INVESTIGATIONS ON THE AIR POLLUTANT SORPTION CAPACITY OF SOME LICHENS FROM SAMPLED URBAN AND PERI-URBAN AREAS OF KADUNA STATE

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FACULTY OF LIFE SCIENCES

AHMADU BELLOUNIVERSITY,

ZARIA NIGERIA

JANUARY, 2018

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A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIA, IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF MASTER OF SCIENCE DEGREE IN BOTANY

DEPARTMENT OF BOTANY,

FACULTY OF LIFE SCIENCES,

AHMADU BELLO UNIVERSITY,

ZARIA, NIGERIA

JANUARY, 2018

DECLARATION

I declare that, this dissertation entitled "**Investigations on the Air Pollutant Sorption Capacity of Some Lichens from Sampled Urban and Peri-Urban Areas of Kaduna State"** has been carried out by me in the Department of Botany, Ahmadu Bello University, Zaria, under the supervision of Professor S. P. Bako and Professor W. S. Japhet. All information derived from existing literature has been duly acknowledged in the text and a list of references provided. No part of this thesis has been presented for another degree or diploma at any other institution.

Isah LABARAN _____ _____

_____ Signature Date

Name

CERTIFICATION

This dissertation titled "**Investigations on the Air Pollutant Sorption Capacity of Some Lichens from Sampled Urban and Peri-Urban Areas of Kaduna State"** by Isah LABARAN meet the regulations governing the award of the degree of Master of science (M.Sc.) of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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Prof. S. Z. Abubakar Dean, School of Postgraduate Studies, Ahmadu Bello University, Zaria	_____ Signature	_____ Date

DEDICATION

I dedicate this to the memory of my late parents and to all my family members and all well-wishers.

ACKNOWLEDGEMENTS

I am most grateful to almighty God for His guidance, protection and keeping me safe and healthy throughout the period of sample collection and laboratory works. Praise be to Him for His favours and Mercy.

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I fondly remember and pray for my Departed Parent, I am grateful for all the support you rendered to me, May the Almighty Allah forgive them all their sin and make Jannatul firdausi their final destination. Ameeen.

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ABSTRACT

Atmospheric deposition of heavy metals like (Pb, Mn, Cd, Cr and Zn), SO_2 and NO_3 was investigated using lichens as suction points. The lichens samples were collected from four study areas namely; ABU Botanical garden, PZ area, (Sabon Gari Local Government) Buruku and Rido village (Chikun Local Government). Samples were collected in two seasons, that is three months in Dry season and three months in Wet season, the sample were collected 300m away from the main road. The representative samples were wet digested in Hydrogen trioxonitrate (HNO_3) and Hydrochloric acid (HCL). Heavy metals content were measured in the extract using Atomic Absorption Spectrometry (AAS); Quantitative analysis of the samples was carried out using Sequential Atomic Absorption Spectrometry (Varian AAS 240FS). Determination of Nitrogen Oxides (NO_3) was carried out using Phenoldisulphate acid method. Sulphur dioxide (SO_2) was determined at 420nm using Bosch and Lomb Spectronic-70. Data obtained was analyzed statistically using Analyses of variance (ANOVA), Duncan's multiple range test (DMRT) was used to separate the means where there is significant differences. The species of lichens collected are*; Phaeophyscia* species, *Xanthoparmelia* spp, *Flavopermelia capirata*, *Dictyonema glabratum*, and *Physcia* species. There is significant difference among the lichens in the accumulation of all the pollutants and *Flavopermelia capirata* has higher accumulation of the most pollutants. The results from all the locations shows that, PZ area is significantly higher in Pb Zn and SO_2, Buruku is significantly higher in Mn and Cd. Cr show no significant difference among the locations, Rido is significantly lower in NO_3 concentration. Also, for the seasonal variation dry season (Jan., Feb., Mar.) shows high content of Zn (0.221), Cr (0.286ppm), NO_3 (0.099mg/L) and SO_2 (355.343mg/L). The high content of Pb (0.183ppm) and Mn (2.146ppm) recorded during wet season (Jul., Aug., Sept.) while the concentration of Cd is uniformly recorded in both dry and wet seasons. The accumulation of heavy metals by lichens species ranged as follows;

Physcia pecies (1.69 – 0.01ppm), *Phaeophyscia* species (1.46 – 0.01ppm), *Dictyonema glabratum* (0.64 – 0.02ppm), *Xanthopermelia caperata* (2.12 – 0.02ppm), *Flavopermelia caperata* (3.84 – 0.02ppm), Manganese (3.84) has the higher concentration in the lichens species and is significantly higher than the metal with lower deposition which is Cadmium (0.02ppm). The concentration of Nitrogen oxide NO_3 in lichens ranged from 0.14 – 0.05mg/L while that of Sulphur dioxide SO_2 ranged from 238.99 – 62.89mg/L. Data Obtained reveal the important contributions towards understanding of heavy metal deposition patterns and provide baseline data, that can be used for identification of areas potential at risk from atmospheric pollutants contamination in the areas and seasons. The use of epiphytic lichens can provide a cost–effective approach for monitoring atmospheric pollutants contamination and may be effectively used in large scale air pollution monitoring programmes.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 LICHENS

The word 'Lichen' (lie ken) was introduced into the Greek literature in about 300 BC by Theophrastus, to describe outgrowths from the bark of olive trees (Hawksworth and McManus, 1989). Lichens are composite organism which are form as a result of symbiotic association between fungus (the mycobiont) with a photosynthetic partner (the photobiont), usually either a green algae or cyanobacterium (Kumar *et al*., 2010). The intimate association of these two microorganisms results in the formation of a macro-organism, i.e. the lichen thallus whose morphology is quite different from that of the original organisms. The association between the algae and fungus is so intimate that, the term symbiosis is often applied to it for its description. Lichens form easily distinguishable coloured patches on tree barks, rocks and soil and are universally distributed organisms occurring in varied climatic conditions ranging from the poles to the tropics (Kumar *et al*., 2010).

Despite the understanding of its important roles in the ecosystem, the study of lichens remains quite neglected throughout the world, though they together with mosses form the dominant organisms in ecosystems covering over 10% of the earth terrestrial habitats, particularly at higher elevations (Nash and Egan, 1988). Lichens were the first examples of symbiosis in which the translocation process was demonstrated especially the movement of carbohydrates from algae to fungi. They have evolved with ability to absorb minute concentrations of water from air or dew and become metabolically active within a few minutes, whereas inversely in scorching sunny conditions, they lose water and become dry and crisp within an hour (Negi, 2003). The Mycobiont part of the Lichen form attachment with substratum and also aids in the absorption of moisture, micro and macronutrients for the

photosynthetic partner to grow and in turn synthesize the carbohydrates for their metabolic activity. This constant supply of carbohydrates enables the fungal partner to continuously grow and reproduce, unlike the free living fungi that appear only upon the availability of moisture and nutrients. Lichens traditionally have been considered a type of fungus due to its dominance of the association. Lichens have diversified extensively in the past 600 years, and occur over more than 10% of the terrestrial surface (Hawksworth and McManus, 1989). About 13,500 species are currently accepted and it is estimated that the actual world total will be in the range of 17,000 - 20,000 (Galloway *et al*., 1995). They form an integral and important part of an ecosystem and serve as ecological indicators too. They are included in the lower groups of plants known as the Cryptogams which reproduce by the means of spores and do not produce seeds. It is believed that the algae, which belong to those families of Chlorophyceae and Myxophyceae that lived on dry land and had become aerial before their association with fungi to form lichens (Galloway *et al*., 1995).

The fungal hyphae can combine with a considerable number of different algae, so that, even as regards the algal symbiont, lichens are truly polyphyletic in origin. Two groups of fungi associated with algae forming lichens are; Basidiomycetes found in only a few genera and Ascomycetes which associate with the various algae and form a bulk of lichen families. Though, lichens have no common origin, they are fitted for much longer existence than that of fungi and can persist through extreme climatic changes (Nayaka *et al*., 2003). The main plant body of the lichen is a vegetative portion known as thallus which is comparable to the vegetative portions of other cryptogams such as mosses and liverworts. The fungal component (mycobiont) is an Ascomycete or Basidiomycete which forms a symbiotic relation with green algae or blue green algae (phycobiont). After this association, both the phycobiont and mycobiont components lose their individuality and the lichen behaves as a single organism, both morphologically and physiologically (Nayaka *et al*., 2003). In lichen

thallus (body) the mycobiont predominates with 90% of the thallus volume and provides shape, structure and colour to the lichen with partial contribution from algae and hence, the lichens are placed in the kingdom – Mycota (Nayaka *et al*., 2003). Lichens have highly organized thallus than corresponding non-lichenized Ascomycetes and also produce vegetative structures not known in other fungi (Hale, 1983).

Lichens are characterized by a variety of vegetative structures on the upper and lower surfaces of the thallus. The colour of the thallus, texture (smooth, rough, warty), presence of finger like projections (isidia), granular powder in groups (soredia), fine powder (pruina), black dots (pycnidia) and whitish decorticated areas (pseudocyphellae) are to be noted on the upper surface of crustose and foliose lichens. The colour of lower surface, presence of any pores, presence or absence of rhizomes (root like structures), their colour, distribution, branching, abundance is to be noted on the lower surfaces of foliose lichens (Nayaka *et al*., 2003).

1.2 Vegetative Classification of Lichens

1.2.1 Classification Based On Habitat

Based on the substratum of growth, Lichens can be broadly classified as – Corticolous (growing on the bark surface of trees), Follicolous (growing on the surface of leaves), Saxicolous (growing on rock surfaces), Terricolous (growing on soil) and Musicolous (growing on mosses) (Nayaka *et al*., 2007).

i Corticolous Lichens

These develop on bark and contain fruticose and foliose species These include the species of *Evernia, Parmelia* and *Usnea*. Growth of lichens on tree bark depends on its stability, texture, pH and water retention ability. The rough barked trees encourage Parmelioid and Physioid lichens along with members of *Buellia, Lecanoraceae, Lecideaceae* and *Pertusariaceae*.

The rough bark help lichens in trapping their spores or vegetative diaspores and retains moisture for longer duration (Nayaka *et al*., 2007).

ii Follicolous Lichen

Species like *Calicium, Cyphelium* and *Strigula* occurring on leaves are called as follicolous lichens.The shiny, smooth evergreen leaves in outer canopy, shady understory, in light gaps and near water bodies provide suitable substratum for follicolous lichens (Nayaka *et al*., 2007).

iii Saxicolous Lichen

Lichen communities developed on rocky substratum are called Saxicolous and these vary according to rock type (Nayaka *et al*., 2007). The type of rock and pH are important factor responsible for colonization of the rock by lichen communities. The species like *Caloplecta, Aspicilia* grow on hard lime stones. *Verrucaria* species can be seen on well lit areas. *Lepraria*, *Cystocoleus* community grows on siliceous rocks (Nayaka *et al*., 2007).

iv Terricolous Lichen

The lichens of this community are growing on the ground or soil and often form a dominant component of the ground vegetation in the extreme environments (Nayaka *et al*., 2007).

V Muscicolous Lichen

These lichens grow on mosses, Some species like *Cladonia, Peltigera* grow along with mosses. They prefer the rough and bushy nature of the mosses which are efficient in trapping the lichen propagules. The hygroscopic nature of the mosses provides better water relation and micro-climatic niche to the lichens growing on them (Nayaka *et al*., 2007).

1.2.2 Classification Based On Growth Forms

The growth forms are usually conspicuous on the substrates, forming grey, green or even orange patches and are categorized primarily based on their morphology and size into three major types viz. Crustose (crust like), foliose (leaf like) and fruticose (shrubby) (Negi, 2003).

The lichens belonging to the first category are usually called microlichens and the latter two are referred to as macrolichens (Negi, 2003).

i Crustose Lichens

These types of lichens lack an organized thallus and are closely attached to the substratum. They consist of an indeterminate hyphal mat which entraps and encloses algal colonies. Such rudimentary thalli occur in the lower species of *Calicium, Pyrenula, Trypethelium, Xylographa* and *Arthonia* (Hale, 1983). Majority of crustose lichens like species of *Lecanora* and *Lecidea* grow on the surface of rocks and trees with distinct thallus (Hale, 1983). The surface is often warty or the entire thallus is marked off into many-sided areas or areoles and is therefore spoken of as areolate. The highest stage in development of crustose lichens is squamulose thallus. In this type the individual lobes still lacking a lower cortex become partially free of the substrate (Hale, 1983). Soil lichens like *Cladonia, Catapyrenium*, *Psora* contains this type of thallus.

ii Foliose Lichens

They are also called as leafy lichens. The thallus in this case is loosely attached to the substratum by rhizines with distinct upper and lower surfaces. The thallus is typically divided into branching lobes as in *Heterodermia*, *Physcia*, *Xanthoria*, *Cetraria* and *Parmelias*. The foliose type of lichens merges into the fruticose type in the ascending series and into the crustose type in the descending series (Hale, 1983).

iii Fruticose Lichens (Shrubby)

These are hair like, shrubby, finger like or strap shaped. Here the lichen thallus is attached to the substratum at one point and the remaining major portion is either growing erect or hanging (Hale, 1983). These vary in size from minute *cladonia* spp (only 1-2 mm) high to strands of *Usnea* spp (up to 5 m long). The internal structure is radial with a dense outer cortex, a thin algal layer, a medulla and more or less hollow centre or a dense central cord.

The thallus is round or flattened and richly branched. It is attached at the central or basal point known as the umbiculus, which consists of a hyphal tissue holding the plant firmly attached to the substratum and taking there from moisture and soluble food-substances (Hale, 1983).

1.3 Lichen Ecology and Distribution

The symbiotic relationship helps the lichens to live in variety of habitats and climatic conditions all over the world including extreme environments. Within a climatically uniform region each particular substrate tends to assume eventually a characteristic and often remarkably uniform lichen community (Yuan *et al.*, 2005). They grow in diverse climatic conditions and on diverse substrates. The ability to quickly absorb and retain water from many sources makes it possible for lichens to live in harsh environments like deserts and polar regions, and on exposed surfaces like bare rocks, walls, roofs, tree branches and man-made substrata like glass, metals etc. They occur in virtually every pioneer terrestrial habitat from Arctic and Antarctic to tropical areas and in many desert areas where they are able to form long lived and stable communities (Hale, 1983)

Since preference for habitats and microhabitats is well-developed in lichens, small differences in chemical (pH and mineral contents) and physical factors (light, temperature, humidity, wind, substrate porosity, toughness and roughness) can explain species replacement. Hale, (1983) also studied factors that influence species composition of epiphytic lichens, have concluded that, the most important factor was macroclimatic gradient followed by the spatial variation and substrate variation. Several researches revealed that, the microclimate has a greater influence on establishing epiphytic communities than the substrate, since the phorophyte is a non continuous variable, unlike the environmental ecological variables that usually establish gradients. Hawksworth and McManus (1989) stated that, variations in the presence of corticolous lichens depends more on the physical

nature of the bark than on tree species, thus, analyzed epiphytic lichens in oak forests and found a homogeneous lichen community on the sides in young trees, while on the older trees the community composition on the trunk sides are modified. According to other Scientists, these changes may be related to trunk roughness and micro-climate. The epiphytic community differs more strongly depending on trunk height, although a difference was also found in the trunk communities on trunks of different ages (Ruchty *et al*., 2001).

Thus, therefore the substrate structure and the physical environmental characteristics are among the principal factors affecting lichen distribution on tree trunks. The physical-chemical characteristics of tree bark, such as texture, hardness, water retention, pH, macro and micro nutrient composition are essential for the establishment of the lichen community (Hawksworth and Hill, 1984; Marcelli, 1996). Trees with smooth bark usually present only crustose forms, many of them with a very thin thallus. When the tree begins to age and the bark roughness, increases other forms of lichens appear, such as crustose species with thicker thallus or large foliose species, as well as fruticose ones. Factors such as tree age, exposure to sunlight and dust are of special importance for the kind of lichen community that will colonize tree trunks. Depending on the circumstances, this community may be poorer or richer than that on the twigs. Likewise, it may happen that, in more advanced stages, many bryophytes, especially mosses, form communities over wide areas, occupying the place of lichens (Hale, 1983).

1.4 Mechanism of association in lichens

Lichens are symbiotic organisms composed of a fungal partner (the mycobiont) and a green or blue-green algal partner (the photobiont) (Garty, 1993; Richardson, 1999). Symbiotic interactions are quite extensive and involve nitrogen metabolism, synthesis of secondary metabolites and the transfer of carbohydrates. Regarding lichen reproduction, many mycologists assume that, once a lichen fungal ascospore has contacted a suitable photobiont,

or once a soredium, isidium or lichen fragment has landed on an appropriate surface, a lichen thallus will develop into mature lichen (Ahmadjian, 1990). For germination, the fungal spores of most lichens do not need the photobiont: they are reported to grow and encircle any spherical structures of suitable size, including glass beads or rods (Ahmadjian, 1990). In liquid cultures, however, the isolated fungus is reported to behave partly like yeast, producing large amounts of single cells, whereas the isolated algae show thickened cell walls (Ahmadjian, 1990).

