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Heavy Metal Levels in Pine (Pinus caribeae Morelet L) Tree Barks as Biomonitors of Atmospheric Pollution in Calabar Municipality, South Eastern Nigeria

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Abstract
Biomonitoring of the air quality in Calabar was carried out by analyzing barks from pine trees (*Pinus caribeae* Morelet). Barks were collected from trees along highways with heavy traffic; residential areas with low traffic and the control (Cross River University of Technology, Staff Residential Area, Calabar); and analysed using atomic absorption spectrophotometer for lead (Pb) and manganese (Mn). The result showed the highest Pb level in the heavy traffic site U. J. Esuene Stadium by Calabar Road, 0.66± 0.02 mg/kg and lowest 0.01mg/kg in the control. Manganese was highest in the heavy traffic site, U. J. Esuene Stadium by Calabar Road 0.57± 0.02 mg/kg and lowest at the control 0.05± 0.01.mg/kg. The apparently low level of lead obtained in this study, compared to values that have been obtained in some other countries might be due to the unleaded petrol imported into this country. However the level of manganese might be due to its inclusion in petrol to improve its antiknock properties.
Keywords: Biomonitoring, Emission, Toxicity, Contamination, Pine bark

Introduction

There is a growing awareness of the dangers posed by heavy metals in the ecosystem. Scientific literature is full of reports of heavy metals and their effects on the environment. Though natural components of the environment, heavy metals are of late, posing great concern because they are being added in increasing amounts to the soil, water and air through human activities. Most heavy metals are essential and needed in small amounts in living organisms, but their excessive amounts are harmful to plants and animals (WHO, 1972). For this reason, heavy metal pollution is becoming a threat to our life support system. Vehicular emissions are a great source of heavy metal accumulation in the surrounding space and plant species (Ward *et al*; 1974, Scerbo *et al;* 2002, Momani *et al*; 2006.).

There are several ways of monitoring air pollution: measure concentration of pollutants in the air (Bellis *et al*; 2001) or rainwater (Jiries *et al*; 2001) and soil (Turer *et al*; 2001) but of all the methods, the use of biological monitors has the advantage of being the cheapest. Biological monitors including plants have been used to measure the atmospheric concentration of trace elements (Onianwa *et al*; 1986, Celik *et al*; 2005). Biological monitors such as plants have been used to measure the atmospheric concentration of trace elements (Onianwa, *et al;* 1986, Onsanaya *et al*; 1993, Celik *et al*; 2005, Ejidike and Onianwa, 2015). Plants are used as the cheapest indicator for monitoring the heavy metal concentration in the atmosphere. Different bioindicators such as mosses, lichens and woody vascular plants are used in monitoring air pollution. The barks of broad-leaved and coniferous trees are used in air pollution studies (Lippo *et al;* 1995, Adeniyi, 1996). Unlike mosses and lichens, tree barks have not been shown to selectively collect heavy metals and other pollutants (Kord and Kord 2011) therefore, they are suitable indicators in urban and industrial areas where other bioindicators are infrequent (Lostchert and Kohm, 1978, Santamaria and Martin, 1997). Pine trees have been studied to assess whether pine species can be used as a biomonitor for the determination of heavy metal pollution. Results of such studies have shown that pine trees are good absorbents of air borne pollutants including anthropogenic heavy metals. Among the studied pine tree barks are Turkish red pine (*Pinus brutia* Ten), Dogan *et al*; (2007); Italian red stone (*Pinus pinea* L) Oliva and Migorance (2006) and Masson Pine (*Pinus massonia* Lamb), Kuang *et al*; (2007). Bingol *et al;* (2008) obtained high values of lead concentrations in the barks of street trees *Sophora japonica* L. in Ankara, Turkey ranging from 11mg/kg dry weight to 199mg/kg dry weight in both control and experimental sites. The aim of this study was to investigate and assess lead (Pb) and manganese (Mn) pollution in the atmosphere of Calabar Municipality, using pine (*Pinus caribeae* Morelet L) barks as biomonitor.

Materials and Methods

Description of Study area: Calabar metropolis is located on Latitude $4^0 57'$N and Longitude $8^0 19'$E and lies in the Tropical Rainfall region in the South Eastern coast of Nigeria. The temperature ranges between 22^0C and 32^0C and an annual average of 26.7^o C. The annual rainfall is about 3239 mm and relative humidity of 85%.

Sampling and Analysis

Tree bark samples were collected from trees of about 20 years old situated along the highways (high traffic areas) and streets in low traffic areas in 2012. Three trees were sampled at each location; heavy traffic, light traffic and control between October and November, 2012. The barks obtained from each site were mixed and put in polytene bags and taken to the laboratory for analysis.

