ISSN: 2231-2196 (Print)
ISSN: 0975-5241 (Online)
Internationally Indexed,
Peer Reviewed, Multidisciplinary
Scientific Journal
ICV: 4.18

International Journal of Current Research and Review
(IJCRR)

Vol 06 / Issue 21 / November 2014
Frequency: Fortnightly
Language: English

Published by:
Radiance Research Academy (Regd.),
Nagpur, MH, India

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Research Article

IJCRR
Section: Technology

ANALYSIS OF MANGANESE CONCENTRATION IN SOME TREE BACKS AND SOILS FROM YOBE STATE NIGERIA

R.O. Akinsola, M.I. Mohammed, D.I. Malami

Department of Pure and Industrial Chemistry, Bayero University Kano, Nigeria.

ABSTRACT

Khaya senegalensis, and *Azadirachta indica* from Yobe State, north east, Nigeria, and the soils around these trees were analysed for their Manganese 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 Mn ranges between 4.59 - 33.32µgg^{-1} in the bark and 4.69 - 28.95µgg^{-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. 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.

Key Words: *Khaya senegalensis, Azadirachta indica,* Manganese, Soil

INTRODUCTION

Manganese is its inorganic species is a ubiquitous essential element in nature. It is hardly present in toxic concentrations. Relatively large dose of manganese can be tolerated without any injury. The concentration of manganese in the earth's crust is approximately 0.1% (Shacklette *et al.,* 1971). Manganese is not found as a free element in nature. It is produced by the reduction of manganese oxide carbon monoxide, hydrogen or silicon into pure metal (Beppler *et al.,* 1978).

Manganese or its compounds are used in the production of alloys (Saager, 1984), depolarized in dry cell batteries and many chemical reactions as catalysts (Boettcher *et al.,* 1985). Manganese ethylene-bis (dithiocarbomate) - $C_4H_6MnN_2S_4$ is used as a fungicide and methyl cyclopentadienyl manganese-tricarbonyl (MMT) – $C_5H_4CH_3Mn(CO)_3$ as anti-knock.

Manganese is emitted into the air as MnO_2 and Mn_3O_4 during mining, crushing, smelting of ores and during steel production. Manganese is also released into the air near workplaces as dust. Emission limits are set for ferro and silico manganese in USA and Federal Republic of Germany. The emission of manganese is limited to 5mg/mg^3 with mass streams of more than 25g/L (Beppler *et al.,* 1978; Mark 1988).

Manganese deficiency causes retardation in growth and yellowing of needles of conifer. In animals, it is associated with menstrual cycle disorder, still birth, and low birth weight (Matrone *et al.,* 1977), neonatal mortality, reduced growth and skeletal anomalies. (Keen and Leach, 1988).

Excess Mn cause chlorosis in plants, impairments of haemoglobin formation and testicular damage in animals (Barlow and Sullivan, 1984). Acute inhalation of Mn cause manganese pneumonia. Inhalation of manganese at concentration above 100mg/day causes serious neurop. Therefore this research aimed to investigate the uptake from the soil of Mn in an arid environment on the basis of concentration in tree barks in the study area, and to compare the suitability of different tree barks as bioindicators of Manganese and to determine a good choice of tree for planting if contamination with this metal is observed.

MATERIALS AND METHODS

In the preparation of reagents, chemicals of analytical grade purity and distilled water were used. All glasswares were socked in (1:4)HNO_3 solution and were rinsed with tap and distilled water before drying in the

Corresponding Author:
R.O. Akinsola, Department of Pure and Industrial Chemistry, Bayero University Kano, Nigeria
Email: omotayo_akinsola@yahoo.com

Received: 10.08.2014 **Revised:** 11.09.2014 **Accepted:** 15.10.2014

oven at 105^{0}C. All weighings were on Toledo AB54 analytical balance. A pipette filler was used in pipetting all solutions.

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^{0}C. All weighings were on Toledo AB54 analytical balance. Pipette filler was used in pipetting all solutions.

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^{0}N and longitude of 12.3^{0}E (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.