The fungal component may comprise some 75% of the total lichen mass (Richardson, 1999), but hardly anything is known about the precise participations of the symbiotic algae and fungi in metal accumulation (Wastlhuber and Loos, 1996). Most commonly, photobionts are located in a layer within the fungal tissue. (Perry, 2007). The layer is generally oriented in a manner that maximizes photosynthesis, and is protected from rapid changes in water availability. Each cell or group of cells of the photobiont is usually wrapped by hyphae, and in some cases penetrated by a haustorium. Moribund cells may be digested by the fungus, but for the most part, the photobiont remains healthy during the functional period of the symbiosis. The increased size of cells of the photobiont indicates that, reproduction is regulated by the symbiosis (Perry, 2007). This photobiont is found within a layer below the surface of the lichen. Cyanobacteria may also be held in small eruptions of or under the surface called cephalopodia. Cyanobacteria can fix atmospheric Nitrogen, and thus, complement the primary activities of the photobiont, energy fixation. The thallus may be covered by or enmeshed in extracellular matrix expressed by the fungus. For instance, some crustose lichens have a polysaccharide layer on the surface, the photobiont is located at the base of the polysaccharide layer. Polysaccharide layers may also be found within the cortex of the thallus where their function may be different (Baron, 1999). The thallus is commonly interleaved by hyphal layers. Some thalli have hydrophobic layers on the surface or within

the thallus. The hydrophobicity appears to be related to the presence of hydrophobins expressed by the fungus. Indeed, different hydrophobins act in different parts of the thallus. Finally, the lower layer of crustose lichens lack hydrophobic materials, indicating a role in the uptake of water and solutes to the tissue. In fruticose lichens, the central core of stems may be hollow, and may have hyphae oriented in a woven pattern, and the hyphae may be thick-walled and multi-layered. The core may serve a number of functions; including strength and stability (Baron, 1999). The matted anatomy of most lichens is particularly important for uptake and storage of water. Though water can be taken up rapidly, even from condensation at night, water is also lost. Thus the anatomy is closely linked to the functioning of the thallus. Water is necessary for metabolic processes, and in the absence of water, the lichen slows or stops its metabolic processes (Baron, 1999)

1.4 Lichens as Bioindicators

Lichens are increasingly being used as air quality biomonitors (Bartoli *et al.,* 1994) because they have several advantages over electronic monitors. Which are expensive and their use and maintenance are not simple or cheap. They are limited to a few elements or chemical compounds and have no intrinsic relationship with the biological effect of the contaminants (Rodrigo *et al.,* 1999). By contrast, biomonitors are available for free and there are millions of them already functioning throughout the world (Ockenden *et al.,* 1998). They integrally reflect the environmental influence over organisms and can be understood and used by the common citizen with minimal training. (Ockenden *et al.,* 1998).

There is a long history of using lichens as indicators of air pollution (Nylander, 1866; Sernander, 1926; James, 1973; Seaward *et al.,* 1981; Brown and Backett, 1984; Garty, *et al.,* 1988; Sawidis *et al.,* 1995). In tropical regions, poor knowledge of lichen taxonomy does not affect basic biomonitoring because, this method does not require species identifications (Carreras *et al.,* 1998). Air biomonitoring is particularly developed in Europe (Faltynowicz,

1997), where the lichen *Hypogimnia physodes* is used as a standard species (Grüninger and Monge-Nájera, 1988). Lichens accumulate and tolerate metals to a high degree because of their relatively large surface area, and slow growth rate. Because of the lack of cuticle and epidermis, and their poikilohydric nature, accumulation of air borne metals occurs by particle trapping (Olmez *et al.,* 1985), active uptake of anions, passive adsorption of cations and ion exchange (Nieboer and Richardson, 1981).

Generally, there are three categories of lichens -one group of lichen disappear when the pollution starts, the second group are resistance to pollution, and the third group appears when pollution begins (Garty *et al.,* 1985). Most of the fruticose lichens are sensitive (Garty *et al.,* 1985) where as foliose and crustose lichens such as *Cladonia convoluta, C. rangiformis, Neophuscelia pulla, Xanthoparmelia taractica, Xanthoria* sp. etc are resistant species and have also been reported as indicator of copper mining areas in Northern Greece (Chettri *et al.,* 1997b). For decades, lichens have been known as good bio-accumulator for heavy metals and other inorganic air pollutants (Nieboer *et al.,* 1978; Puckett, 1988; Herzig, 1993; Sawidis *et al.,* 1995; Chettri *et al.,* 1997). Application of biomonitors is the one of the suitable method to monitor these metals in Kathamndu, as some crustose and foliose lichens are available in and around Kathmandu (Chettri *et al.,* 1999). There is very close statistical relationship between the accumulated heavy metal contents in lichens and the heavy metal pollution measured in air (Sloof *et al.,* 1988; Herzig, 1993). For example, a remarkable correlation was found between the deposition values and the corresponding accumulation values of exposed samples of *Hypogymnia physodes* in an emission related examination around a Danish steel works (Pilegaard, 1979). It is now well known that the production of geothermal energy may affect the surrounding environment. Excluding geological and geophysical effects, the environmental impact is related to the emission in to the atmosphere of significant amounts of uncondensable greenhouse gases, as well as elements and

compounds of toxicological relevance which may be dangerous to public health (Axtman, 1975; Ármannsson and Kristmannsdóttir, 1992). They can be used as sensitive indicators to estimate the biological effects of pollutants by recording changes at the community or population level, and as accumulative monitors of persistent pollutants, which can be assessed by assaying their trace element content (Ferry *et al*., 1973). The use of lichens as biomonitors of geothermal air pollution from a physiological perspective, there are three specific areas where there is a considerable amount of information available; on the patterns of species distribution in relation to contrasting substrates that have differing ionic environments, on metal ion uptake and on sulphur dioxide substrate interactions.

Kershaw (1984) classified the origin of elements found in lichen thalli as two-fold; particulate atmospheric fallout and ionic solutions drops, the latter delivered as rainfall or as surface runoff. Neiboer *et al.* (1978) indicated a large range in the elemental uptake of lichens that varied according to elemental characteristics of the substrate and environmental factors. The response of lichens to air pollutants is well understood. No one has suggested that lichens are not useful for indicating the effects of air pollutants, to the contrary that, the lichens are reliable indicators of change in emissions effects. Lichen response to pollutants has been questioned, the field is not without challenges to the basic concepts, and most of these are based on a careful assessment. For example, Rydzack (1954) rejected the concept of lichen species response to sulphur dioxide, and proposed that, drought was responsible for major declines in lichen species diversity. However, this was debunked by Coppins (1973), but Nimis (1985) went on to show that, drought and other effects could interfere with a species response to sulphur dioxide.

Air pollution effects theories have been challenged in other venues as well. For example, the concept of forest decline in Europe and North America (Krahl-Urban *et al.* 1988) was challenged and found wanting (Innes, 1992; Kandler and Innes, 1995). The most problematic

issue facing biomonitoring currently is the shift in pollutant character from acidity due to sulphurous compounds to that from nitrogenous compounds. Lichen biomonitoring and bioindication has striven to make lichen bioindication relational to the response of other ecosystem components. For example, Rao and LeBlanc (1966) correlated lichen zonation with soil sulphates concentration around an iron sintering plant at Wawa, Ontario. Their zones of damage corresponded with damage zones to vegetation extending 32 kms from the plant as defined by Gordon and Gorham (1963), including areas where damage to tips of emergence tree crowns were slightly injured by sulphur dioxide.

The consistency of the relationship between sulphur dioxide, lichen response and vascular plants was critically assessed and accepted by Muir and McCune (1988). Due to the concern surrounding air pollution effects in the early 1980's. Richardson (1988) recognized the mistrust on the part of non-biologists toward bioindication and biomonitoring with lichens, but provided ample evidence that lichen bioindication and biomonitoring has been accepted and developed on a variety of scales from local to national (Sloof and Wolterbeek 1991; Murphy *et al*., 1999). Since 1970 - 2000, the number of research dealing with lichen bioindication has increased exponentially and has branched into respected and dedicated air quality journals

1.5 Statement of the problem

Air pollution load is increasing day by day as result of human activities so the need to check mate the atmospheric environment is becoming necessary and there is lack of sufficiently sensitive and inexpensive techniques that permit the simultaneous analyses of many air contaminants (Puckett, 1988). The need of using sensitive lower organism lichens as biomonitors is very necessary although, there are some groups of lichens that become less conspicuous when pollution becomes so persistent (Garty *et al.*, 1985).

1.6 Justification

This research provides information on the presence of pollutants in the atmospheric environment using lichens as biomonitors. This because Air pollution is something that we cannot really ignore now-a-days. This is evident from the moment we step out of our house and are greeted with black coloured smog that hits us directly reminding us that breathing clean air is more of a distant dream. The majority of these come from automotive engines and industries. Since air pollution cause damages to the vegetation and materials on earth apart from damaging the human and animal health, so a high degree of air pollution control is essential (Perry, 2007).

Lichens have been used, accepted, and developed for monitoring of air pollution effects earlier than most other plant groups (Seaward, 1993; Sloof and Wolterbeek, 1991; Murphy *et al*., 1999). Application of lichens as biomonitors of air quality is one of the suitable methods to monitor heavy metals in cities (Adamo *et al.*, 2007). 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).

1.7 Aim

To assess the level of air pollution in some Urban and Peri-urban areas in Kaduna state using Lichens as biomonitors.

1.8 Objectives

1 To identify the common lichen species encountered across the sampled areas.

2 To determine the concentration of some atmospheric pollutants such as Heavy metal (Pb, Mn, Cd, Cr and Zn), SO_2 and NO_3 in lichens found in the various locations.

3. To determine seasonal variability of the level of atmospheric pollutants such as Heavy metal, SO_2 and NO_3 in lichens found in the locations.

3. To determine the suitability and effectiveness of lichens species in pollution monitoring of the sampled area

5. To determine the correlation of atmospheric pollutants with absorbed pollutants in the lichens

1.9 Hypotheses

1. There no significant difference between the diversity of common species encountered in the various locations.
2. There is no significant difference in the concentration of atmospheric pollutants in lichens at the various locations
3. There is no significant difference in the seasonal concentration of atmospheric pollution in lichens in the dry and wet seasons.
4. Lichens species are not suitable and effective in pollution monitoring.
5. There is no significant correlation between atmospheric pollutants and absorbed pollutants in lichens

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Biomonitoring of air pollution

According to Conti and Cecchetti (2001), the use of composite organisms to asses pollution has developed notably during the last few decades. Pollutants from ecotoxicological perspective, they are consider as contaminants or producers of environmental stress. They are also defined as chemical compounds that are released into the environment as a result of human activities, and which cause damage to living organisms (Moriarty, 1999).

2.2 Lichens as Biomonitors of air pollution

Lichens are considered the result of a symbiotic association between fungus and algae. More precisely, the term algae indicates either a cyanobacteria or a chlorophyceae; the fungus is usually an ascomycetes, although on rare occasions it may be either a basidiomycetes and or a phycomycetes (Hale, 1983). In this association, the algae is the part responsible with the production of nutrient, since it contains chlorophyll, while the fungus supplies the alga with water and minerals. These organisms are perennial and maintain a uniform morphology over time. They grow slowly; have a high dependence upon the environment for their nutrition, and differently from vascular plant. Furthermore, their lack of cuticle or stoma means that the different contaminants are absorbed over the entire surface of the organisms (Hale, 1983). As far back as 1866, a study was published on epiphytic lichens used as bioindicators (Nylander, 1866). Lichens are the most studied bioindicators of air quality (Ferry et *al.*, 1973). They have been defined as permanent control system'' for air pollution assessment (Nimis *et al.*, 1989). During the last 30 years, many studies have stressed the possibility of using lichens as biomonitors of air quality in view of their sensitivity to various environmental factors, which

can provoke changes in some of their component and/or specific parameters (Brodo, 1961; Rao and LeBlanc, 1966; Conti and Cecchetti 2001). Indeed many physiological parameters are used to evaluate environmental damage to lichens, such as rate of photosynthesis (Catayud *et al*., 1999) and chlorophyll content (Garty *et al*., 1988; Balaguer and Manrique, 1991). Many studies show a positive correlation between the Sulphur content of lichens and SO_2 present in the atmosphere (Conti and Cecchetti, 2001). Various authors report that, the concentration of chlorophyll *a+b* is altered by vehicular released pollutants (LeBlanc and Rao, 1975; Ronen and Galun, 1984; Carreras *et al*., 1998), and by urban emissions (Conti and Cecchetti, 2001). In general, lichens that are transferred into areas with intense vehicle traffic showed an increase in chlorophyll *a+b* concentration that was proportional to the increase in emission. Such effects are generally caused by traffic emission in particular, sulphur and Nitrogen Oxides. Air traffic, and in particular the effect of kerosene and benzene, seems to have less effect on the lichens population than vehicle traffic. This has been demonstrated in a study of Hamburg airport. Lichens may be used as bioindicators and/or biomonitors in two different ways (Richardson, 1988; Seaward, 1993)

i. By mapping all species present in a specific area (method A)

ii. Through the individual sampling of lichens species and measurement of the pollutant that accumulate in the thallus; or by transplanting lichens from an uncontaminated area to a contaminated one, then measuring the morphological changes in the lichen thallus and/or evaluating the physiological parameters and/or evaluating the bioaccumulation of the pollutants.

2.3 Heavy metals accumulation in lichens

The accumulation of metals in plants depends upon many factors, such as the availability of elements; the characteristic of the plant (lichens), such as species, age, state of health, type of

reproduction, etc and other parameters such as temperature, available moisture, substratum characteristics, etc. Contaminants deposits on lichens through normal and indirect precipitation (Conti and Cecchetti, 2001). This later includes mist, dew, dry sedimentation and gaseous absorption. Indirect precipitation occurs in highly stable atmospheric conditions and contains higher nutriment and contaminant concentrations of different orders of size when compared to normal precipitation (Conti and Cecchetti, 2001).

In general, three mechanism have been put forward with regard to the association of metals with lichens (Richardson *et al* 1995)

1) Intracellular absorption through an exchange process;

2) Intracellular accumulation; and

3) Entrapment of particles that contain metals. (Szczepaniak and Biziuk, 2003).

Many experts have attempted to increase knowledge of this bonding process, that is, the interaction between lichen and metal using various analytical techniques, such as nuclear magnetic resonance, electron paramagnetic resonance, and luminescence. It should however, be noted that knowledge regarding the understanding of the entire process that is responsible for metal absorption and accumulation in lichens is still scarce. A new approach has recently been attempted, where metal− lichen interaction studied by applying micro calorimetric techniques with the aim of obtaining enthalpic measurement data (Szczepaniak and Biziuk, 2003). To carry out these tests and to process the micro calorimetric data, the metal−lichen complexes considered as an overall coordinating agent, given that it is not possible at this time to know which particular molecule is responsible for coordination with metal, considering the equilibrium and the enthalpy trend for *Evernia prunastri*, the following trend has been found; Pb››Zn›Cd›Cu›Cr; which indicates a good correlation between a metal bond

and the enthalpy values in the absorption process (metal uptake). Lichens are also excellent bioaccumulators of trace elements, since the concentration found in their thalli can be directly correlated with those in the environment (Anderson *et al.,* 1978; Sloof and Wolterbeek, 1991; Herzig, 1993). Studies made of transplanted *Evernia prunastri* highlight the fact that the capacity of Pb accumulation expressed as the relationship between the concentration in the latest sample and the initial concentration value, is 10.2 in the Fontainebleau site (france), 3.7 for the Wurzburg site (Germany); and 4.4 for the city of Rome (Italy); (Bartoli *et al*., 1994). In Italy, different biomonitoring studies carried out using lichen have shown that Pb is still very widespread in spite of introduction of lead free petrol. This indicates that high levels of this metal are still released (and/or suspended) by vehicle traffic (Monaci *et al.,* 2000). Vehicular traffic seems to be the main source of atmospheric Cr, Cu and Pb in the central Italian sites (Loppi *et al*., 1998). The direction in this pollutant are transported by the wind is most surely fundamental in determining their main fallout points (Nimis *et al.,* 1985) correlates pollution from an industrial pole. (Northern Italy) with that at a distant agricultural centre, situated in the predominant wind direction.

It well known that heavy metal content in lichen thalli tend to alternate over time in phases of accumulation and subsequent release. The causes of these differences may lie in the incidence on this phenomenon of acid rain. Conti and Cecchetti (2001) indicates that the periodic release of Pb that occur in lichens may depend upon lixiviation induced by acid precipitation. Heavy metals do in any case, influence water loss in lichen thalli, and the accumulation effect of Pb, Cu and Zn on water loss, after absorption of a mix of metals in solution has been observed in the laboratory (Chettri *et al*., 1997b). Altitude seems to play an important role in Pb and Cd concentrations as studied in *Hypogymnia physodes* (Krahl-urban *et al.,* 1988). The concentration of both increase in linear as altitude increases, except that Cd increase up to 900- 1100m. In general, the higher amount of heavy metal in the thallus found after summer

period, may be due to the increased hydration that results from autumn rainfall (Nieboer *et al.,* 1978). In Nigeria Cadmium (Cd) concentrations in lichen samples ranged from 0.001 to 0.092 μg g^{-1} with a mean concentration of 0.027 ± 0.031 μg g^{-1}. The concentrations of Cd of 0.05 – 0.70 μg g^{-1} have been reported in related studies in other regions in Nigeria (Onianwa and Ajayi, 1987). Several studies have reported varying concentrations of Cd in lichen samples. Examples; 0.027±0.02 (Aniefiok *et al.,* 2014), 0.10+0.64 (Uluozlu *et al.,* 2007). In (Aniefiok *et al.,* 2014), the highest concentration of Cd of 0.092 μg g^{-1} obtained at Ikot Udoma can be attributed to anthropogenic activities such as combustion of fossil fuels and emissions from motor vehicles (Uluozlu *et al.,* 2007), metal works and waste burning (Aksoy *et al.,* 2010). The concentrations of Cd were not significantly correlated with concentrations of other metals. Plants from unpolluted natural environments contain 0.01 – 0.3 μg g^{-1} Cd (Allen, 1989) and ambient air usually has a low concentration of Cd in particulate form (Nordberg *et al.,* 2007). The concentrations of Cd measured in Nordberg *et al.,* (2007) study are within the range of values obtained in similar studies in the developed countries like United State of America (U.S.A) and Europe.