The tree barks were dried to a constant weight. The dried samples were pounded using wooden mortar and pestle into fine powder. Analysis was done according to Association of the Official Analytical Chemists (AOAC), (1990). One (1) gram of dried powdered and sieved sample was weighed and put into a conical flask after which 5ml of 60% perchloric acid was added. This was then poured into a crucible and ignited to ash in a muffle furnace at 300^{0}C for 2 hours. It was allowed to cool and then 10ml of 60% perchloric acid was added and heated to digest the charred sample into a solution. This procedure was replicated three times. For each sample, the digest was diluted to 100ml with deionized water. It was then used for analysis using Buck Scientific Atomic Absorption Spectrophotometer Model Buck 210 VG at Chemistry Laboratory, University of Calabar, Nigeria.

Results and Discussion

Heavy metal concentrations in the sampled barks are presented in Tables 1 and 2. Pine barks in both the heavy and light traffic sites accumulated the heavy metals lead and manganese in varying amounts as shown in Tables 1 and 2. U. J. Esuene Stadium by Calabar Road had 0.66±0.02 mg/kg for lead (Pb), followed by Calabar Urban Development Authority (CUDA) by New Ikang Road 0.06 ±0.01 mg/kg. Barracks Road by the Cenotaph had 0.05±0.01 mg/kg. The control had the least 0.01 mg/kg. Manganese (Mn) was highest at U. J. Esuene Stadium by Calabar Road 0.57±0.02 mg/kg followed by CUDA by New Ikang Road 0.52±0.02 mg/kg. Barracks Road by the Cenotaph had 0.16±0.04 mg/kg. The control had the least, 0.05± 0.01mg/kg.

In the light traffic sites the levels of Pb and Mn were lower than the heavy traffic sites. The concentration of lead was the same at Etta Agbo Layout and Satellite Town 0.05±0.01 mg/kg, while Unical Hotel had the highest 0.07±0.01 mg/kg with the control being 0.01 mg/kg. Manganese was lower in the light traffic sites than the heavy traffic sites. Etta Agbo Layout and Satellite Town had almost the same concentration of 0.16±0.02 mg/kg and 0.16 ±0.01 mg/kg respectively; Unical Hotel was not much different at 0.15 ±0.01 mg/kg. The control was least at 0.05 ± 0.01mg/kg.

The lead levels were lowest at the control and highest at U. J. Esuene Stadium by Calabar Road a heavy traffic site. The values of lead obtained in this study were relatively low because, atmospheric lead pollution on a local level in the area investigated is caused by emission from motor vehicles using imported unleaded petrol. This is at variance with the high levels ranging from 11mg/kg dry weight to 199mg/kg dry weight of lead obtained by Bingol *et al;* (2008) at Ankara Turkey, which was attributed in part to the use of leaded petrol by motor vehicles. The levels of lead at low traffic sites were higher than that of control but lower than the values at the high traffic sites indicating that there is a correlation between lead concentrations in the pine barks and traffic density. This agrees with the findings of other investigators (Hampp and Höll, 1974; Ward *et al*; 1974, Laaksovirta *et al*; 1976).

Table 1: Mean concentration (mg/kg) of Pb and Mn in Heavy traffic sites.

Sites	Pb	Mn
Calabar Road by U. J. Esuene Stadium	0.66±0.02	0.57± 0.02
CUDA by New Ikang Road	0.06± 0.01	0.52±0.02
Barracks Road by Cenotaph	0.05±0.01	0.16±0.04
Control	0.01	0.05±0.01

Means of triplicates ± standard deviation

Table 2: Mean concentration (mg/kg) of Pb and Mn in light traffic sites.

Sites	Pb	Mn
Etta Agbo Layout	0.05±0.01	0.16±0.02
Satellite Town	0.05±0.01	0.16± 0.01
Uncial Hotel	0.07±0.01	0.15±0.01
Control	0.01	0.05±.01

Means of Triplicates ± standard deviation

The values of manganese also reflected the traffic density. It was highest at Calabar Road by U. J. Esuene Stadium and lowest at the control site. The accumulation of manganese in the *Pinus caribeae* (Morlete L) bark might be due to its inclusion in petrol for its antiknock properties.

The result of this study suggests that pine tree *Pinus caribeae* (Morlete L) is a good biomonitor of heavy metal pollutants in the air. The surface structure of the bark (coarse and rough) makes it suitable for passive accumulation of heavy metal pollutants in the air. The result observed in this study shows that the amounts of these air pollutants have not reached toxic levels in Calabar yet. However it is important for government to initiate measures that will prevent the potential risks posed by their increase. It is documented that human exposure to lead results in decreased sperm quality, altered sperm morphology and general reproductive dysfunction (Ejidike and

Onianwa, 2015). It is also reported that elevated lead level in the environment can cause decreased growth and reproductive rate in plants and animals (EPA, 2017).

We recommend regular bio-monitoring of the environment so as to have the necessary information that will guide government environmental policies.

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