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#### Research Article

## Lead Content of Lichens in Metropolitan Harare, Zimbabwe. Air Quality and Health Risk Implications

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#### ABSTRACT

Many studies have shown that inhaled lead is one of the major contributors of lead poisoning. Lead poisoning affects all systems within the body. Lead amount in metropolitan Harare atmosphere was estimated by measuring the amount of lead in lichens found in the area. Lead pollution of the atmosphere is of major concern because continuous exposure of low levels of lead may cause serious effects. Furthermore there are no agreed safety limits for children. The concentration of Pb in different species was determined by atomic absorption spectrometry. Lead concentration varied from not detectable quantities to  $3.31 \pm 0.04$  ppm. Harare central hospital recorded the highest lead content  $3.31 \pm 0.04$  ppm in *Parmelia* species while the lowest was observed at centers far from the CBD, Botanic gardens, Christonbank and Mwenje dam. Generally the relationship between distance, lead content and species diversity was significant for most lichens except that for *Lecanora caesiopallens* (r = 0.72) and *Lecanora atraaeformis* (r = 0.71) student t-test p > 0,05 showing presence of increased pollution in the CBD. It is suggested that all possible sources of lead poisoning and their contributions to atmospheric lead content should be ascertained to determine the actual daily exposure rate. Such data would help in formulating policies to reduce lead poisoning in the general public.

Keywords: Lead content, lichens, air quality, health implications.

#### INTRODUCTION

Exposure to low levels of lead through contaminated air has adverse health implications (Ferner 2001; Jarup 2003; Arora et al. 2008). Most importantly, it is the long-term effects of lower levels of lead exposure that cause concern. Many studies have shown that heavy metals such as lead are extremely persistent in the environment. They are non biodegradable and therefore they can readily accumulate to toxic levels (Grzebsz et al 2002; Ma et al 2001; Adie and Osibanjo 2009; Bergamasdini et al. 2004). Long-term exposure may result in general fatigue, headaches, blood circulation problems, reduced kidney function, reduced fertility, reduced brain function and other neurological problems (Ogwuegbu and Muhanga 2005). Children are considered to be mostly affected than adults to the effects of lead WHO, (1995). It has been widely recognized that lead at exposure levels well below those mentioned for acute lead poisoning has the potential to impair children's brain development and learning (Navas-Acien et al. 2007). Lead is also harmful to adults. Adults can suffer from, reproductive problems for both men and women, high blood pressure and hypertension, nerve disorders, memory and concentration problems and muscle and joint pain (Wilson, 2008; Lanntech, 2004). Many countries have successfully enacted laws and regulations to limit the use of leaded petrol, however the developing world including Zimbabwe have been slow in enforcing such laws. Worldwide leaded petrol has been implicated as the major source of lead poisoning in human beings (Luilo and Othman 2006). Other sources of lead contamination include paints and street dust. The quantity of the lead absorbed by humans via the lungs depends on the concentration of lead in the environment. Chronic lead poisoning occurs when small amounts of lead are taken in over long periods of time. Exposure to lead is most commonly monitored by measuring blood lead levels (Schwartz and Hu 2007; Menke et al. 2006; Kosnett and Wedeen 2007; Hu et al. 2007; AOEC 2007), however long term exposure can rarely be ascertained from blood lead records. No one in general population has an adequate blood measurement history. The ability of lichens to absorb and accumulate xenobiotics makes them useful as indicators of air quality (Mimis et al. 2002; Bargagli and Mikhailova 2002; Garty, 2001). They depend on surface absorption of nutrients. Lichens lead measurements allow the direct measurement of long term lead exposure. At present little is known about the range of chronic environmental exposure to the general population in Harare. Thus this study has the potential to give an insight on the effects of low levels of lead exposures.

#### MATERIALS AND METHODS

All reagents were analytical grade. HNO<sub>3</sub> and HClO<sub>4</sub> were obtained from Merck, New Jersey, USA. Calibration and Certified reference materials were obtained from Aldrich, Steinheim, Germany. Double deionized water was used for all analysis. Analysis of heavy metal content was performed using AAS, Varian model AA 1275 series atomic absorption spectrophotometer equipped with a single slot burner and a built in digital read out.