Chromium (Cr) concentrations in lichen and moss samples ranged from 0.004 to 8.793 μg g^{-1} with a mean concentration of 3.155 ± 2.284 μg g^{-1}. The highest concentrations of Cr were observed in rural settlement at Ikot Odiong (8.793 μg g^{-1}) and Ikot Obio Amana (8.654 μg g^{-1}) compared to the lowest concentration of Cr of 0.004 μg g^{-1} measured at Atabong Road, which is an urban site with high anthropogenic activities. The highest concentrations of Cr at these rural sites are attributed to long–range transport of trace metals in ambient aerosols (Onianwa, 2000) and local point sources such as a metal works, automobile workshop and wastes incineration located near the sampling sites. In addition, aerial fallout of windblown dust contribution from metal corrosion and soil of the study area might have increased the contamination load of the surrounding atmosphere. Several studies have

reported varying concentrations of Cr in lichen and moss samples. Examples of the concentrations of Cr in lichen and moss samples obtained from other studies include 1.4 μg g^{-1} (Grodzinka *et al.*, 2003); 1.60μg g^{-1} (Mendil *et al.*, 2005); 3.6 μg g^{-1} (Riget *et al.*, 2000); 1.6μg g^{-1} [Loppi *et al.*, 2000]; 111μg g^{-1} (Pandey and upreti, 2000); 1.20μg g^{-1} (Uluozlu *et al.*, 2007]; 1.00μg g^{-1} (Abdullahi *et al.*, 2012), and 0.07μg g^{-1} (Aksoy *et al.*, 2010).

Manganese (Mn) concentrations in lichen samples ranged from 10.530 to 153.320 μg g^{-1} with a mean concentration of 73.962 ± 43.737 μg g^{-1}. The concentrations of Mn in lichen samples were still at background levels at most of the sampling sites. The elevated concentrations of Mn were measured at samplings sites in the urban areas compared to the rural areas. In urban and rural areas without significant manganese contamination, annual averages of manganese concentration are mainly in the range of 0.01 – 0.07 μg m^{-3} (WHO, 2000). Several studies have reported varying concentrations of Mn in lichen and moss samples. Examples of the concentrations of Mn in lichen samples obtained from other studies include 93.00μg g^{-1} (Onianwa and Ajayi, 1987); 3.91μg g^{-1} (Jazwik 1990); 22.70μg g^{-1} (Mendil *et al.*, 2005); 57.30μg g^{-1} (Jeran *et al.*, 2002); 25.80μg g^{-1} (Uluozlu *et al.*, 2007), and 9.50 μg g^{-1} (Abdullahi *et al.*, 2012). The concentrations of Mn in the ambient air in the rural areas are probably reflecting the contribution of vegetation inputs (Abdullahi *et al.*, 2012). However, it is known that, Mn toxicity limits in plants are in the range of 400 – 1000 μg g^{-1} (Zhu *et al.*, 2011). The atmospheric deposition of Mn is associated with local and/or anthropogenic activities in the urban areas and the distribution of Mn is more regional compared to Zn. Lead (Pb) concentrations in lichen samples ranged from 0.001 μg g^{-1} with a mean concentration of 3.149 ± 4.488 μg g^{-1}. The concentrations of Pb in lichen and moss samples were still at control levels at most of the sampling sites (Aniefiok *et al.*, 2014). The highest Pb concentrations of 16.70 μg g^{-1} were measured at the urban sites with the highest

vehicular traffic density, frequent traffic queues and various anthropogenic activities. The background concentrations of Pb of 5.00 μg g^{-1} have been reported in few related studies in other regions in Nigeria (Onianwa and Ajayi, 1987). Several studies have reported varying concentrations of Pb in lichen and moss samples. Examples of the concentrations of Pb in lichen samples obtained from other studies include; 1.06 μg g^{-1} (Riget *et al.*, 2000); 27.30 μg g^{-1} (Jeran *et al.*, 2002); 11.00 μg g^{-1} (Grodzinka *et al*., 2003); 4.03μg g^{-1} (Uluozlu *et al*., 2007); 2.80 μg g^{-1} (Abdullahi *et al*., 2012), and 3.10 μg g^{-1} (Aksoy *et al*., 2010).

Zinc (Zn) concentrations in lichen and moss samples ranged from 23.530 μg g^{-1} with a mean concentration of 61.948 ± 20.883 μg g^{-1}. The concentrations of Zn in lichen samples were also at elevation levels in most of the sampling sites. The highest concentration of Zn of 130.60 μg g^{-1} was obtained at Atabong Road, an urban site with high vehicular traffic density, frequent traffic queues and other local anthropogenic activities (Aniefiok *et al.*, 2014). The elevated concentrations herein reported at most of the sampling sites in this study are higher than Zn concentration of 9 – 15 μg g^{-1} reported for the Olympic and Mt. Rainier National Park, Washington, U.S.A. (Frenzel *et al.*, 1990). The background Zn concentrations of 26.30 – 153.00 μg g−1 have been reported in South West region of Nigeria (Onianwa and Ajayi, 1987). Several studies have reported varying concentrations of Zn in lichen and moss samples. Examples of the concentrations of Zn in lichen samples obtained from other studies include; 6.48 μg g^{-1} (Reget *et al.*, 2000); 37.00 μg g^{-1} (Loppi *et al.*, 2000); 35.00 μg g^{-1} (Pandey *et al.*, 2002); 39.00 μg g^{-1} (Grodzinka *et al.*, 2003); 23.70 μg g^{-1} (Mendil *et al.*, 2005); 14.50 μg g^{-1} (Uluozlu *et al.*, 2007); 8.70 μg g^{-1} (Abdullahi *et al.*, 2012), and 23.50 μg g^{-1} (Aksoy *et al.*, 2010). Although the normal concentrations of Zn in plants are in the range of 10 – 100 μg g^{-1} (Allen, 1989) , concentration of Zn in lichens > 100 μg g^{-1} is an indication of environmental contamination (Adamo *et al*., 2003).

Satya and Upretti (2015) also investigated the concentration of micro-elements contents (Mn, Cu, Zn, Cr, Fe, Ni, Pb) to determine the influence of traffic load on distribution pattern of micro-elements, which were accumulated by *Ramalina sophodes* in the study area. The data represented that, the sites having high-traffic load, shows maximum concentration of six micro-elements (Mn, Zn, Cr, Fe, Ni and Pb) except Cu. The study indicated that the concentration of Fe was found highest (1152.56 μg g^{-1} to 4962.86 μg g^{-1}) in comparison to other micro-elements. Some reports showed that traffic activities increases the Fe concentration on roadside soil (Monaci *et al.*, 2000). However, according to him Pb is second most accumulated element (492.76 μg g^{-1}). High level of these elements may be attributed to industries like Tanneries, Fertilizers, Paints as well as traffic load. The average value of Mn content obtained by Monaci *et al* (2000) ranged from 43.44 to 103.14 μg g^{-1}. The site 1 and 2 were located close to major motor vehicle traffic manifested the highest level of Mn having 103.14 μg g^{-1} and 95.81 μg g^{-1}, respectively. Motor vehicles are known to be a source of Mn in urban areas (Monaci *et al.*, 2000). The highest level of Zn in the *Ramalina sophodes* was found in the site-1 (53.83 μg g^{-1}), then site-2 (32.71 μg g^{-1}) and site-3 (31.00 μg g^{-1}). Zn belongs to a group of trace metals, which is essential for the growth of humans, animals & plants and is potentially dangerous for the biosphere when present in high concentrations (Gowd *et al.*, 2010).

The vehicular traffic and industrial emissions are supposed to be the main source of Zn in the study area. Romic and Romic (2003) reported that, the main sources of the Zn pollution are industries and the huge of liquid manure, composted materials and agro chemicals such as fertilizers and pesticides in agriculture. The present study is presented to 300 tanneries along the bank of river Ganga. It is a prominent center for leather processing, especially for the manufacture of saddler products (Gupta *et al.*, 2011). The Cr content was correlated with industrial as well as traffic influence. The Cr concentration was found highest at the site-1

with 13.22 µg g^{-1}. However, it was observed that the average concentration of Cr in *Ramalina sophodes* was decreased with the increase of distance from the road site. Similarly, Aslam *et al.* (2011) reported that, the concentration of total Cr in soil was decreased with the increase of destination from the road side. In the recent study shows that, the higher concentration of Pb was recorded in traffic area. The increase in Pb concentration in traffic/urban area is probably confirmed by the amount of this metal deriving from the exhaust gases. A notably higher Pb concentration was also characteristic of the industrial sites (Biolonskan and Dayan, 2005). Site-2 with maximum human activities, together with motor garage, high vehicular density congestion showed the highest Pb level with the value of 492.76 µg g^{-1}. Cansaran -Duman *et al.* (2009) concluded that maximum concentration of Pb indicated highest vehicular density. The results of the present study indicated that the accumulation patterns of macroelements Some industrial activity in and around the city sites may also have a contribution to the urban pollution. Highest concentration of Mn, Zn, Cr, Fe, Ni and Pb content at highly polluted areas are directly indicated that the city is suffering from vehicular emissions. On the other hand, it is possible to differentiate the effect of traffic released pollutants on the different studied sites, which helps raise the issue of the need to carry out better controls on the quality of the air in our country, as well as to control the level of pollutant emissions in the vehicles circulating.

2.4 Sulphur compounds accumulation in lichens

The effect of sulphur compound on lichens have been extensively studied. For indeed many studies are generally concerned with the effect of SO_2 fumigation of exposed lichens (Gries *et al*., 1995),or with the effect of simulated acid rainfall (Tarhanen *et al.,* 1998). Other works deal with respiration rate, Photosynthesis and chlorophyll fluorescence (Deltoro *et al*., 1999). For the most part,these studies aim to evaluate the effects of sulphur compound on the physiology of lichen thalli and/or the integrity of photobiont chlorophyll. Chlorophyll

analysis is usually carried out following the method proposed by Ronen and Galun (1984). Phaeophytin is a product of chlorophyll degradation. The variation in the normal chlorophyll-phaeophytin ratio is an indication of suffering in lichens. and this is considered to be an appropriate index for measuring the impact of high concentration of SO_2 in lichens , or for evaluating the effect of heavy metals pollution in transported lichens (Garty, 1987). Any reduction in this value indicates chlorophyll degradation with ensuing stress to the organisms. Gonzales *et al.* (1998) report a value of 1.44 for the Chl/Ph ratio of *Ramalina duriaei* in the control site, while for a polluted site with high level of vehicle traffic, that found a value of 0.80. In general, an alteration of the Chl/phaeophytin ratio has been found, indicating the toxic effect of a combination of gaseous and non-gaseous pollutants.

Sulphur content is determined by transforming molecular sulphur into SO^{+}_{4} ions, which occurs through the acid suspension method using Barium chloride expressed in mg-1 dry weight. Also Some authors (Gonzalez *et al*., 1998; Carreras *et al*., 1998) report that data relating to sulphur accumulation and obtained indirectly from the bioindicator, seem to show that, the influence of SO_2 from industry (cardoba, Argentina), is rather restricted compared to that, which comes from vehicle traffic. Sensitivity to SO_2 and to other atmospheric pollutant in general, varies according to species, *Lobaria pulmonaria* is considered to be one of the most sensitive species according to the scale of Hawksworth and Rose (1976); 30 µg m^{-3} for average winter concentration of SO_2. This species high degree of sensitivity is probably due to the present of vegetative structure on the upper surface of the thallus and which plays a role in asexual reproduction. The isidia increases the absorption surface of thallus per unit of mass (Conti and Cocchetti, 2001). *Hypogymnia physodes* is on the contrary, a species that is particularly resistant to SO_2, indeed, it has been seen that its exposure to H_2SO_4 in highly acid condition, produces no effect (Garty *et al.*, 1995). *Hypogymnia physodes* has also been used in the area surrounding the fertilizer plant in Finland, where sulphur level of 3000 ppm had

been found (Palomaki *et al.*, 1992). Typical ultra structure damage caused by the action of sulphur on photobiont cells is seen within the first two weeks of the transplant. Without the sulphur concentration levels being particularly high.

Another interesting field of research is that which correlates sulphur content and the composition of sulphur isotopes (Takala *et al.*, 1991). A study report the spatial variation of the sulphur isotope composition of 83 epiphytic lichen samples (Conti and Cocchetti, 2001). The study reveals a positive correlation between isotope composition and different sources of sulphur emission in the site under study. It is interesting to note the fact that lichens are also sensitive to the sulphur salts that come from sea. Indeed the degree of sulphur concentration has been seen to cause decrease in lichens. The role of sugars in alga-fungus interaction is most important in lichen biology. Chronic SO_2 fumigation of lichens may cause interference in the flow of such nutrient as carbonhydrate, thus creating damage to symbiont. SO_2 causes reducing sugar to increases and non reducing sugars to decrease; this effect is probably due to a breakdown in the polysaccharide that are rich in reducing sugars.

Spectroscopic measure, carried out to study changes in the spectral reflectance response of lichen thalli have been exposed in contaminated sites as against those exposed in control sites (Garty *et al.*, 1997). In spectra of lichens transplanted to contaminated side, the red edge (700 nm) is much less pronounced and the plateau is very low. This indicates a clear situation of organisms stress (Garty *et al.*, 1997). In extreme cases, for example in plant that are subjected to high stress level, or which are already dead, the spectrum shows a continuous lines that rises gradually. Membrane protein are damaged by the present of SO_2, which may cause a reduction in protein biosynthesis in some lichens, or there may be negative effect on the nutritional interchange between symbionts with, as a consequence, an alteration of their delicacy balance. The structural protein found in cells membranes and the lichens enzymes

can have considerable damage in the presence of high level of SO_2 concentration, this process concern the delicate interchange of nutrient between symbiont and can damage the delicate equilibrium of the association. Thus, the damage to cell membrane can be used as an indicator of environmental stress. Indeed it has been demonstrated that SO_2 such as O_3 and NO_2 are powerful catalyst of lipid membrane peroxidation (Gonzalez *et al.*, 1998). Experiment where lichens were exposed to 1 ppm of SO_2 in aqueous solution show a slight reduction in the overall content of phospholipids and an increase in unsaturated fatty acids, this later type of response to SO_2 may considered to be of the adaptive type (Conti and Cocchetti, 2001).

The effect of SO_2 can also be evaluated by dry weight/fresh weight ratio. This ratio has been proposed an indication of the influence of the environment on the bioindicator, it has indeed been observed that in highly polluted areas (e.g. where traffic is intense), there is a tendency in lichen to lose moisture (Takala *et al.*, 1991). Finally the production of ethylene is another indicator of stress in lichens. Lichens exposed to solution containing sulphur in an acid environment have different levels of ethylene production, in general, these solution increases the solubility of particles containing heavy metals that are trapped within the hyphae. This phenomenon may lead to an increase in production of endogenous ethylene in lichen when they are exposed to chemical agents containing sulphur, to acid rain and to their polluted environment with heavy metals (Garty *et al.*, 1995).

2.5 Nitrogen compounds accumulation in lichens

Although lichens have already been proposed as bioindicators of Ammonia (NH_3) (De bakker, 1998). only in the last two years has a clear positive correlation have been established between nitrophytic lichens and atmospheric NH_3 concentration; even if responses are always greater to SO_2, Tree bark analyses in sites in Holland demonstrate that Nitrophytic lichen

species do not response directly to nitrogen level found in the environment but that they are favoured by the high pH value in the bark, which are related to the high level of NH_3 in the environment (van Dobben and Ter Braak, 1998). *Clardonia portentosa* is an excellent bioindicator for the study of precipitation chemicals and nitrogen. Hyvarinen and Crittenden (1998) have found concentrations in the range of 0.08-1.82% for nitrogen and 0.04-0.17% for phosphorous (per unit of dry weight) in apex (5 mm top part) and thalli (bases) in various comparison sites. The concentration levels found for this element are 2-5 times higher in the apex than in bases and furthermore, both the apex and bases part show a high positive correlation between elements. The correlation between Nitrogen deposition and Nitrogen accumulated in the lichen are positive; becoming higher when referred to concentrations found in the thalli rather than in the apex. On the other hand nitrogen concentrations in the thallus are little correlated with the N value in precipitation. The nitrogen found in the thalli is however highly linked to moist nitrogen deposit, but it is also correlated positively with the NO_2 present in the air, as well as *Cladonia potentosa, Hypogymnia physodes* has also been proposed as bioindicator of Nitrogen total deposit (wet and dry) (Jeran *et al.,* 2002).

High level of SO_2 and NO_2 can cause reduction of pH of lichen thalli, to this respect, it shall be highlighted that atmospheric pollution of this kind has led to the reduction of *Lobaria pulmonaria and Ramalina farinacea.* The measurement of the pH lichen thallus surface can supply information with regard to the state of pollution of a site. Various authors report that *Lobaria pulmonaria* is endangered in some sited subject to acid rain and pH=5 has been indicated as a treshold value below which lichen is unable to survive (Gilbert *et al.,* 2007).

CHAPTER THREE

3.0 MATERIALS AND METHOD

3.1 Locations and description of the study areas.

3.1.1 Selected Areas in Kaduna State

The following areas were chosen for the study

1. Rido village (7º25″8.434″E, 10º24″43.224″N) is located in Chikun Local Government area, Kaduna state.
2. PZ, Zaria (7º43' 16.395″E, 11°6' 9.986N) is located in Sabon Gari Local Government Area, Kaduna State.
3. Buruku village (6°56' 53.399″E, 10º 41' 8.463″E) village is located at Kaduna – Birnin Gwari road and is also under Chikun local Government area, Kaduna state.
4. Botanical Garden, Ahmadu Bello University, Zaria (7º 37' 56.239″E, 11º 9' 52.169″N) is also under Sabon Gari Local Government area, Kaduna state. (figure 1)
   (GPS model 010 – 01534 – 01)

3.2 Criteria for selection of study areas

Rido village: This was chosen due to its proximity to the Kaduna Refining and Petrochemical Company (KRPC) and there is high traffic of heavy trucks conveying petroleum products, a highly polluted area (HPA),

Buruku village: This is local area with significant amount of heavy truck shuttling from northern to south western part of Nigeria and its proximity to dumping site. Considered to be least pollution area (LPA).