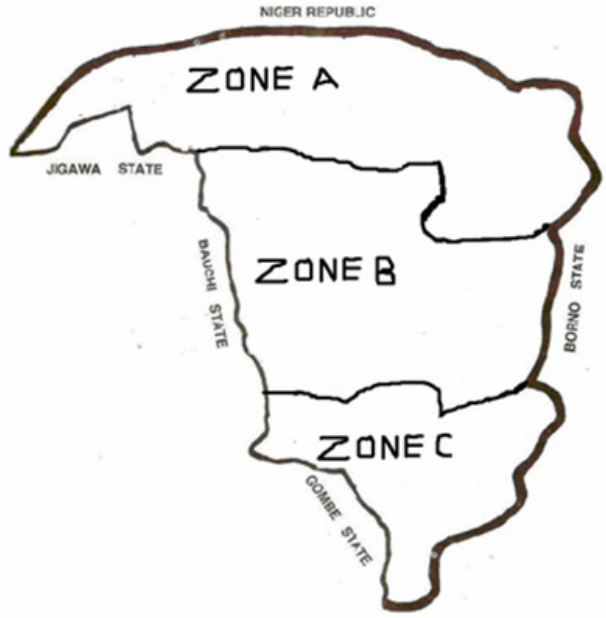

Figure 1: Yobe State showing sampling sites

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).

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.

Sample Preparation

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).

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 to50ml volumetric flask and diluted to volume.

Elemental Analysis

The Mn 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.

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).

RESULTS AND DISCUSSION

The concentrations of the element in the bark and soil vary among trees analyzed in the state thus a number of samples from a population were analysed and the results treated statistically for a meaningful correlation. Yobe was divided into three sampling zones, which were chosen in such a way that samples collected at these sites gave an overview and represent the entire state, based on the abundance of these plant species and activities taking place in the state.

The distribution pattern for Mn in the bark of *Khaya senegalensis* is as shown in (Fig.2). The distribution is multimodal with a mean and standard deviation of 15.12 ± 0.75μgg^{-1}. Mn is a naturally occurring element that is found in rock, soil and water. It is ubiquitous in the environment and occupies about 0.1% of the earth crust. Crustal rock is a major source of manganese found in the atmosphere. Ocean spray, forest fires, vegetation and volcanic activity are other major natural atmospheric sources of manganese. Important sources of dissolved manganese are anaerobic environments where particulate manganese oxides are reduced, the direct reduction of particulate manganese oxides in aerobic environments, the natural weathering of Mn (II)-containing minerals, and acidic environments (IPCS, 2004). The distribution pattern for the Mn in the soil around *Khaya senegalensis* is as shown in (Fig. 2). The distribution is multimodal and is skewed towards high concentrations of low frequencies with a mean and standard deviation of 14.29 ± 0.37μgg^{-1}. The major pool of m*anganese* in soils originate from crustal sources. Other sources including direct atmospheric deposition, wash-off from plant and other surfaces, leading from plant tissues, and the shedding or excretion of material such as leaves dead plant, animal material and excrement of animals. The major anthropogenic sources of environmental manganese include municipal wastewater discharges, sewage sludge, mining and mineral processing, emissions from alloy, steel and iron production, combustion of fossil fuels and to a much lesser extent, emissions from the combustion of fuel additives (Bankovitch et al; 2003). Comparing the Mn concentrations 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 Mn concentrations in *K. senegalensis* was compared with its concentration in other trees from the state.

The distribution pattern for Mn in the bark of *Azadirachta indica* is as shown in (Fig. 3). The distribution is multimodal with a mean and standard deviation of 12.15 ± 0.66μgg^{-1}. Mn is released to air as particulate matter. The fate and transport of the particles depend on their size, density, wind speed and direction. Some manganese compounds are readily soluble in water, and exist as Mn^{2+} and Mn^{4+}. Movement between these two forms occur by oxidation and reduction reactions that may be abiotic or microbially mediated. The environmental chemistry of manganese is governed by pH and redox conditions (Bankovitch et al; 2003). The distribution for Mn in the soil around *Azadirachta indica* is as shown in (Fig. 3). The distribution is multimodal and is skewed towards low concentrations of high frequencies with a mean and standard deviation of 10.17 ± 0.70μgg^{-1}. Mn in water can be bioconcentrated by aquatic biota at lower trophic levels. Uptake of manganese by aquatic invertebrates and fish increases with temperature, decreases with pH, and increases with decreasing salinity (IPCS, 2004). Comparing the Mn concentrations 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 Mn concentrations in *A. indica* was compared with its concentration in other trees from trees from the state.