#### **Sampling Sites**

Samples were collected from five sampling stations along a 47,5km transect in the city of Harare. The five sampling stations were Harare Kopje, Harare central hospital National Botanic gardens, Christonbank and Mwenje dam. Harare Kopje is located in the heart of the Central Business District (CBD) while Harare central hospital is entirely surrounded by factories. The National Botanic Gardens are located in a low density residential area while Christonbank and Mwenje Dam are in the outskirts of the CBD.

#### Sample collection

Samples were collected from trees of the same species (*Brachystegia*) of approximately the same age as determined by their diameters. Samples were collected at face height ± 15 cm using a pocket knife into clean labeled polythene bags and transported straight to the laboratory. Fifty trees were sampled from each area. The lichens were identified by taxonomist from the Harare National herbarium. Some species could only be identified by the family only.

#### Sample preparation

Samples were washed with minimum deionized water and shade dried for two weeks. Dried lichens were then ground in a hand mill to a uniform size by sieving through a 2  $\mu$ m sieve. A mass of 1g of each lichen species was weighed into a flask and 21 ml of 6:1 mixture of concentrated HNO<sub>3</sub> and 15 % HClO<sub>4</sub> was added. Five replicate samples were prepared for each species for each area. The mixture was gently heated to 80°C and then the temperature was raised to 150°C to achieve complete dissolution. The final solution was filtered into 50ml flasks and diluted to the mark with 2M HNO<sub>3</sub>. Lead concentration in the species was determined using an atomic absorption spectrophotometer.

#### Quality assurance and quality control

Suitable quality control and assurance protocols were carried out to ensure reliability of the results. Double deionized water was used throughout the study. Glassware was properly cleaned, and the reagents used were of analytical grade. Reagents blank determinations were used to correct the instrument readings. All analyses were performed five times. Certified reference materials (CRM) were used for validation of the analytical procedure. The results of measurements of CRMs are summarized in Table 1.

Sample	Certified value	Measured value	Recovery (%)
CRM 1	120 ± 0,6	119 ± 0,5	99
CRM 2	$73 \pm 0,5$	$73 \pm 0,5$	100

#### Table 1. Certified reference material concentrations (ppm) mean ± SD, n = 5

#### Statistical analysis

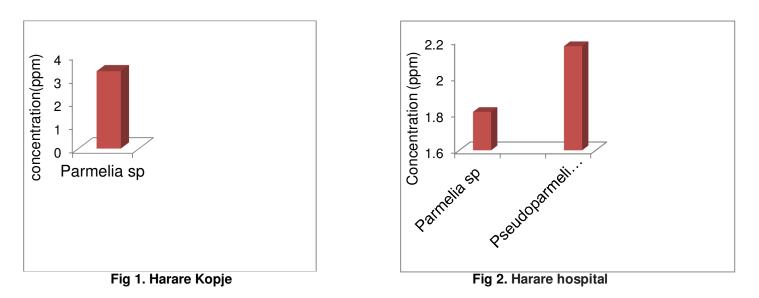
Data gathered from different sampling area were subjected to (ANOVA) and separation of means was done using Duncan test at p<0.05 of SPSS Version 16.0 (SPSS Inc., Chicago, IL, USA) with replications as random effects. Spearmen product correlation moment (r) and Student t test at 0.05 significant level was applied to determine relationships between lead concentration with distance and species diversity.

#### **RESULTS AND DISCUSSION**

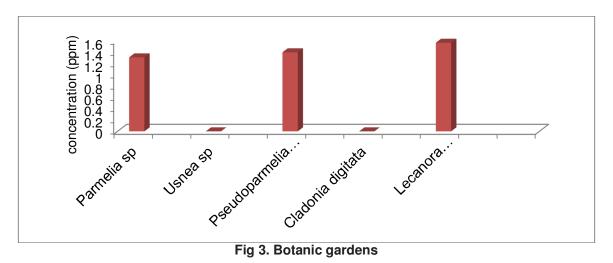
Lichens have long been recognized as sensitive indicators of environmental pollution (Adams et al 2007; Turhan et al 2005; Ekmekyapar et al. 2006). Application of lichens as bioindicators of air quality is one of the suitable methods to monitor heavy metals in cities. There is a very close statistical relationship between heavy metal contents in lichens and the heavy metal pollution measured in air Coskun, (2006). Biomonitoring studies provide valuable information about the quantity and quality of pollutants in the atmosphere and can be very effective as an early warning system to detect environmental changes (Bajpai et al. 2004).