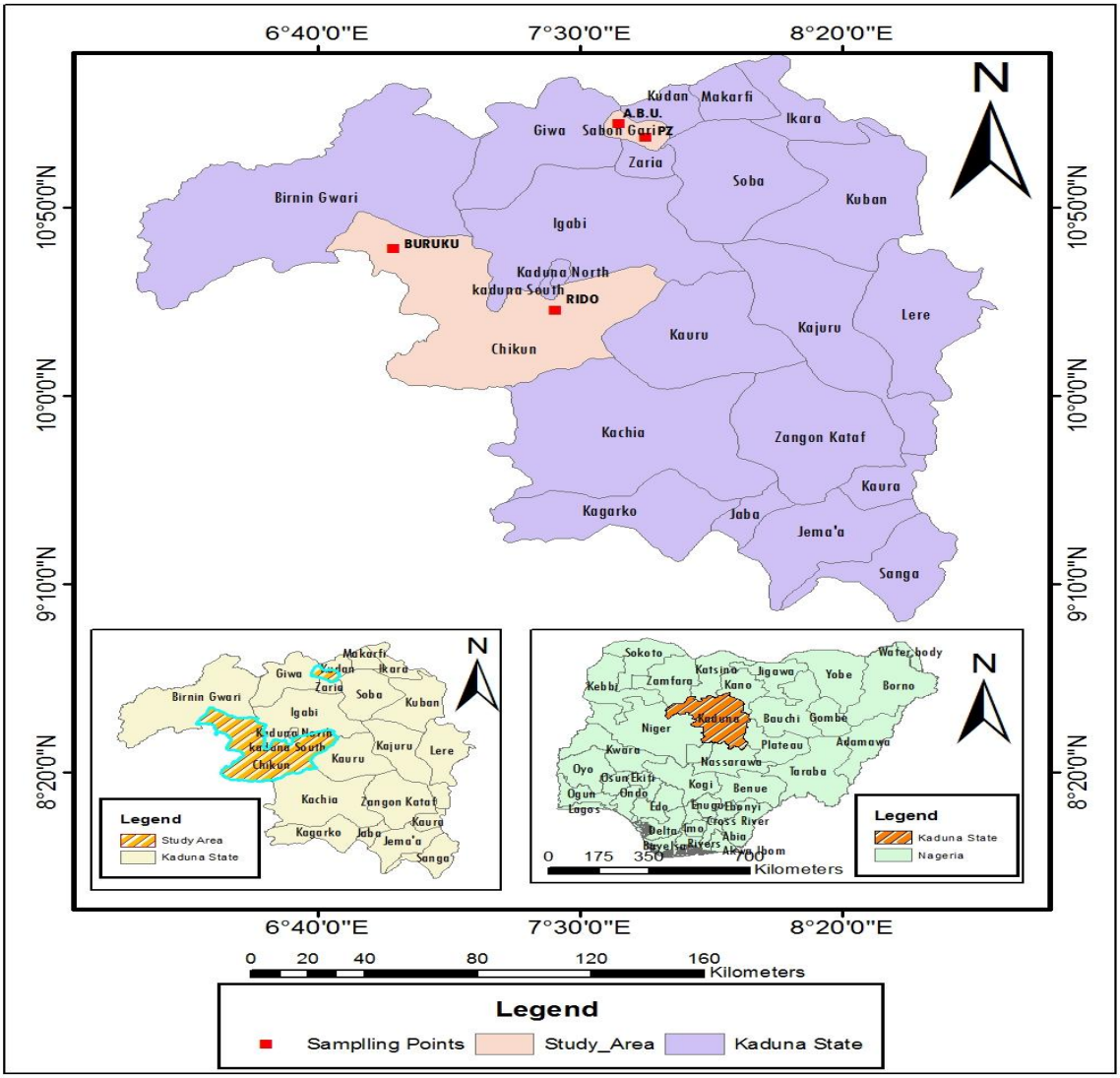

Figure 1; Map of Kaduna state showing the study areas

PZ areas: This is commercial area with higher traffic density, is considered to be High pollution area (HPA)

Botanical garden, Ahmadu Bello University was used as a control, Botanical garden can be said to be pollution free and naturally conserved, with little anthropogenic human activities, except for educational purposes, this is Considered to be Non pollution area (NPA)

3.3 Sample collection

Lichen distribution is directly influenced by substrate nature, moisture content and sunlight availability. All available substratum and habitat at each reference site were carefully examined, sufficient amount of lichen species were removed directly from the substrate. Lichen sampling was carried out during wet season (three months ie; July, August and September 2014) and dry season (three months ie; January, February and March 2015). For each month lichen sample was collected from three sites in the location selected. The lichen samples were collected within the range of 2 to 8m high from the ground of the trees. And the samples were collected in plastic bags and taken to the laboratory for further analysis, such as identification of samples and determination of target pollutants. Samples were taken to Herbarium in the Department of Biological Sciences Ahmadu Bello University Zaria for identification. The lichens was identify using 'key to nature' Natural history museum (Pieri *et al.,* 2009) with the help of expert in Taxonomy.

3.4 Location of the study site

Sites selected in each area were located up to 300 meters from main roads and densely traffic areas, and were more widely located (ie, above 300 meters) in industrial areas like Kaduna Refining and Petrochemical Company (KRPC). This is to avoid collection of samples from areas suspected to be of low deposition of heavy metals, and also to avoid collection of

samples from areas of pollution sources which will give no desire result. Three sampling sites were selected at each sample location from which collection was made.

3.5 Sample preparation

The collected lichens samples were prepared according to Chettri *et al.,* (1997) for metal analysis. Lichen samples were thoroughly cleaned, followed by washing the external surface in running distilled water. Representative samples for each sampling site were washed with deionized water and shade dried for two weeks. The dried lichens were then ground in a hand mill (using mortar and pestle) to a uniform size by sieving through a 2 μm sieve.

3.6 Determination of heavy metals

Heavy metals determinations were carried out at Multi-user Research Laboratory, Ahmadu Bello University, Zaria. A mass of 1g of each lichen sample were weighed into a flask and 21 ml of 6:1 mixture of concentrated Hydrogen trioxonitrate (HNO_3)and 15 % of hydrochloric acid (HCl) was added. The mixture was gently heated to 80^{o}C and then the temperature was raised to 150^{o}C to achieve complete dissolution. Representative samples were wet digested in Hydrogen trioxonitrate (HNO_3) and the heavy metals (Pb, Cd, Cr, Mn and Zn) were measured in the digest using Atomic Absorption Spectrometry (AAS) according to the procedure of Sawidis *et al.* (1995) and Chettri *et al.* (1997). Quantitative analysis of the samples was carried out using Sequential Atomic Absorption Spectrometry (Varian AAS 240FS)

3.7 Determination of NO_3

Determination of Nitrogen (v) oxides (NO_3) was carried out at Soil Science Laboratory, Department of Soil Science, Ahmadu Bello University, Zaria. Phenoldisulphate acid method (APHA, 2005) was used to measure nitrate- nitrogen in the sample. About 50mls of the

sample was evaporated to dryness and 1ml of Phenoldisulphate acid added to the residue. This was left to stand for 10minutes, before 10ml of distilled water was added to it until the residue was completely dissolved. Then 5ml of 0.12N potassium hydroxide was added to the solution, this was again diluted with distilled water to 50ml, and a yellow colour was formed. the absorbance of the yellow coloured was measured using Hach Spectrophotometer model DR/890 at 493.

3.8 Determination of SO_2

Determination of Sulphur dioxides (SO_2) was carried out at Soil Science Laboratory, Department of Soil Science, Ahmadu Bello University, Zaria. According to Chettri *et al.,* (1997) a mass of 1g of each lichen sample was weighed into a flask and 21 ml of 6:1 mixture of concentrated Hydrogen trioxonitrate (HNO_3) and Hydrochloric acid (HCl) was added. The mixture was gently heated to 80^oC and then the temperature was raised to 150^oC to achieve complete dissolution. Sulphur dioxide (SO_2) was determined according to (APHA, 2005) at 420nm using Bosch and Lomb Spectronic -70.

3.9 Statistical analysis

The Mean values of the pollutants such as heavy metals, NO_3 and SO_2 at the period of sampling for all locations and for all lichens species were calculated. Seasonal variability in the values of the pollutants was determined using t-test. Data obtained was analyzed statistically using analysis of variance (ANOVA) to test the differences in individual concentration in each species found in the different locations. Duncan's multiple range test (DMRT) was used to separate the means where there is significant differences. Statistical Package for the Social Science (SPSS) version 19.0.0.247 (2016).

CHAPTER FOUR

4.0 RESULT

4.1 Lichens species diversity in the study areas

Five lichens species were found; the most common species were foliose and fruticose forms. Tree Trunks contain the large number of foliose species.(see plates 1-5) in Appendix I

i, *Dictyonemma glabratum;* a fruticose lichen is formed by the symbiosis between cyanobacteria and basidiomycete fungi. It is also known as Basidiolichens. It was collected from ABU Botanical garden, during dry season.

ii, *Flavoparmelia caperata:* a foliose lichen was collected from Rido during the dry and wet seasons and Buruku during wet season. Medium to large foliose lichen that has a very distinctive pale yellow green upper cortex when dry. The rounded lobes, measuring 3–8 mm (0.1–0.3 in).

iii, *Physcia* spp: also foliose lichen. This was discovered and collected from PZ area and Buruku village during dry season.

iv, *Phaeophyscia sp* (Neck.) Moberg: this was collected from PZ area during wet season. Presence of closely pressed narrow radiating lobes, variable in colour (grey, green-grey to brown, green when wet). Widespread on nutrient-enriched bark and other surfaces, tolerant of Nitrogen pollution they are foliose that normally colonize rough bark of the old trees. Thallus foliose, often forming rounded colonies with evenly radiating lobes, light to dark or brownish grey, green when wet, soralia rounded and convex, mostly laminar, but narrower and marginal towards the periphery of the colony, lower medulla white, orange pigment sometimes developing in the soralia and on damaged areas of cortex, apothecia infrequent,

with rather thick, smooth margins and dark discs. Widespread and common on bark, walls and concrete.

V. *Xanthopermelia spp:* this was found in and around the ABU Botanical garden during wet season. The summary of all these are shown in (Table 1).

4.2 Heavy metals pollution load in lichens from sampled areas

The heavy metals concentration in all lichens species collected from all the study areas. Significant difference are taken as $P \leq 0.05$. Pb concentration in lichens species ranged from 0.098 – 0.279ppm *Phaeophyscia* spp collected from PZ area recorded the higher concentration (0.279ppm) while the lower concentration (0.098ppm) was recorded in *Physcia* spp collected from Buruku. Mn concentration in lichens ranged from 0.642 – 3.839ppm for the *Dictyonema glabratum* 0.642ppm the lower and *Flavoparmelia caperata* 3.839ppm the higher collected from Botanical garden and Buruku respectively. The concentration of Cadmium (Cd) ranged from 0.010 – 0.025ppm both lower and higher concentration was recorded in *Physcia* spp collected from PZ area and Buruku respectively. Cr concentration ranged from 0.208 – 0.329ppm for the *Flavoparmelia caperata* (0.208ppm) collected from Buruku and *Xanthoparmelia* spp (0.329ppm) from Botanical ABU, and there is significant difference within the range. Zn concentration in lichens spp also ranged from 0.069 – 0.439ppm it was recorded in *Physcia* spp collected from Buruku as (0.069ppm) and PZ area

as (0.439ppm) respectively. (See table 2)

TABLE 1: LICHENS SPECIES FOUND IN FOUR LOCATIONS IN KADUNA STATE

		LICHENS SPECIES			
LOCATIONS	**DESCRIPTION**	**WET SEASON**	**DESCRIPTION**	**DRY SEASON**	**DESCRIPTION**
PZ	HPA	*Phaeophyscia spp*	Foliose	*Physcia spp*	Foliose
ABU	NPA	*Xanthoparmelia spp*	Foliose	*Dyctyonema glabratum*	Fruticose
Rido	CPA	*Flavoparmelia capirata*	Foliose	*Flavoparmelia capirat*	Foliose
Buruku	LPA	*Flavoparmelia* capirata	Foliose	*Physcia species*	Foliose

Keys: HPA: High pollution area, CPA: Controlled pollution area, LPA: Least pollution area, NPA: Non pollution area

Table 2: MEAN CONCENTRATION OF HEAVY METALS, IN LICHENS SPECIES COLLECTED FROM FOUR LOCATIONS IN KADUNA STATE

		Heavy metals concentration (ppm)					
Lichens	**Locations**	**Pb**	**Mn**	**Cd**	**Cr**	**Zn**	**Mean**
Physcia spp	PZ Area	0.261 ± 0.030^{a}	1.199 ± 0.376^{bc}	0.010 ± 0.003^{b}	0.303 ± 0.022^{ab}	0.439 ± 0.107^{a}	**0.44± 0.11**
Phaeophyscia spp	PZ area	0.279 ± 0.047^{a}	1.463 ± 0.351^{bc}	0.013 ± 0.002^{bc}	0.327 ± 0.043^{a}	0.314 ± 0.065^{ab}	**0.48 ± 0.10**
Dictyonema glabratum	ABU	0.179 ± 0.013^{b}	0.642 ± 0.178^{c}	0.020 ± 0.004^{a}	0.315 ± 0.018^{a}	0.190 ± 0.024^{bc}	**0.26 ± 0.05**
Xanthoparmelia caperata	ABU	0.178 ± 0.009^{b}	2.117 ± 0.358^{b}	0.019 ± 0.000^{ab}	0.329 ± 0.010^{a}	0.099 ± 0.013^{c}	**0.55 ± 0.08**
Flavoparmelia caperata	RIDO	0.132 ± 0.024^{bc}	0.816 ± 0.200^{c}	0.020 ± 0.000^{a}	0.323 ± 0.027^{a}	0.184 ± 0.058^{bc}	**0.29 ± 0.06**
Flavoparmelia caperata	RIDO	0.134 ± 0.009^{bc}	0.845 ± 0.173^{c}	0.022 ± 0.002^{a}	0.230 ± 0.048^{ab}	0.180 ± 0.073^{bc}	**0.28 ± 0.06**
Physcia spp	BURUKU	0.098 ± 0.009^{c}	1.689 ± 0.249^{bc}	0.025 ± 0.002^{a}	0.211 ± 0.029^{b}	0.069 ± 0.008^{c}	**0.42 ± 0.06**
Flavoparmelia caperata	BURUKU	0.142 ± 0.009^{bc}	3.839 ± 0.658^{a}	0.023 ± 0.002^{a}	0.208 ± 0.035^{b}	0.090 ± 0.012^{c}	**0.86 ± 0.14**
Mean		**0.17 ±0.02**	**1.57±0.32**	**0.02±0.00**	**0.28±0.03**	**0.19±0.05**	
P-value		**0.000****	**0.000****	**0.000****	**0.013***	**0.000****	

Note: Value are express as mean ± SE (Standard error) mean with different superscript down the column are significantly different at p≤0.05

***Highly significant diferent **highly significant, *significant**

The concentration of heavy metals in all the study areas for the two seasons, The value of Lead (Pb) ranged from 0.100 – 0.300ppm, Manganese (Mn) ranged from 0.800 – 3.500ppm, Cd ranged from 0.010 – 0.030ppm, Cromium (Cr) ranged from 0.200- 0.300ppm, and Zinc (Zn) ranged from 0.070 – 0.500ppm, and the values are significantly different at $p \leq 0.05$. The locations with highest and lowest concentration of individual heavy metals are shown in (Figure 2-6) which state that, PZ area is significantly higher in lead (Ld) and Zinc (Zn) concentration. Buruku is significantly higher in Manganese Mn and Cadmium Cd while there is no significant difference among location in Chromium Cr concentration.

For the mean monthly variation of heavy metals accumulation from January to September irrespective of locations shows in (Table 3) where the values of Pb ranged from 0.145 – 0.203ppm, Mn ranged from 0.934 – 2.622ppm, Cd ranged from 0.017 – 0.022ppm, Cr ranged from 0.284 – 0.300ppm, and Zn ranged from 0.125 - 0.318ppm. In January heavy metal accumulation recorded Mn with highest deposition in all the locations with 1.799±0.297ppm and Cd is reported with lowest deposition in all the locations with 0.019±0.002ppm, the order of arrangement from higher to lower is as follow (Mn>Cr>Pb>Zn>Cd). In February the heavy metal accumulation are reported from higher to lower as; Mn>Pb>Cr>Zn>Cd. February is reported to have high in both Pb and Mn. In march the heavy metal accumulation is reported as follows; Mn>Cr>Zn>Pb>Cd, and Cd is reported to be lowest. The accumulation of heavy metal in July is reported from high to lower content as; Mn>Zn>Cr>Pb>Cd, month of July is said to have high content of Cd, Cr, and Zn. In the month of August also the metals concentration are in order of Mn>Cr>Zn>Pb>Cd. in August also Mn is reported to have higher content of 0.934±0.259ppm. Also September is reported to have Mn as highest and Cd as lowest; Mn>Cr>Zn>Pb>Cd. The mean concentration of heavy metals at PZ area as shown in (Table 4). Pb concentration ranged from 0.393 – 0.194ppm,