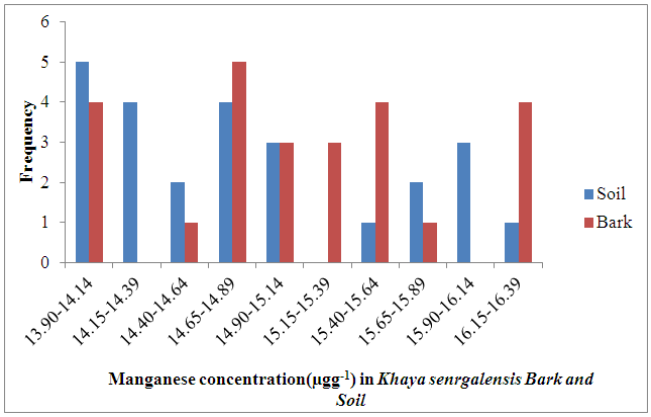

Figure 2: Frequency Distribution pattern for Manganese in *Khaya senegalensis*

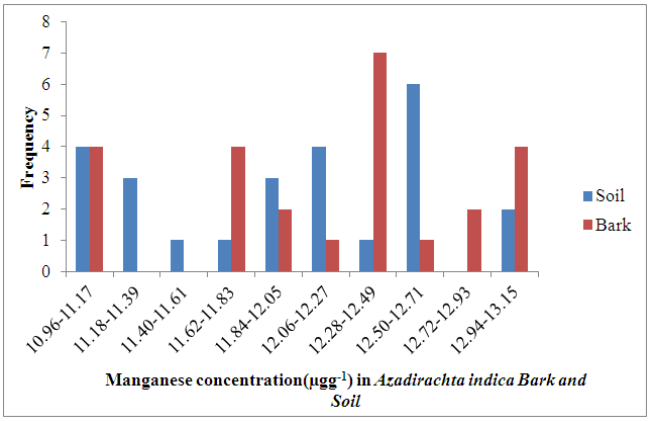

Figure 3: Frequency Distribution pattern for Manganese in *Azadirachta indica*

CORRELATION TABLES FOR MANGANESE

Table 1: Correlation of Mn levels between Bark and Soil for Khaya senegalensis

Correlations			
		Mnbark	Mnsoil
Mnbark	Pearson Correlation	1	.941(**)
	Sig. (2-tailed)		.000
	N	25	25
Mnsoil	Pearson Correlation	.941(**)	1
	Sig. (2-tailed)	.000	
	N	25	25

** Correlation is significant at the 0.01 level (2-tailed).

Table 2: Correlation of Mn levels between Bark and Soil for Azadirachta indica

Correlations			
		Mnbark	Mnsoil
Mnbark	Pearson Correlation	1	.969(**)
	Sig. (2-tailed)		.000
	N	25	25
Mnsoil	Pearson Correlation	.969(**)	1
	Sig. (2-tailed)	.000	
	N	25	25

** Correlation is significant at the 0.01 level (2-tailed).

CONCLUSION

The concentrations obtained varied from one sampling area to another. The concentrations of Mn may be in line with the nature of activities (natural and antropogenic) peculiar to the state.

The concentrations of Manganese in the bark can be expected to be an indicator of trace metal loading at the time of sampling. The study demonstrated the suitability of the investigated trees to successfully absorb and uptake Managanese from the soil. It also justifies the usefulness of *Khaya senegalensis*, and *Azadirachta indica* as an indicator of local soil deposition for this metal, due to variation in its concentrations among the soil and tree barks.

ACKNOWLEDGEMENT

Authors acknowledge the immense help received from the scholars whose articles are cited and included in references of this manuscript. The authors are also grateful to authors/editors/publishers of all those articles, journals and books where literature for this article has been reviewed and discussed.

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