The Potentials of Eucalyptus camaldulensis for the Phytoextraction of Six Heavy Metals in Tin – mined Soils of Barkin Ladi L.G.A. of Plateau State, Nigeria

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Abstract
Formal and informal tin mining has devastated farmlands in Barkin Ladi L.G.A. of Plateau State leaving numerous mounds and ponds containing heavy metals and radioactive elements. *E. camaldulensis* were planted on filled – in shafts to restore the landscape of few of the devastated lands. The ability of *E. camaldulensis* to clean - up the soil of heavy metals was tested by analyzing the levels of accumulation of six heavy metals in its tissues using flame atomic absorption spectroscopy (FAAS). The samples were collected from July – September 2006. The concentrations of Pb ranged from 6.23mg/kg in roots to 15.26mg/kg in leaves. Zn was accumulated much in the tissues (88.30mg/kg in leaves and 51.23mg/kg in roots) but the soil had a lower concentration of 35.67mg/kg. The concentration of Nickel in soil (26.71mg/kg) was twice that in leaves (12.05mg/kg) and almost 3 times that in the roots (9.99mg/kg) .Cr concentration in leaves (183.31mg/kg) and roots (182.72mg/kg) were higher than Cr in the soil (102.92mg/kg). The concentration of copper in the soil, leave and roots were 24.55mg/kg 9.56mg/kg and 15.00mg/kg respectively. The concentration sequence of Sn was soil > roots > leaves with the values of 2479.47, 1885.29 and 181.68mg/kg respectively. The concentrations of Cr and Sn were above the environmental thresholds. From the data, *E. camaldulensis* did not accumulate substantial amount of the metals into its leaves and may only be used to phytoextract Zn, Cr and Pb with soil amendments but for Sn, Ni and Cu, other plants like corn that grow faster on the contaminated tin – mined soil on fertilization could be tried.

Key words: Metal Accumulation, *Eucalyptus camaldulensis,* Phytoextraction *and FAAS*.

Introduction
For decades, both formal and informal mining of tin have been carried out on the Plateau. In spite of its economic benefits, a myriad of environmental problems has been the attendant accompaniment. For example, over 316km^2 of farmlands in the state were devastated by tin mining, leaving numerous ponds and mounds containing radioactive elements (e.g. U-238, U-235, Th-232, and K-40) and heavy metals [1]. Chemicals like heavy metals, once introduced by any one particular method, may spread to the various environmental components in different forms due to different natures of interactions with various factors of the environment [2]. Accumulation of these heavy metals in the environment and particularly in aquifers and soils, from which they may be transferred to living organisms, either via groundwater or the food chain (crops, cultivated food plants) and feed chain (fish, animals) is continuously an environmental concern [3].
Plateau State Government, environmentalists and the citizenry are becoming aware of the health threat posed by tin-mining activities in the State [4] but, there has never been a measure put in place (if any, it may not have been enforced) by the government to control the continuous activities of informal miners primarily responsible for such pollution. There are also no proper cleaning methods put in place to rid the environment of heavy metals pollution as a result of tin mining. The only means of restoring the landscape of devastated lands instituted was to plant *E .camaldulensis* (Rastata) afforestation on the filled-in mined shafts. In addition to restoring the lands structure, *E. camaldulensis* may also be used as a device to clean-up the contaminated soil if plant is able to accumulate high concentrations of heavy metals in its tissues by the method known as phytoremediation. Phytoremediation is the use of plants to remove, detoxify or immobilized environmental contaminants in a growth matrix (soil, water or sediments) through natural, biological, chemical, physical activities and processes of the plants [5]. Thus, phytoremediation is an emerging technology which should be considered for remediation of contaminants because of its cost effectiveness, aesthetic advantages and long term necessary for the removal of heavy metals. Phytoremediation requires technical strategy, expert project designers with field experience that can choose metals and regions [6]. Some plants like Alfafa, sunflower and millet can take up lead, copper, cadmium, iron and mercury. While most plants exposed to high level of soil toxins may die off, Scientists have discovered that certain plants are resistant to these toxins and even a smaller group actually thrive. Both groups of plants are of interest, but the thriving plants show a particular potential for remediation because some of them actually transport and accumulate

extremely high levels of soil pollutants within their bodies. They are aptly named hyper accumulators [7, 8]. *E. camaldulensis* trees thrive on the filled-in mined shafts of Barkin Ladi that are contaminated with heavy metals. *E. camaldulensis* also have massive shoot system which should be able to accumulate high concentrations of heavy metals thereby cleaning the soil of heavy metals [9]. To our knowledge there has not been any study that has identified heavy metal accumulator or tolerant plant species from tin mined contaminated soils that is native to Jos Plateau. The aim of this work is to access the levels of six (6) heavy metals (Pb, Zn, Ni, Cr, Cu and Sn) in the tissues of *E. camaldulensis* and its potential utilization after metal sequestration.