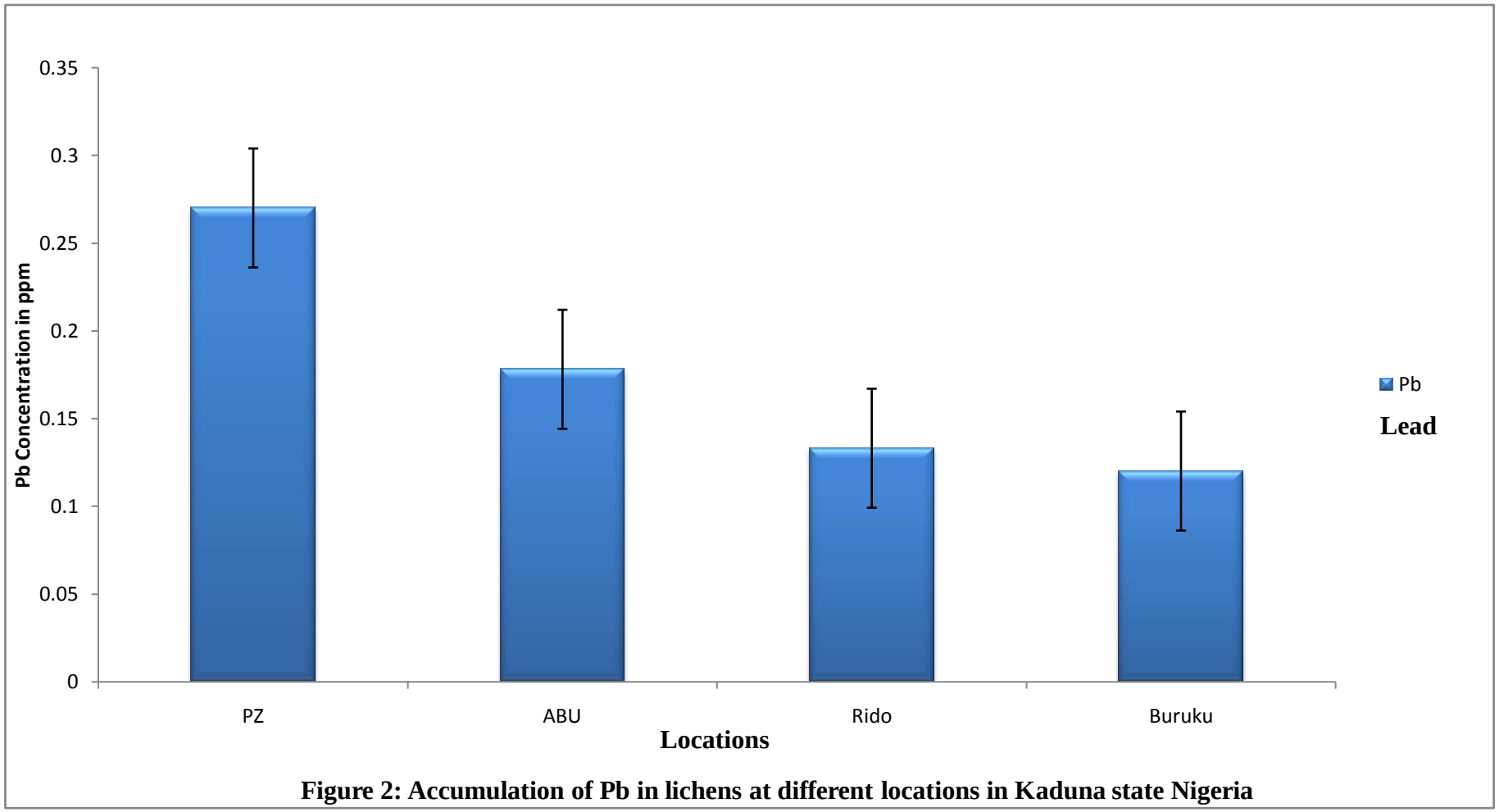

Figure 2: Accumulation of Pb in lichens at different locations in Kaduna state Nigeria

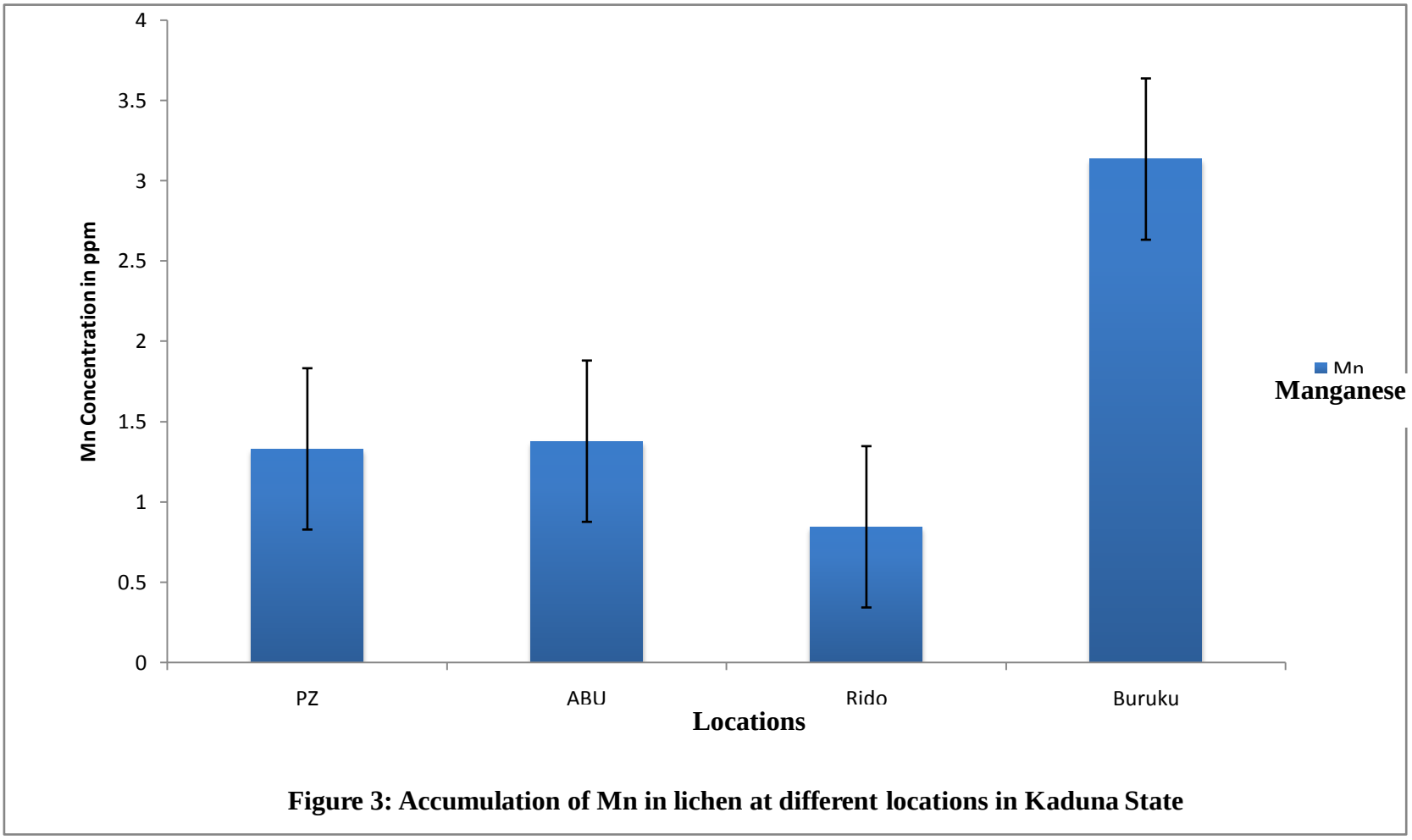

Figure 3: Accumulation of Mn in lichen at different locations in Kaduna State

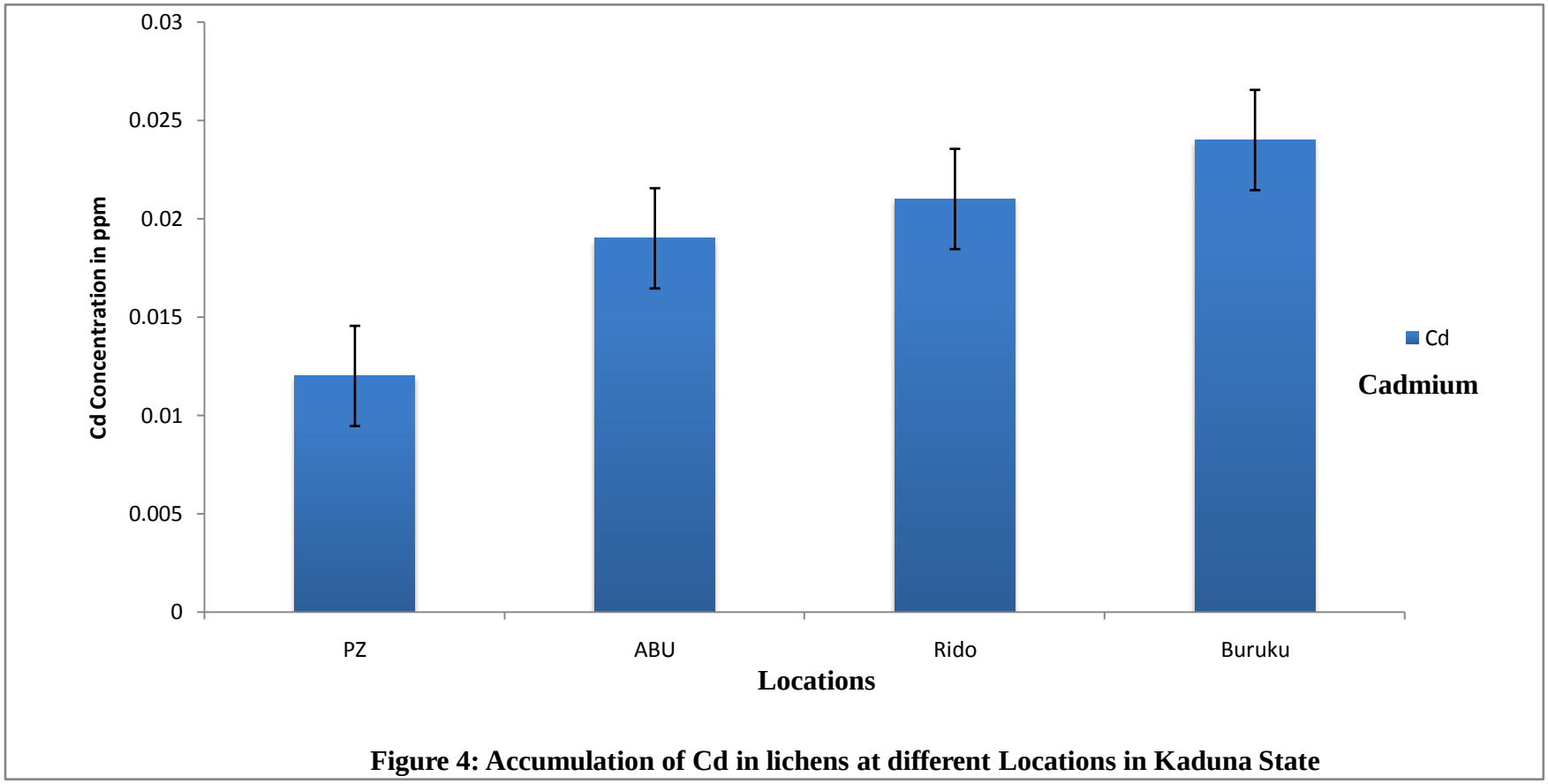

Figure 4: Accumulation of Cd in lichens at different Locations in Kaduna State

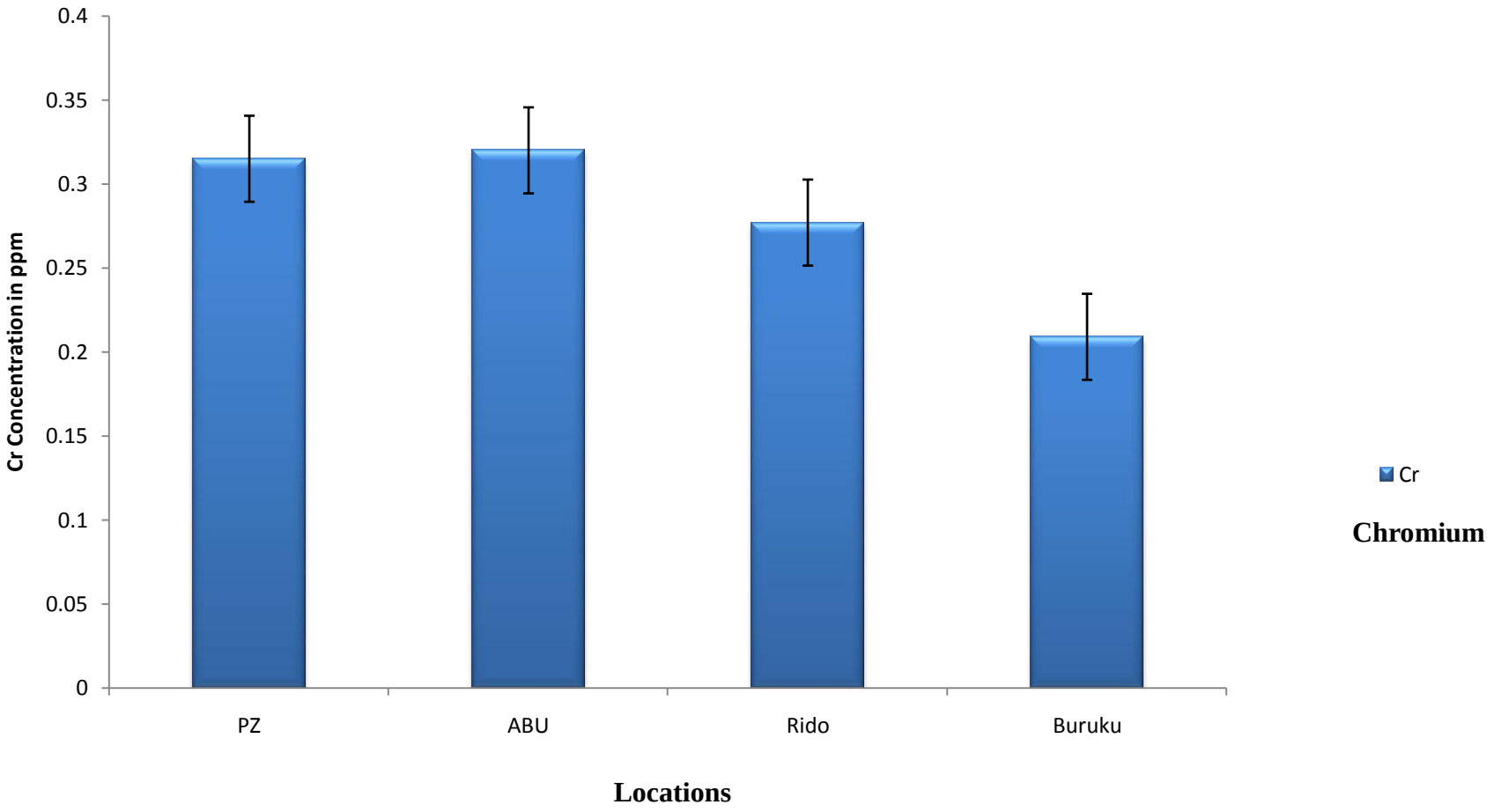

Figure 5: Accumulation of Cr in lichens at different locations in Kaduna State

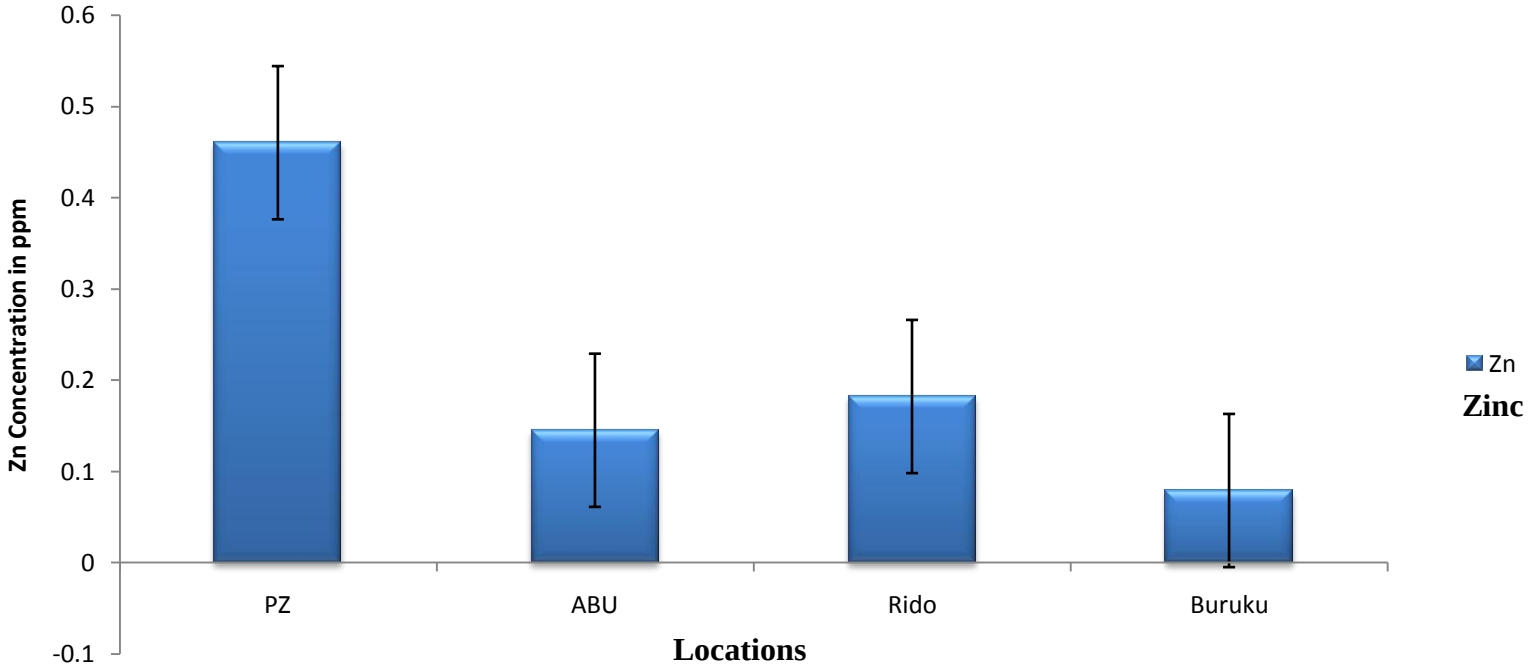

Figure 6: Accumulation of Zn in lichens at different locations in Kaduna State

TABLE 3: MEAN CONCENTRATION VALUES OF HEAVY METALS IN LICHENS SAMPLED ACROSS THE MONTHS IN SABON-GARI AND CHIKUN LOCAL GOVT AREA OF KADUNA STATE

Months	Heavy Metal Concentrations (ppm)				
	Pb	**Mn**	**Cd**	**Cr**	**Zn**
January	0.152±0.013[a]	1.799±0.297[a]	0.019±0.002[a]	0.282±0.034[a]	0.125±0.027[a]
February	0.203±0.049[a]	2.622±0.669[a]	0.020±0.001[a]	0.248±0.040[a]	0.242±0.125[a]
March	0.195±0.015[a]	2.017±0.691[a]	0.020±0.002[a]	0.293±0.038[a]	0.272±0.063[a]
July	0.196±0.039[a]	1.380±0.318[a]	0.022±0.003[a]	0.300±0.010[a]	0.318±0.100[a]
August	0.161±0.022[a]	0.934±0.259[a]	0.017±0.003[a]	0.273±0.021[a]	0.167±0.053[a]
September	0.145±0.018[a]	1.284±0.389[a]	0.018±0.003[a]	0.287±0.039[a]	0.178±0.038[a]
Mean	**0.17±0.03**	**1.68±0.44**	**0.02±0.00**	**0.28±0.03**	**0.22±0.07**
P-value	**0.58[ns]**	**0.17[ns]**	**0.70[ns]**	**0.89[ns]**	**0.48[ns]**

Note: Values are expressed as means ± SE (standard error), significant different are taken at p-value ≤0.05. Non-significant difference is taken at p-value >0.05, [ns] = not significant

TABLE 4: MEAN CONCENTRATION VALUES OF HEAVY METALS IN LICHENS SAMPLED FROM PZ AREA IN ZARIA METROPOLIS, NIGERIA

Months	Heavy Metal Concentrations (ppm)				
	Pb	**Mn**	**Cd**	**Cr**	**Zn**
January	0.194±0.019[a]	1.951±0.941[a]	0.011±0.001[a]	0.206±0.041[a]	0.242±0.026[a]
February	0.393±0.108[a]	1.500±0.499[a]	0.016±0.005[a]	0.376±0.043[a]	0.738±0.328[a]
March	0.253±0.014[a]	0.938±0.443[a]	0.012±0.002[a]	0.400±0.049[a]	0.463±0.005[a]
July	0.349±0.041[a]	2.193±0.791[a]	0.016±0.007[a]	0.321±0.028[a]	0.755±0.010[a]
August	0.232±0.016[a]	0.642±0.018[a]	0.006±0.000[a]	0.267±0.053[a]	0.332±0.134[a]
September	0.203±0.001[a]	0.764±0.095[a]	0.008±0.001[a]	0.322±0.036[a]	0.233±0.011[a]
Meam	**0.27±0.03**	**1.33±0.46**	**0.01± 0.03**	**0.33±0.04**	**0.33±0.08**
P-value	**0.12[ns]**	**0.38[ns]**	**0.39[ns]**	**0.12[ns]**	**0.13[ns]**

Note: Values are expressed as means ± SE (standard error), significant different are taken at p-value ≤0.05. Non-significant difference is taken at p-value >0.05 [ns =] not significant

Mn concentration ranged from 0.642 - 2.193ppm, Cd concentration ranged from 0.206 – 0.400ppm. Zn concentration ranged from 0.233 – 0.755ppm respectively.