#### Lead concentration and number of lichen species at each site

Two lichens species were found at Harare Kopje while one was observed at Harare central hospital (Fig 1 and 2). At Harare Kopje lead content was found to be  $1.81 \pm 0.08$  ppm in *Parmelia* species and  $2.17 \pm 0.01$ ppm in *Pseudoparmelia* species Fig 1. Harare hospital recorded the highest lead content of  $3.31 \pm 0.04$  in *Parmelia* species Fig 2.

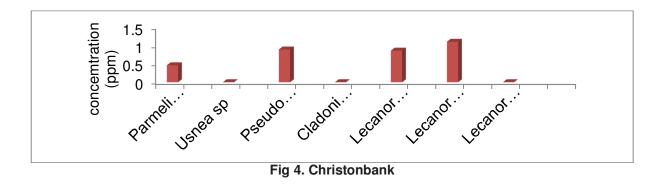


Five lichens species were observed at Harare botanic gardens Fig 3. Lead content was found to be  $1.31 \pm 0.07$  in *Parmelia sp*,  $1.40 \pm 0.01$  in *Pseudoparmelia sp*,  $1.57 \pm 0.07$  in *Lecanora Caesiopallens* while *Usnea sp* and *Cladonia digitata* levels were beyond detectable limits Fig 3.

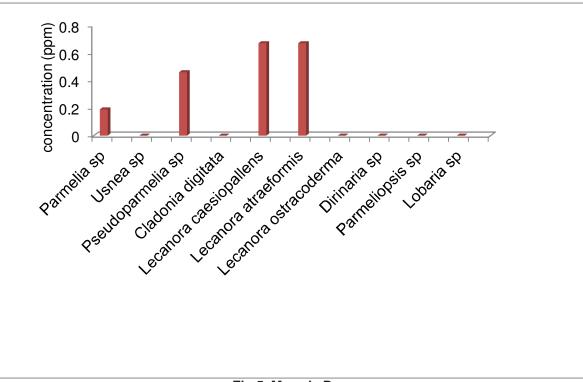


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A total of eight lichen species were recorded at Christonbank site Fig 4. Lichens lead content varied from  $0.46 \pm 0.06$  to  $1.10 \pm 0.07$ . *Lecanora atraaeformis* recorded the highest levels while *Parmelia* species recorded the lowest. *Usnea, Cladonia Digitata* and *Lecanora ostracoderma* lead content were not detectable.

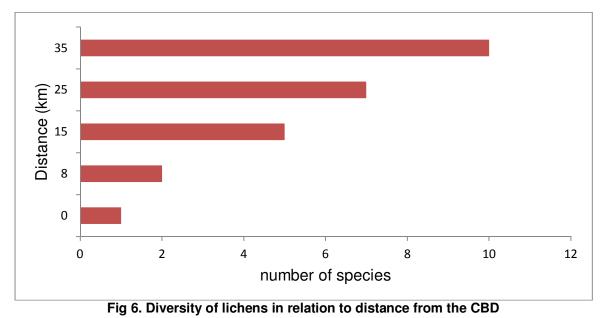


Among all the areas studied Mwenje Dam recorded the highest number of species Fig 5. A total of 10 species were observed. Lead levels ranged from  $0.19 \pm 0.06$  in *Parmelia* to  $0.67 \pm 0.07$  in *Lecanora atraaeformis*. Levels in *Usnea sp, Cladonia Digitata ,Lecanora ostracoderma, Dirinaria sp, Parmeliopsis sp* and *Lobaria sp* were beyond detectable limits.



#### Fig 5. Mwenje Dam

Lichen species diversity increased with increase in distance from the CBD from 1 to 10 Fig 6. *Parmelia* species were present in all the selected areas while *Lecanora* species favored areas far from the CBD where lead levels were low.



Generally the relationship between distance and species diversity was significant for most lichens (Table 1) except that for *Lecanora caesiopallens* (r = 0.72) and *Lecanora atraaeformis* (r = 0.71) student t-test p > 0.05. The increase in the diversity of lichens on *Brachystegia* trees with distance from the CBD was also reported by (Hawksworth and McManus 1989; Carreras and Pignata 2007). In both cases the number of species in all substrates declined along a 10 km transact towards the city centre. Reported values were significantly correlated to lead concentration in lichen thalli. In the present study levels of lead were significantly related to distance and species diversity for most of the lichens student t-test p > 0.05. Lawrey, (2011) observed that lichen communities in urban parks closest to Washington, DC were lowest in species diversity and coverage, and had no pollution-sensitive species.