Methodology

Sampling: The roots and leaves of *E. camaldulensis* (n = 122) were collected from the reclaimed tin mined sites (areas *with E. camaldulensis* afforestations) of Barkin Ladi L.G.A. of Plateau State from July to September, 2006. These were pulverized and air dried for two weeks. At the same place where the roots and the leaves were obtained, the surface soils (0-10cm) were also collected.

Sample Treatment:

***E. camaldulensis* Samples**: The pulverized samples were again dried in an oven at 105 ^{0}C for eight (8) hours prior to digestion. This was further pulverized and sieved through 2mm sieve. 1g of the sieved sample was weighed into an already labeled beaker that was dried and cooled. 10ml of concentrated HNO_3 was added into the beaker and digested on a hot plate in a fume cupboard and several volumes of HNO_3 were added until a clear solution was obtained. The clear solution was allowed to cool and filtered into a 100ml volumetric flask and made up to the mark with deionised water and stored. The solution was analyzed for six (6) heavy metals using Flame Atomic Absorption Spectrophotometer (Unicam 969 AAS).

Soil Samples: The soil sample that was air dried for two (2) weeks was again placed in oven at 105^{0}C until a constant weight was obtained after 15 hours. The sample was crushed using pestle and mortar and sieved with 2mm sieve. 1g of the soil sample was treated as with the *E. camaldulensis* tissues.

Results

The concentration (mg/kg) of six heavy metals accumulated by the tissues of *E. camaldulensis* (leaves and roots) and the soils on which the plant were grown in Barkin Ladi L.G.A. are tabulated in Table 1. The concentration factors of the metals in the tissues of *E. camaldulensis* are recorded in Table 2

Table 1: Concentrations (±SD, n = 3) of six (6) heavy metals (mg/kg) in the tissues of *E. camaldulensis* and the soils of the tin mined areas of Barkin Ladi L.G.A.

Concentration (±SD) of heavy metals (mg/kg)						
Samples	Pb	Zn	Ni	Cr	Cu	Sn
E. camaldulensis (leaves)	15.26 ±2.5	88.30 ±9.4	12.05 ±3.3	188.13 ±13.1	9.56 ±1.5	181.68 ±3.5
E. camaldulensis(roots)	6.23 ±1.4	51.23 ±5.2	9.99 ±2.1	182.72 ±23.4	15.00 ± 1.2	1885 ±15.4
Soil (pH=5.2)	13.85 ±3.1	35.67 ±5.3	26.71 ±3.4	102.83 ±7.4	24.55 ±4.1	2479.47 ±45.6
Environmental threshold*	300	300	60	50	60	50

*Troung (2000) [10]

Table 2: The concentration factors (CF) of the heavy metals in leaves and roots of *E. camaldulensis*

Sample	Pb	Zn	Ni	Cr	Cu	Sn
E.camaldulensis(leaves)	1.10	2.48	0.45	1.78	0.38	0.07
E.camaldulensis (roots)	0.45	1.44	0.37	1.78	0.61	0.76

Discussion

Barkin Ladi L.G.A. of Plateau State was famous in the State and beyond because of tin mining activities. The Local Government has the highest area of wastelands in the State as evident by the numerous ponds, mounds and some abandoned tin mined equipment, even in the heart of the city. The mining activities have contaminated the area with heavy metals and radioactive elements [1].

From Table 1, lead (Pb) concentration was in the order of leave > soil > root. The concentration factor (CF) of Pb in the leaves and the roots were 1.11 and 0.45 respectively. Zhuang et al (2007) [8] reported CF of eighth tested plant species and found that CF values for Pb were lower than 0.2 for all the eight tested plants. The concentrations of the metal were below the environmental threshold of 300mg/kg. The plant was able to translocate most of the metals to the leaves; however, the concentration of the metal accumulated by the plant was