Also, Pb, and Cd are recorded higher in February with 0.393±0.041 and 0.016±0.005ppm, Mn and Zn recorded higher in July with 2.193±0.791 and 0.755±0.010ppm, Cr was recorded higher in March with 0.400±0.049ppm.

Table 5, show the mean values of heavy metal obtained from ABU Botanical garden, The Pb content ranged from 0.162 -0.200ppm, Mn ranges from 0.300 – 0.423ppm, Cd ranged from 0.016 – 0.028ppm, Cr content ranged from 0.287 – 0.347ppm, Zn content ranged from 0.088 – 0.226ppm respectively. Pb and Mn were recorded higher in February with 0.200±0.017 and 3.00±0.064ppm, Cd was recorded higher in January with 0.347±0.006ppm, Zn was recorded higher in August with 0.226±0.058ppm. The mean concentration of heavy metal obtained from Rido village (Table 6), Pb concentration ranged from 0.402 – 1.032ppm, Cd content ranged from 0.019 – 0.025ppm, Cr ranged from 0.173 – 0.407ppm, Zn content ranged from 0.037 – 0.407ppm. Pb Cd and Zn recorded higher in March with 0.206±0.004, 0.023±0.002 and 0.407±0.047ppm respectively, Mn and Cr was recorded higher in January with 1.032±0.0133 and 0.366±0.062 respectively. (Table 7), shows the mean concentration of heavy metals obtained from Buruku village through the whole months. Pb content ranged from 0.085 – 0.161ppm, Mn content ranges from 1.717 – 5.255ppm, Cd content ranged from 0.022 – 0.030ppm, Cr values ranged from 0.130 – 0.290, Zn values ranged from 0.060 – 0.099ppm. Pb and Zn, were recorded in march with 0.161±0.002 and 0.097±0.028ppm respectively, Mn recoded higher in February with 5.255±0.612ppm, Cd reported higher in September 0.027±0.001ppm, Cr was recorded in July with 0.280±0.031ppm.

TABLE 5: MEAN CONCENTRATION OF HEAVY METALS IN LICHENS SAMPLE FROM ABU BOTANICAL GARDEN

Months	Heavy Metal Concentrations (ppm)				
	Pb	**Mn**	**Cd**	**Cr**	**Zn**
January	0.169±0.006[a]	2.205±0.327[a]	0.018±0.001[a]	0.347±0.006[a]	0.090±0.019[a]
February	0.200±0.017[a]	3.000±0.064[a]	0.019±0.001[a]	0.309±0.029[a]	0.088±0.004[a]
March	0.162±0.016[a]	1.145±0.279[b]	0.019±0.001[a]	0.341±0.006[a]	0.121±0.037[a]
July	0.171±0.014[a]	0.423±0.013[b]	0.028±0.011[a]	0.310±0.004[a]	0.202±0.028[a]
August	0.198±0.038[a]	0.977±0.550[b]	0.016±0.000[a]	0.287±0.054[a]	0.226±0.058[a]
September	0.167±0.016[a]	0.528±0.027[b]	0.017±0.001[a]	0.330±0.015[a]	0.144±0.035[a]
Mean	**0.18±0.02**	**1.37±0.21**	**0.02±0.00**	**0.32±0.02**	**0.15±0.03**
P-value	**0.65[ns]**	**0.00****	**0.52[ns]**	**0.61[ns]**	**0.12[ns]**

Note: Values are expressed as means ± SE (standard error), means with different superscript down the columns are significantly different at p-value ≤0.05. Non-significant difference is taken at p-value >0.05 **highly significant, [ns =] not significant

TABLE 6: MEAN CONCENTRATION VALUES OF HEAVY METALS IN LICHENS FROM RIDO VILLAGE

Months	Heavy Metal Concentrations (ppm)				
	Pb	**Mn**	**Cd**	**Cr**	**Zn**
January	0.113 ± 0.008^{a}	1.032 ± 0.592^{a}	0.022 ± 0.002^{a}	0.366 ± 0.062^{a}	0.083 ± 0.009^{bc}
February	0.084 ± 0.022^{a}	0.735 ± 0.059^{a}	0.022 ± 0.001^{a}	0.152 ± 0.055^{a}	0.052 ± 0.011^{c}
March	0.206 ± 0.004^{a}	0.859 ± 0.166^{a}	0.023 ± 0.002^{a}	0.173 ± 0.013^{a}	0.407 ± 0.047^{a}
July	0.179 ± 0.065^{a}	1.032 ± 0.450^{a}	0.021 ± 0.001^{a}	0.290 ± 0.004^{a}	0.245 ± 0.071^{abc}
August	0.108 ± 0.011^{a}	0.402 ± 0.133^{a}	0.020 ± 0.001^{a}	0.320 ± 0.005^{a}	0.037 ± 0.005^{c}
September	0.109 ± 0.031^{a}	1.015 ± 0.353^{a}	0.022 ± 0.000^{a}	0.360 ± 0.092^{a}	0.272 ± 0.113^{ab}
Mean	**0.13 ± 0.03**	**0.85 ± 0.29**	**0.053 ± 0.00**	**0.28 ± 0.4**	**0.18 ± 0.04**
P-value	**0.16^{ns}**	**0.76^{ns}**	**0.47^{ns}**	**0.09^{ns}**	**0.02***

Note: Values are expressed as means ± SE (standard error), means with different superscript down the columns are significantly different at p-value ≤0.05. Non-significant difference is taken at p-value >0.05, *significant, ^{ns} = not significant

TABLE 7: MEAN CONCENTRATION VALUES OF HEAVY METALS IN LICHENS SAMPLED FROM BURUKU VILLAGE

Months	Heavy Metal Concentrations (ppm)				
	Pb	**Mn**	**Cd**	**Cr**	**Zn**
January	0.131± 0.018^{a}	2.008 ± 0.561$^{\mathbf{b}}$	0.024 ± 0.001^{a}	0.210 ± 0.071^{a}	0.085 ± 0.029^{a}
February	0.135 ± 0.024^{a}	5.255 ± 0.612$^{\mathbf{a}}$	0.024 ± 0.001^{a}	0.156 ± 0.024^{a}	0.089 ± 0.019^{a}
March	0.161 ±0.002^{a}	5.127 ± 0.346$^{\mathbf{a}}$	0.025 ± 0.000^{a}	0.258 ± 0.089^{a}	0.097 ± 0.028^{a}
July	0.085 ± 0.022^{a}	1.872 ± 0.267$^{\mathbf{b}}$	0.023 ± 0.001^{a}	0.280 ± 0.031^{a}	0.070 ± 0.005^{a}
August	0.109 ± 0.006^{a}	1.717 ± 0.755$^{\mathbf{b}}$	0.025 ± 0.002^{a}	0.217 ± 0.030^{a}	0.073 ± 0.015^{a}
September	0.099 ± 0.022^{a}	2.829 ± 0.891$^{\mathbf{b}}$	0.027 ± 0.001^{a}	0.135 ± 0.028^{a}	0.063 ± 0.024^{a}
Mean	**0.13 ± 0.02**	**0.85 ± 0.29**	**0.05 ± 0.00**	**0.28 ± 0.04**	**0.18 ± 0.04**
P-value	**0.16^{ns}**	**0.02***	**0.24^{ns}**	**0.42^{ns}**	**0.86^{ns}**

Note: Values are expressed as means ± SE (standard error), means with different superscripts down the columns are significantly different at p-value p≤0.05. Non-significant difference is taken at p-value p>0.05, *significant, ^{ns} = not significant

The mean seasonal variation of heavy metals of all the study areas shown in (Table 8). Pb concentration ranged from 0.160 – 0.185ppm, Mn ranged from 1.190 – 2.150ppm, Cd fall on the same range as 0.019ppm, Cr ranged from 0.270 – 0.290ppm, Zn ranged from 0.210 – 0.225ppm. Where significant difference recorded only in Mn values.

4.3 NO_3 and SO_2 pollution load in lichens from sampled areas

The concentration of NO_3 ranged from 0.051 – 0.140mg/L which was recorded in *Xanthoparmelia caperata* and *Flavoparmelia caperata*. And SO_2 concentration ranged from 62.892 – 238.989mg/L the content recorded from *Xanthoparmelia* spp and *Physcia* spp collected from Buruku which also reported with highly significant different at $P \leq 0.05$ respectively (Table 9). The mean concentration of SO_2 and NO_3 also like heavy metals is determined in all locations and seasons. Values are expressed as means ± SEM (standard error of mean), NO_3 ranged from 0.091 – 0.102mg/L, SO_2 values ranged from 72.954 – 496.845mg/L, the values of the locations are shown in (Figure 7 and 8) as PZ area is significantly higher in SO_2 concentration while Rido is significantly lower in NO_3 concentration respectively. The mean monthly concentration of SO_2 and NO_3 shows that NO_3 ranged from 0.075 – 0.125mg/L, SO_2 ranged from 133.959 – 786.791mg/L (Table 10). Table 11; shows the mean concentration of NO_3 and SO_2 at PZ area, NO_3 ranges from 0.062 – 0.158mg/L, and SO_2 ranged from 45.285 – 260mg/L. NO_3 were recorded higher in January with 0.0.158±0.018 and SO_2 recorded higher in July with 260.780±150.220mg/L. ABU Botanical garden the mean concentration of NO_3 and SO_2. NO_3 ranged from 0.053 – 0.185mg/L, SO_2 content ranged 37.735 – 105.655mg/L. NO_3 and SO_2 were recorded higher in July with 0.185±0.044 and 105.655±15.095mg/L see (Table 12). The Rido village as shown in (Table 13), the mean concentration of NO_3 and SO_2, the content of NO_3 ranged from 0.040 – 0.184mg/L, SO_2 content ranged from 188.675 – 303.765mg/L. NO3 and SO_2 are recorded higher in January and with 0.184±0.114 and 303.765±7.545 The mean

concentration of NO_3 and SO_2 in Buruku, Show that the values of NO_3 ranged from 0.071 – 0.132ppm and SO_2 values ranged from 196.220 – 218.860mg/L, with highest content recorded in the month of March and July. NO_3 and SO_2 were recorded in March with 0.132±0.027 and 218.860±7.550mg/L (Table 14). The mean seasonal variation of NO_3 and SO_2 show that the value of NO_3 ranged from 0.096 – 0.100mg/L, SO_2 ranged from 140.505 – 355.343mg/L (Table 15).

TABLE 8: MEAN VALUES OF SEASONAL VARIATION OF HEAVY METALS CONCENTRATION IN LICHENS SAMPLED FROM FOUR STUDY AREA IN KADUNA STATE

Heavy metals (ppm)	Season	Mean	*P-value*
Lead concentration (ppm)	Dry	0.167 ± 0.016^{a}	**0.50^{ns}**
	Wet	0.183 ± 0.018^{a}	
Manganese concentration (ppm)	Dry	1.199 ± 0.184^{a}	**0.02***
	Wet	2.146 ± 0.329^{b}	
Cadmium concentration (ppm)	Dry	0.019 ± 0.002^{a}	**0.77^{ns}**
	Wet	0.019 ± 0.001^{a}	
Chromium concentration (ppm)	Dry	0.286 ± 0.015^{a}	**0.64^{ns}**
	Wet	0.274 ± 0.021^{a}	
Zinc concentration (ppm)	Dry	0.221 ± 0.041^{a}	**0.90^{ns}**
	Wet	0.213 ± 0.047^{a}	

Note: Values are expressed as means ± SE (standard error), Non-significant differences between wet and dry seasons are taken at p-value >0.05, while significant different are taking at p- value p≤0.05, *significant, ^{ns} = not significant

TABLE 9: MEAN CONCENTRATION OF SO_2 AND NO_3 IN LICHENS SAMPLE FROM FOUR LOCATIONS IN KADUNA STATE

Lichens	Locations	NO_3 (mg/L)	SO2(mg/L)	Mean
Physcia spp.	PZ area	0.094 ± 0.012^{ab}	121.988 ± 59.553^{bc}	**61.04 ±29.78**
Phaeophyscia spp.	PZ area	0.111 ± 0.017^{ab}	90.532 ± 14.051^{bc}	**45.32 ± 7.03**
Dictyonema Glabratum	ABU	0.129 ± 0.027^{a}	83.015 ± 10.125^{bc}	**41.57 ± 5.08**
Xanthoparmelia caperata	ABU	0.051 ± 0.005^{b}	62.892 ± 15.301^{c}	**31.47 ± 7.65**
Flavoparmelia caperata	Rido	0.126 ± 0.038^{a}	158.498 ± 29.873^{ab}	**79.31 ± 14.96**
Flavoparmelia caperata	Rido	0.094 ± 0.015^{ab}	216.359 ± 10.064^{a}	**108.23 ± 5.04**
Physcia spp.	Buruku	0.079 ± 0.007^{ab}	238.989 ± 10.614^{a}	**119.53 ± 5.31**
Flavoparmelia caperata	Buruku	0.140 ± 0.036^{a}	206.288 ± 5.031^{a}	**103.21 ± 2.53**
Mean		**0.10 ± 0.02**	**147.32 ± 18.69**	
P-value		**0.144^{ns}**	**0.000****	

Note: Value are express as mean ± SE (Standard error) significant different area taken at p≤0.05 while non significant different are taken at p>0.05, **highly significant, ^{ns} = not significant

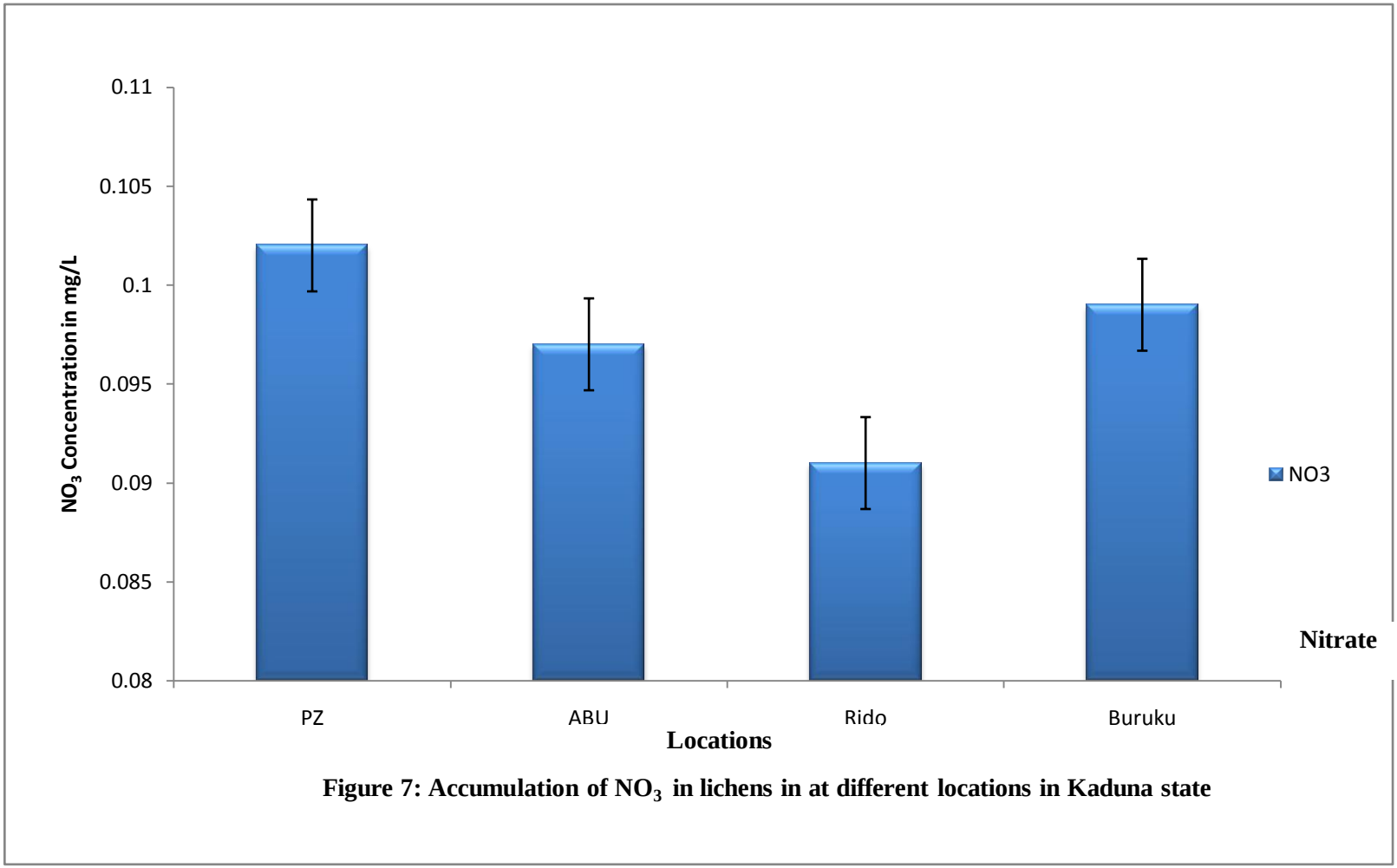

Figure 7: Accumulation of NO_3 in lichens in at different locations in Kaduna state