Species	Α	В	С	
Parmelia sp	0.89	0.94	0.90	
Usnea sp		0.99		
Pseudoparmelia sp	0.83	0.84	0.87	
Cladonia digitata		0.87		
Lecanora caesiopallens	0.92	0.72*	0.95	
Lecanora atraeformis	0.32*	0.71*	0.90	
Lecanora ostracoderma		0.95		
Dirinaria sp		0.99		
Parmeliopsis sp		0.96		
Lobaria sp		0.94		

Table 1 Correlation between distance and lead concentration (A), distance and species diversity (B) and	
species diversity and lead concentration (C) $P = 0.05$	

\* = no significant difference, p = 0.05, Student t-test.

#### Air quality and Health implication

Lichens are widely used for biomonitoring of atmospheric heavy metals (Bargagli and Mikhailova 2002; Garty, 2001; Adams et al 2007; Turhan et al 2005; Ekmekyapar et al. 2006; Yazıcı and Aslan 2006; Bingol et al. 2009). There is very close statistical relationship between the accumulated heavy metals in lichens and the heavy metal pollution measured in air (Monna et al. 2012; Bajpai et al. 2011; Herzig 1993; Sloof and Wolterbeek 1998). Lichen species develop structural changes in response to air pollution that may include reduced photosynthesis and bleaching.

Pollution can result in the death of the lichen algae, reduced growth of the lichen fungus, or kill the lichen completely. With time all sensitive species may be replaced by pollution tolerant species. Therefore it follows that the species of lichens present in an area and the concentration of pollutants measured in those lichens can tell us a lot about air quality. The presence of lead in lichen thallus exhibits its airborne origin. Quantities of lead absorbed via the lungs by humans depend on the concentrations of lead in the air through which a person passes in the course of a day.

Presence and distribution of lichens in Harare show that the air in Harare is polluted with lead. High levels of lead in lichens around Harare central hospital can be rationalized by increased pollution from cars and industries surrounding the area. Species diversity in this area was greatly diminished as compared to other areas. Levels of lead decreased significantly with increasing distance from the CBD (ANOVA p > 0.05). Several studies share similar results as found in this research. Gombert et al. (2003) found out that lichen species diversity diminished around polluted sites. High levels of pollution eventually kill the lichens and only those species that can tolerate such levels survive. Health implications of high levels of lead in the air refer to the harmful effects of lead to the body when being consumed above the bio-recommended limits. Recent studies have shown that the magnitude of change in blood lead of adults caused by changes in concentration of lead in inhaled air show that for every 1µg of Pb per m<sup>3</sup> of air contributes 0.3 µg Pb/100 g of blood. World Health Organization (1995) task force basing on the analysis of occupational data reported that each 1 µg Pb per m<sup>3</sup> of breathed air contributes about 1g Pb per100 g of blood.

There is no definite relationship reported for children. Some studies have found out that average intake of lead from air appears to be below quantities that are thought to produce adverse health effects (Navas-Acien et al. 2007). Constant exposure of low levels of lead can lead to harmful effects because of its teratogenic effect. Lead poisoning also inhibits the synthesis of haemoglobin; disturb the well functioning of kidneys, joints, reproductive systems, cardiovascular and the Central Nervous System (Ogwuegbu and Muhanga 2005). Lichens are very important as bioindicators of air pollution because they assist in the interpretation of epidemiological patterns of respiratory diseases.

#### CONCLUSION

The presence of lead metal in lichens and the significant correlation between distance from the CBD, lead concentration in lichens and species diversity generally indicate the presence of lead in the ambient air of metropolitan Harare. The presence of lead in the atmosphere is now of greater concern because many studies have found out that average intake of lead from air appears to be below quantities that are thought to produce adverse health effects. Long-term exposure of low levels of lead may result in fatigue, headaches, blood circulation problems, reduced kidney function, reduced fertility, reduced brain function and other neurological problems. Furthermore the actual permissible safe limit in children is not certain. Because of presence of lead in the atmosphere as shown by lichens, it is therefore important to conduct further monitoring of the quality of foods grown or prepared in Harare and water sources. All possible sources of lead poisoning and their contribution should be ascertained to determine the actual daily exposure rate. Such data would help in formulating policies to reduce lead poisoning of the population in cities. It may also be useful to map the overall contribution of other pollutants such as SO<sub>2</sub> and other heavy metals to improve the accuracy of the findings.

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