too low to consider phytoremediation of the metal to be the sole objective. Chen and Cutright [11] reported that, plants grow normally without extracting much Pb in contaminated Pb soils, but the plants absorb a high concentration of lead once EDTA (a complexing agent) was added to the soil.
The zinc (Zn) concentrations occur in the sequence leave > root> soil. In agricultural soils, the roots Zn are expected to be more than ten (10) times the leaves Zn but for the hyper accumulators, the Zn shoots concentration should exceed the roots by the multiples of ten [12]. In this work, the Zn in the leaves barely exceeded the roots' Zn; *E.camaldulensis* could not be regarded much as a hyper accumulator of Zn. Also in the work of Zhuang et al (2007) [8] reported CF of eighth tested plant species and found that Zn CFs of all plants varied between 0.06 and 6.30, with the lowest CF in V. zizanioides and the highest CF in S. alfredii.
The concentration of nickel (Ni) analyzed were lower than the concentration of Zn in both root and leave, but Ni also has higher concentration in the leaves than in the roots. It was reported that the metal most commonly accumulated is (Ni) [13].The concentration factors of Ni in the tissues of *E.camaldulensis* indicated that it will take cycles of plantations to clean up the contaminated soil because of the low accumulation of the metal. Unfortunately, the plant takes several years to grow fully. It is therefore advisable to search for an alternative plant for the purpose of phytoremediation.
The concentrations of chromium (Cr) in the tissues of *E.camaldulensis* were higher than in the soil in the work. The combination of high biomass of *E.camaldulensis* and the high accumulation of the metal and its tolerance to hash growing conditions on the mined soil should make this plant suitable agent of phytoremediating Cr. The high concentration of Cr in tin mined soils is an issue of great concern as children play and carelessly ingest the tin mined sand that are often used for building construction. Cr exists as Cr^{3+} and Cr^{6+} forms. The Cr^{3+} is an essential trace metal needed for the glucose metabolism in humans and animals. It is relatively innocuous and immobile when compared to Cr^{6+}. Because of the high charge of Cr^{6+}, it is hydrolyzed to form oxo- anions, CrO_4^{2-} and $Cr_2O_7^{2-}$, depending on the pH. The pH of aqueous solution is an important operational parameter in the absorption process and the form in which a particular metal exists. This is because it affects the solubility of the ion, concentration of the counter ion on the functional groups of the adsorbent and the degree of ionization of the adsorbent during reaction [14, 18]. Acute exposure to Cr^{6+} causes nausea/diarrhea, liver and kidney damage, irritation and ulceration. Skin contact with Cr^{6+} will result to systematic poisoning or even severe burns and interference with healing of cuts. Eye exposure to Cr^{6+} causes permanent damage [14].
The concentration of copper (Cu) follows the sequence soil > leaf > roots, with values of 24.55, 15.05 and 9.56mg/kg respectively. Cu presented low values but E. camaldulensis would be effective in the phytoremediation of the metal from the contaminated tin mined soil of Barkin Ladi.
Tin (Sn) concentrations were the highest among the metals investigated. This is not unconnected with its mining in the area of study. Sn is said to be the component of many soils that binds with soil and sediment of the water. Sn is regarded to be generally immobile [15]. With the high concentration of Sn in the area, people living in these areas are exposed to Sn by breathing Sn dust or getting Sn compounds on their skin. Children sometimes ingest the contaminated soil while playing. Ingested inorganic Sn travels through the intestine and leaves the body in the feaces, some through the urine. Sn that passes through the nostril may be trapped in the lungs. Inorganic Sn leaves the body very quickly; most are within a day, some spent up to 2-3 months but are not harmful. However, when large amount of inorganic Sn is swallowed, one suffers stomach ache, anemia, liver and kidney problems [15, 16].
Finally, *E. camaldulensis* cannot be said to be hyperaccumulator of any of the six metals studied but soils conditions can be altered to favor some metals. This also agrees with the work of (Naseem et al, 2010) [17]. After studying the phytoextraction of six heavy metals by sixteen plant species in Pakistan, they found that none of the plant species was identified as hyper accumulator.

Conclusion

E. camaldulensis cannot be said to be a hyper accumulator of any of the metals analyzed. Nevertheless, it accumulated higher concentrations of Pb, Zn and Cr in its tissues (particularly in the shoots) than in the soil. *E. camaldulensis* could therefore be adapted to phytoextract these metals by the addition of biodegradable chelating agents such as methylglycine diacetate (MGDA), ethylene succinic acid (EDTS), L-glutamic acid diacetate (GLDA), L-aspartic acid diacetate (ASDA). Cu, Ni and Sn had very low concentration factors in the plants' shoot, and *E. camaldulensis* cannot be used to clean up these metals from the contaminated tin mined soil, except if the soil is amended. Cr and Sn concentrations were higher than the environmental threshold and may pose children to health risk as they ingest the soil while playing. Other plant species should be tried for the phytoremediation of these metals, especially that it takes a very long period for the *E.camaldulensis* plant to grow. The work demonstrated the need of multidisplinary approach in order to achieve effective phytoremediation of heavy metals and other environmental contaminants from the mined area.

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