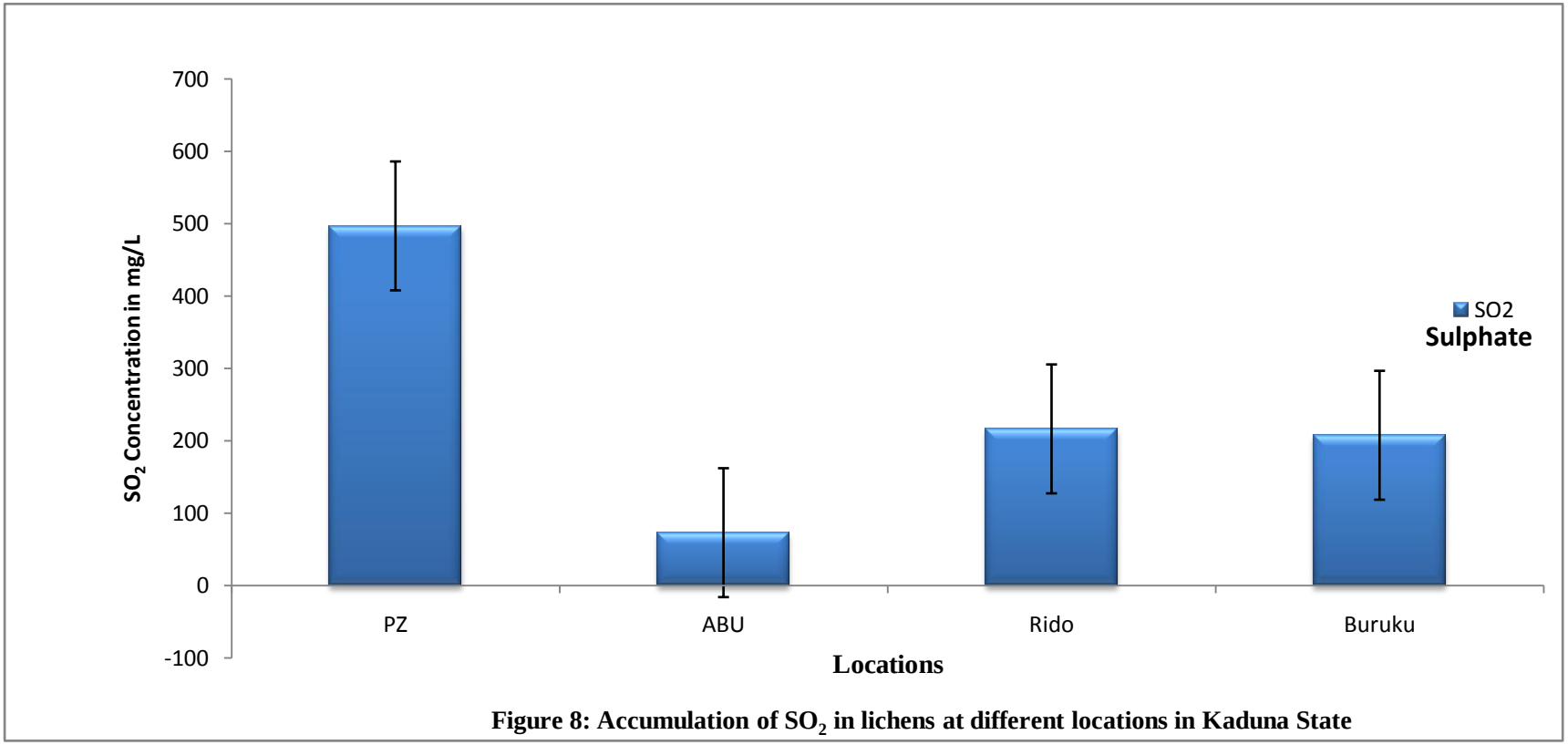

Figure 8: Accumulation of SO_2 in lichens at different locations in Kaduna State

Table 10: MEAN CONCENTRATION OF NO_3 AND SO_2 IN LICHENS SAMPLE ACROSS THE MONTHS IN SABON-GARI AND CHIKUN LOCAL GOVT AREA OF KADUNA STATE

Months	NO_3 (mg/L)	SO_2 (mg/L)
January	0.125 ± 0.027^{a}	141.504 ± 24.025^{a}
February	0.075 ± 0.008^{a}	133.959 ± 28.587^{a}
March	0.090 ± 0.013^{a}	149.051 ± 31.691^{a}
July	0.119 ± 0.022^{a}	786.791 ± 492.992^{a}
August	0.092 ± 0.015^{a}	133.959 ± 25.583^{a}
September	0.086 ± 0.011^{a}	145.279 ± 30.043^{a}
Mean	**0.09 ± 0.02**	**248.42 ± 31.65**
P-value	**0.32^{ns}**	**0.16^{ns}**

Note: Values are expressed as means ± SE (standard error), significant different are taken at p-value ≤0.05. Non-significant difference is taken at p-value >0.05, ^{ns} = not significant

Table 11: MEAN CONCENTRATION OF NO_3 AND SO_2 IN LICHENS SAMPLE FROM PZ AREA

Months	NO_3 (mg/L)	SO_2 (mg/L)
January	0.158 ± 0.018^{a}	113.200 ± 22.640^{a}
February	0.088 ± 0.018^{bc}	90.565 ± 30.185^{a}
March	0.088 ± 0.018^{bc}	67.920 ± 22.640^{a}
July	0.123 ± 0.018^{ab}	260.780 ± 154.220^{a}
August	0.097 ± 0.009^{bc}	60.375 ± 15.095^{a}
September	0.062 ± 0.009^{c}	45.285 ± 15.090^{a}
Mean	**0.10 ± 0.02**	**106.35 ± 43.31**
P- value	**0.04***	**0.13^{ns}**

Note: Values are expressed as means ± SEM (standard error of mean), means with different superscript down the columns are significantly different at p-value ≤0.05. Non-significant difference is taken at p-value >0.05, *significant, ^{ns} = not significant

Table 12: MEAN CONCENTRATION OF NO_3 AND SO_2 IN LICHENS SAMPLED FROM ABU BOTANICAL GARDEN

Months	**NO_3 (mg/L)**	**SO_2 (mg/L)**
January	0.079 ± 0.009^a	52.830 ± 7.550^a
Februay	0.053 ± 0.000^a	37.735 ± 7.545^a
March	0.062 ± 0.009^a	67.925 ± 7.545^a
July	0.185 ± 0.044^a	105.655 ± 15.095^a
August	0.097 ± 0.062^a	75.470 ± 0.000^a
September	0.106 ± 0.018^a	98.110 ± 37.730^a
Mean	**0.09 ± 0.02**	**72.95 ± 12.57**
P-value	**0.19^{ns}**	**0.18^{ns}**

Note: Values are expressed as means ± SE (standard error), significant different are taken at p-value ≤0.05. Non-significant difference is taken at p-value >0.05, ^{ns} = not significant

Table 13: MEAN CONCENTRATION OF NO_3 AND SO_2 IN LICHENS SAMPLED RIDO VILLAGE

Months	NO_3 (mg/L)	SO_2 (mg/L)
January	0.184 ± 0.114^{a}	303.765 ± 7.545^{a}
February	0.071 ± 0.018^{a}	211.315 ± 30.185^{a}
March	0.079 ± 0.026^{a}	241.500 ± 30.190^{a}
July	0.040 ± 0.005^{a}	218.870 ± 22.650^{a}
August	0.097 ± 0.044^{a}	188.675 ± 7.545^{a}
September	0.079 ± 0.044^{a}	233.955 ± 7.545^{a}
Mean	**0.09 ± 0.04**	**192.76 ± 17.61**
P-value	**0.58^{ns}**	**0.53^{ns}**

Note: Values are expressed as means ± SE (standard error), significant different are taken at p-value ≤0.05. Non-significant difference is taken at p-value >0.05, ^{ns} = not significant

Table 14: MEAN CONCENTRATION OF NO_3 AND SO_2 IN LICHENS SAMPLE FROM BURUKU VILLAGE

Months	NO_3 (mg/L)	SO_2 (mg/L)
January	0.071 ± 0.018^a	196.220 ± 0.000^a
February	0.088 ± 0.018^a	196.220 ± 0.000^a
March	0.132 ± 0.027^a	218.860 ± 7.550^a
July	0.132 ± 0.009^a	218.860 ± 7.550^a
August	0.079 ± 0.009^a	211.315 ± 15.095^a
September	0.097 ± 0.009^a	203.765 ± 7.545^a
Mean	**0.09 ± 0.01**	**207.54 ± 6.29**
P- value	**0.13^{ns}**	**0.28^{ns}**

Note: Values are expressed as means ± SE (standard error), significant different are taken at p-value ≤0.05. Non-significant difference is taken at p-value >0.05, $^{ns\ =}$ not significant

Table 15: MEAN SEASONAL VARIATION OF NO_3 AND SO_2 CONCENTRATION

	Pollutants	
Seasons	**NO_3 (mg/L)**	**SO_2 (mg/L)**
Dry	0.099 ± 0.010	355.343 ± 169.888
Wet	0.096 ± 0.011	141.505 ± 15.652
Mean	**0.09 ± 0.01**	**248.42 ± 92.77**
P – value	**0.82^{ns}**	**0.22^{ns}**

Note: Values are expressed as means ± SEM (standard error of mean), Significant difference are taken at p≤0.05 while non-significant differences between wet and dry seasons are taken at p-value >0.05, ^{ns} = not significant

CHAPTER FIVE

5.1 DISCUSSION

Dictyonema glabratum found at ABU Botanical garden during dry season, a fruticose was formed by the symbiosis between algae/Cyanobacteria and Basidiomycete fungi it is also known as Basidiolichens, and also known as macrolichens, it is common and widely available lichen species and considered to be ecologically important to Nigeria as it is one among many lichens that fix atmospheric Nitrogen into the Soil, which makes them (the lichens) natural fertilizers. *Dictyonema glabratum* grows in curly masses around objects, such as tree trunks (Lawrey *et al.*, 2007).

Flavopermelia capirata: The lobes of the thallus of this species may be smooth, but quite often have a wrinkled appearance especially in older specimens. Widespread on well-lit acid-barked trees, wood and other surfaces, now colonising urban and other disturbed sites, previously affected by acid rain.

Physcia species: The name of lichen originated from the Greek *physckέ*, used to describe the large intestine, a sausage or a blister and referring to thalli with hollow lobes. *Physcia* is a cosmopolitan genus of 75 species. It is distinguished from most other foliose Physciaceae mainly by its pseudoparenchymatous upper cortex in combination with atranorin as a cortical substance (Elix, 2011). *Physcia* species was also found by Bako *et al.* (2008) in Nigerian guinea Savannah which coincides with areas where this research was conducted.

Phaeophyscia species: This was collected during wet season at PZ area. All the lichens collected are foliose and fruticose species which are mainly found on old tree trunk with rough bark, because roughness increases humidity which is the factor contributing toward the survival of the lichens, This is according to Suzana *et al.* (2011) that, humidity caused by

bark roughness may be an important factor in establishing different species that attach themselves more easily to irregular surfaces, but less to smooth surfaces.

The genus *Xanthoparmelia* (Vain.) Hale, comprised of approximately 750 species, constitutes a major part of the family Parmeliaceae Zenker (Blanco *et al*., 2004). All *Xanthoparmelia* species share key taxonomic characters, including the degree of attachment to the substrate, colour of the lower surface (pale brown to ebony black), presence of isidia of different types (cylindrical to globose), shape of the lobes and the medullar chemistry (Hale, 1971; Kurokawa, 1989). The history of *Xanthoparmelia* as an individual genus has been relatively brief, as all *Xanthoparmelia* species were only separated from *Parmelia* as recently as 1974, and few publications on this genus even existed up until 1959. Only since 1964 have virtually all of the 300 or so additional new species of *Xanthoparmelia* been described, with a total of 750 species reported (Park, 1990; Kashiwadani *et al*., 2002; Hur *et al.*, 2005).

Lichens have a higher capacity to accumulate and store heavy metals for a long time because of their morphological and ecological peculiarities. Lichens are widely used as plant material to investigate or biomonitor airborne heavy metals (Esmira *et al*., 2006). In this study *Phaeophyscia* spp was found to have higher concentration of Pb, This may be attributed to the anthropogenic activities in the collection area (PZ area), such as vehicular movement, automobile workshop etc, which is among the sources of Pb and other pollutants. This is in line with what Rai *et al.* (2011) reported, *Phaeophyscia hispidula* accumulates higher amount of Pb ranging from 8600±395 to 12433±185 µg g-1. Thus, in *Hypogymnia* physodes and *Unnea hirta* the highest concentration of Pb can be related to selective cation uptake as reported previously by Cansaran-Duman *et al*. (2009).

Flavoparmelia caperata collected from Buruku is said to have higher concentration of Mn and NO_3 this could be attributed to the species morphology (ie, it foliose nature) and the little

anthropogenic and or agricultural activities in the area where the species was collected, as reported by Pandey and Shama, (2001) that the anthropogenic activities in the collection area play a vital role in the trapping of pollutants by lichens. *Physcia* spp was reported to have higher concentration of Cd, SO_2 and Zn from Buruku and PZ area respectively. *Xanthoparmelia caperata* which was collected from ABU Botanical garden is reported to have higher concentration of Cr. Since chromium compounds cannot volatilize from water, transport of chromium from water to the atmosphere is not likely, except by transport in windblown sea sprays (Alimonti *et al.*, 2000). Chromium is released into the atmosphere mainly by anthropogenic stationary point sources, including industrial, commercial, and residential fuel combustion, via the combustion of natural gas, oil, and coal (Kimbrough *et al*. 1999; Pacyn and Pacyn 2001; Seigneur and Constantinous 1995). Other potentially small sources of atmospheric chromium emission are cement –producing plants (cement contains chromium), the wearing down of asbestos brake linings that contain chromium, incineration of municipal refuse and sewage sludge, and emission from chromium-based automotive catalytic converters. Emissions from cooling towers that previously used chromate chemicals as rust inhibitors are also atmospheric sources of chromium (EPA, 1990).

The high concentration of Cr in this garden could be as result of the domestic cooking and abundance of asbestos roofing in the surrounding environment. Heavy metal concentrations in this study were in line with the data obtained by Nimis *et al*. (2001) who studied foliose lichens. Fruticose *Cladonia* spp were significantly different from foliose species in terms of heavy metal concentrations where there is higher concentration of pollutants in foliose lichens. Pandey *et al*. (2002) stated that thallus types play an important role in determining the accumulation of heavy metals. *Collema furfuraceum*, *Dermatocarpon luridum* and *Xanthoria calcicola* were the best accumulator of heavy metals as compared to the other species in the present study and all of these lichen species are foliose lichens. McCune and

Geiser, (1997) stated these genus are heavy metal-tolerant and based on the results of the present study these species can be used safely in biomonitoring process.

