples were generally followed by same or high metal levels in the bark. These high levels may be as a result of great input of the metal from dry and wet atmospheric deposition originating probably from Sahara desert (Yahaya *et al.,* 2011).

According to Biney et al., (1994), many heavy metals emitted mostly from anthropogenic sources have now exceeded or equalled their natural emissions and have been posing a serious threat to the ecosystems. This may be as a result of rapid population growth, urban sprawl and industrial activities expansion which has affected the release of chemical substances into our environment more and more (Kuang et al., 2007). However, this reflects the close relationship between the metal uptake and its accumulation in the bark of sampled tree barks. The levels in sequence were almost similar in the bark with those in the soil for statistically, significant ($P < 0.01$ and $P < 0.05$) correlations between the soil concentrations and the bark levels were found. This suggests that levels of Co in the bark were associated with the metal concentrations in the soil beneath the trees and the ability to bio accumulate them.

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