The heavy metals concentration in all locations was shown in (Table 2) , ABU Botanical garden has low concentration of lead (Pb) 0.178±0.0081pmm, while the high concentration was recorded at PZ area 0.270±0.027pmm.The high lead (Pb) concentration in PZ area is as a result of high vehicular movement in the area, This can be attributed to what Aniefiok *et al.* (2014) reported, the elevated concentration of Pb reported are mainly attributed to emission from vehicular traffic, exhaust gasses associated with fossil fuel combustion, metal works, automobile repairs and municipal waste incineration. Cansaran-Duman *et al*. (2009) concluded that maximum concentration of Pb indicated highest vehicular density. The authur stated that long term exposure to Pb concentration may cause complex human health, such as chronic and peripheral neuropathy especially in children. The increase in Pb concentration in traffic area is probably confirmed by the amount of this metal deriving from the exhaust gases. A notably higher Pb concentration was also characteristic of the industrial sites (Biolonskan and Dayan, 2005). With maximum human activities, together with motor garage, high vehicular density congestion showed the higher atmospheric level of Pb. Cansaran-Duman *et al*. (2009) concluded that maximum concentration of Pb indicated highest vehicular density. Mn (Manganase) high concentration 3.155±0.487ppm was recorded at Buruku while the low concentration was recorded at Rido. According to the WHO (2000) Urban and rural areas without significant manganese concentration recorded have the annual averages of manganese concentration are mainly in the range of 0.01±0.07μgg^{-1}. Several studies have reported varying concentration of Mn in lichen samples, Example of the concentration of Mn in other studies include 93.00μgg^{-1} (Onianwa and Ajayi, 1987), 3.91μgg^{-1} (Jozwik 1999), 222.70μgg^{-1} (Mendil *et al.*, 2005) and 25.80μgg^{-1} (Uluozlu *et al.*, 2007). The concentrations of Mn in the ambient air in the rural areas are probably reflecting the

concentration of vegetation input (Abdullahi *et al.,* 2012). The atmospheric deposition of Mn is associated with local and anthropogenic activities in the urban areas and the distribution of Mn is more regional than Zn. Several studies have reported varying concentration of Cd in lichens sample, example; 0.027±0.02 (Aniefiok *et al.,* 2014), 0.10+0.64 (Uluozlu *et al.,* 2007). The concentration of Cd obtained in Buruku can be attributed to anthropogenic activities such as combustion of fossil fuel and emission from vehicles (Uluozlu *et al.,* 2007). Plants from unpolluted environment contain 0.01 – 0.3µgg^{-1} Cd (Allen, 1989), and ambient air usually has a low concentration of Cd in particulate form (Nordberg *et al.,* 2007), the background concentration of Cd measured in this study are within the range of values obtained in similar studies in Nigeria and other developed countries. The concentration of Cr is recorded highest in ABU Botanical garden with 0.320±0.10ppm and lowest in Buruku with 0.209±0.22ppm, with all anthropogenic activities. Since chromium cannot volatilize from water, transport of chromium from water to the atmosphere is not likely (Alimonti *et al.,* 2000), so the presence of chromium in atmosphere may not be as result of washing soaps. Chromium is released into the atmosphere mainly by anthropogenic stationary point sources, including industrial, commercial, and residential fuel combustion, via the combustion of natural gas, oil, and coal (Kimbrough *et al*. 1999; Pacyn and Pacyn 2006). Other potentially small sources of atmospheric chromium emission are cement –producing plants (cement contains chromium), the wearing down of asbestos brake linings that contain chromium, incineration of municipal refuse and sewage sludge. Chemicals as rust inhibitors are also atmospheric sources of chromium (EPA, 1990). The high concentration of Cr in this garden could be as result of the domestic cooking and abundance of asbestos roofing in the surrounding environment. In addition aerial fallout of windblown dust contribution from metal corrosion and soil of the study area might have increased the contamination load of the surrounding atmosphere (Aniefiok *et al.,* 2014). However, it was observed that the average

concentration of Cr in lichens decreased with the increase of distance from the road site. Similarly, Aslam *et al.* (2011) reported that the concentration of total Cr in soil was decreased with the increase of destination from the road side.

Zn content in lichen is reported higher in PZ area with 0.460±0.078ppm and lowest content was obtained in Buruku with 0.079±0.007ppm. The highest content of Zn obtained at PZ area was due to high traffic density and other local anthropogenic sources. Zn belongs to a group of trace metals, which is essential for the growth of humans, animals & plants and is potentially dangerous for the biosphere when present in high concentrations (Gowd *et al.,* 2010). The vehicular traffic and industrial emissions are supposed to be the main source of Zn in the study area. Romic and Romic (2003) reported that the main sources of the Zn pollution are industries and the huge of liquid manure, composted materials and agro chemicals such as fertilizers and pesticides in agriculture. According to Aniefiok *et al.* (2014), high Zn contencentration are attributed to traffic density and local anthropogenic sources. The NO_3 and SO_2 background content was reported high in PZ area while lowest was reported in Rido with 0.102±0.010 and 0.09±0.021mg/L respectively. The Nitrogen found in thalli was however highly linked to moist Nitrogen deposits, but was also correlated with NO_3 present in air as well as in the lichen species (Van Dobben *et al.,* 2001). SO_2 content was also reported higher in PZ area with 496.854±342.143mg/L while the lowest value was recorded in ABU Botanical garden with value of 72.954±8.877mg/L the result of measured atmospheric SO_2 showed the highest pollution at the PZ area since SO_2 can be transported far away from its emission site. It is true to say that this gaseous phototoxic pollutant is one of the most important factors which have negative effect in epiphytic vegetation even at remote site (Van Dobben *et al.,* 2001). According to Conti and Cecchetti (2001) high level of SO_2 and NO_3 can cause a reduction of pH of lichen to this respect, it shall be highlighted that atmospheric pollution of this kind has lead to the less abundance of

some lichen species like *Lorama pulmonaria* and *Ramalina farinacea.* So with this the scarce abundance of lichen in PZ area is attributed to the higher level of this pollution. According to Mark *et al.* (2013), the number of pollutants intolerant of lichens species drops from 10 to 5 with an associated decline in species number when the wet and dry seasons NO_2 concentrations are greater than 0.46 ppb and 0.15 ppb (respectively the median wet and dry seasons pollutants concentrations observed in this study). The presence of the intermediate tolerant lichen species when the NO_2 is above 0.46 ppb is roughly unchanged but the species number is lower than when the NO_2 concentration is below 0.46 ppb (Conti and Cecchetti 2001). Two of the pollutant tolerant species of lichen (*Phaeophyscia rubropulchra* and *Pyxine sorediata*) are absent from the sites that experience NO_2 concentrations above 0.46 ppb. However, two pollution tolerant species (*Parmelia sulcata* and *Melanelia subaurifera*) appear not to be impacted by NO_2 concentrations above 0.46 ppb. On the other hand, it is possible to differentiate the effect of traffic released pollutants on the different studied sites, which helps raise the issue of the need to carry out better controls on the quality of the air in our country, as well as to control the level of pollutant emissions in the vehicles circulating (Satya and Upreti, 2015).

The mean monthly variation of heavy metal, SO_2 and NO_3 accumulation. Showed that in January heavy metal accumulation of Mn was the highest 1.799±0.297 Mn>Cr>Pb>Zn>Cd, while SO_2 high than NO_3 and NO_3 high content is recorded in January and lowest in February. In February the heavy metal accumulation was in the following order; Mn>Pb>Cr>Zn>Cd, while the highest content of Pb is recorded in February and the lowest is in September. February had reported to have high accumulation of both Pb and Mn. August is reported to have lowest content of Mn and Cd. Also September is reported to have Mn as highest and Cd as lowest, Mn>Cr>Zn>Pb>Cd, The mean seasonal variation of heavy metal accumulation in all the location. In this it shows high content of Cd, Cr, Zn, NO_3 and SO_2

during Dry season while Pb and Zn show high content in the wet season. In having lower content in the wet season, similar result was obtained by Backor and Loppi (2009) who observed that metal content in the lichen was lower during the wet period and higher in the dry season, are mainly due to rainfall variation. While the high contents of Pb and Zn in the wet season instead of dry season is possible because, Kularatne and Freitas (2012) stated that the total (on thallu plus in thallus) accumulation increases with time irrespective of season or rainfall. With this the accumulation of heavy metals in lichens or any plants specimens can attain higher or lower contents in respective of seasonal variability. And the morphology of lichens and mosses does not vary with seasons; thus accumulation can occur throughout the year. Lichens and mosses usually have considerable longevity, which led to their use as long-term integrators of atmospheric deposition (Szczepaniak and Biziuk, 2003).

CHAPTER SIX

6.0 CONCLUSSION AND RECOMMENDATION

6.1 Conclusion

Lichens species found in all locations were; *Dictyonema glabratum, Flavomarmelia caperata*, *Phaeophyscia* spp, *Xanthoparmelia caperata* and *Physcia* spp. There was significant difference among the lichens for all the pollutants studied. *Flavomarmelia caperata* have the higher accumulation of the most pollutants with the mean value of (97.39 ± 7.64ppm). The highest concentration of pollutants was recorded in PZ area with the mean value of (248.96 ± 6.08ppm). ABU Botanical garden had the lowest content of most of the pollutants with mean value of (36.94 ± 2.26ppm), SO_2 has the highest deposition in lichens in all the locations. Monthly variation shows that Cd recorded with lowest content while Mn is the highest of all heavy metals in most of the month. In all locations Mn shows significant difference in both ABU Botanical garden and Buruku, while Zn and NO_3 shows significant difference at P-value≤0.005 in Rido and PZ area respectively. Dry season has the higher concentration of all the pollutants such as heavy metal, (Cr (0.286±0.015), Zn (0.221±0.041), NO_3 (0.099±0.010) and SO_2 (355.343) while it correlate in Cd concentration. This work has provided an insight into the geospatial and seasonal variation of pollutants in all the study areas, and an area whose air quality status has not previously been studied like Buruku. The study has shown that anthropogenic sources such as metals work shop, agro-chemicals fossil combustion etc) of air pollution appear to be the predominant influence on NO_3 concentrations and potentially also on the lichen species diversity in most of the study areas, especially in the PZ area. The study has shown that monitoring programs such as a lichen desert and lichen forest can reveal the locations where ecological detriment is occurring that maybe associated with air pollution even at low levels. The improved sensitivity to this

passive biomonitoring methodology applied here will also be applicable to other monitoring studies of ambient pollutants.

6.2. RECOMMENDATION

The continuous study of lichens species is recommended considering their significance in determining air quality in our environment. The use of epiphytic lichens biomonitoring particularly; *Dictyonema glabratum*, *Flavopermelia capirata*, *Xanthoparmelia* species, *Physcia* species and *Phaeophyscia* species is recommended because it provides a cost–effective approach for monitoring of atmospheric pollutants. It also recommended continuous monitoring and investigating the pollutants, as it is being done in some countries, considering the toxicological effect they posed to human health and environment.

6.3 CONTRIBUTION TO KNOWLEDGE

1. Establishing the presence of the common lichen species such as; *Dictyonema glabratum*,(Fruticose lichen) *Flavopermelia carperata*, *Xanthopermelia caperata*, *Phaeophyscia* species and *Physcia* species (Foliose lichen) in the study area.
2. Quantifying the relative concentration of the pollutants adsorbed by lichens;

i Heavy metals; Mn (1.58 ± 0.32ppm) is the highest heavy metals absorbed by lichens, followed by Cr (0.28 ± 0.03ppm), Zn (0.19 ± 0.05ppm), Pb (0.17 ± 0.02ppm) and Cd (0.02 ±0.00ppm).

ii. NO_3 and SO_2 were recorded as (0.10 ± 0.02mg/L) and (147.32 ± 18.69mg/L) respectively, where as SO_2 is the highest pollutants absorbed by lichens.

iii. *Flavoparmelia caperata* trapped highest content of pollutant with (97.39 ± 7.64ppm), *physcia* species (90.74 ± 17.63ppm), *Phaeophyscia* specie (45.80 ± 7.36ppm), *Dictyonema glabratum* (41.84 ± 5.12pppm), and *Xanthoparmelia caperata*, (32.02 ± 7.73ppm).

iv. PZ area had the highest content of pollutants with (248.96 ± 6.08ppm) which make it the highly polluted area, Rido with (108.51 ± 2.07ppm), Buruku with (104.53 ± 1.95ppm), and ABU Botanical garden with (36.94 ± 2.26ppm).

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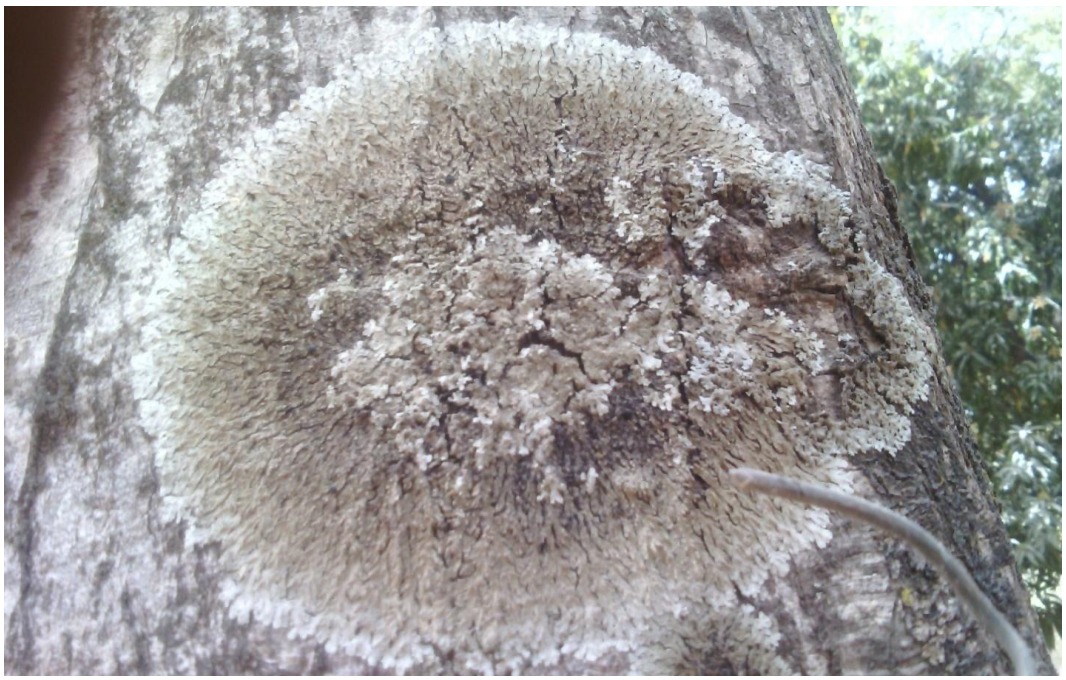
APPENDIX I

Dictionema glabratum:
Body form: Fruticose
Habitat: Coticolous
Description: this lichens is formed by symbiosis between a basidiomycete fungus and cyanobacterium, making it both a basidiolichen and a cyanolichen, which is a very rare combination This makes *Dictyonema* more closely related to mushrooms than it is to most other lichens.



Xanthoparmelia caperata
Body form: Foliose
Habitat: Coticolous
Description: The genus *Xanthoparmelia* (Vain.) Hale, comprised of approximately 750 species, All *Xanthoparmelia* species share key taxonomic characters, including the degree of attachment to the substrate, color of the lower surface (pale brown to ebony black), presence of isidia of different types (cylindrical to globose)

Phaeophyscia spp
Body form: Foliose
Habitat: Coticolous
Description: Shelf-like filamentous, up to 7 cm across, composed of loosely interwoven but compacted, more or less horizontally arranged, erogenous fibrils bordered by a narrow, white margin. Thallus in section 0.5–1 mm thick, composed of an irregular photobiont layer and a thin medulla forming a white hypothallus; photobiont layer composed of numerous cyanobacterial filaments wrapped in a closed hyphal sheath formed by jigsaw puzzle-shaped cells;

Flavopermelia caperata
Body form: Foliose
Habitat: Coticolous
Description: Common greenshield lichen is a medium to large foliose lichen that has a very distinctive pale yellow green upper cortex when dry, usually have patches of granular soredia arising from pustules. The lobes of the thallus may be smooth, but quite often have a wrinkled appearance especially in older specimens. The lower surface is black except for a brown margin

Physcia spp*:* Body form: Foliose
Habitat: Courticours and some are Saxicolours
Description: Is a genus of lichenized fungi in the family Physciaceae. The genus name means "inflated" or "sausage-like. According to a 2008 estimate, the widespread genus contains 73 species.

APPENDIX II

Pb

Descriptives

HM

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	6	.2610	.07422	.03030	.1831	.3389	.20	.39
2	6	.2798	.11511	.04700	.1590	.4006	.18	.50
3	6	.1785	.03136	.01280	.1456	.2114	.15	.24
4	6	.1768	.02365	.00966	.1520	.2017	.15	.22
5	6	.1317	.05839	.02384	.0704	.1929	.08	.24
6	6	.1342	.05900	.02409	.0723	.1961	.06	.21
7	6	.0975	.02261	.00923	.0738	.1212	.06	.12
8	6	.1422	.02382	.00972	.1172	.1672	.11	.16
Total	48	.1752	.08194	.01183	.1514	.1990	.06	.50

ANOVA

HM

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.174	7	.025	7.041	.000
Within Groups	.141	40	.004		
Total	.316	47			

HM

Duncan

SPP	N	Subset for alpha = 0.05		
		1	2	3
7	6	.0975		
5	6	.1317	.1317	
6	6	.1342	.1342	
8	6	.1422	.1422	
4	6		.1768	
3	6		.1785	
1	6			.2610
2	6			.2798
Sig.		.244	.233	.586

Means for groups in homogeneous subsets are displayed.

Mn

Descriptives

HM

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	6	1.1993	.92161	.37625	.2322	2.1665	.62	2.98
2	6	1.4630	.85983	.35102	.5607	2.3653	.50	2.89
3	6	.6423	.43675	.17830	.1840	1.1007	.41	1.53
4	6	2.1165	.87676	.35794	1.1964	3.0366	.87	3.06
5	6	.8155	.49064	.20030	.3006	1.3304	.27	1.48
6	6	.8445	.42462	.17335	.3989	1.2901	.44	1.67
7	6	1.6898	.60902	.24863	1.0507	2.3290	.96	2.47
8	6	3.8378	1.61216	.65816	2.1460	5.5297	1.45	5.87
Total	48	1.5761	1.26374	.18240	1.2092	1.9431	.27	5.87

ANOVA

HM

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	45.365	7	6.481	8.730	.000
Within Groups	29.696	40	.742		
Total	75.061	47			

HM

Duncan

SPP	N	Subset for alpha = 0.05		
		1	2	3
3	6	.6423		
5	6	.8155		
6	6	.8445		
1	6	1.1993	1.1993	
2	6	1.4630	1.4630	
7	6	1.6898	1.6898	
4	6		2.1165	
8	6			3.8378
Sig.		.070	.099	1.000

Means for groups in homogeneous subsets are displayed.

Cd

Descriptives

HM

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	6	.0100	.00651	.00266	.0032	.0168	.01	.02
2	6	.0130	.00420	.00171	.0086	.0174	.01	.02
3	6	.0203	.00916	.00374	.0107	.0299	.02	.04
4	6	.0190	.00089	.00037	.0181	.0199	.02	.02
5	6	.0200	.00063	.00026	.0193	.0207	.02	.02
6	6	.0217	.00408	.00167	.0174	.0260	.02	.03
7	6	.0250	.00548	.00224	.0193	.0307	.02	.03
8	6	.0233	.00516	.00211	.0179	.0288	.02	.03
Total	48	.0190	.00681	.00098	.0171	.0210	.01	.04

ANOVA

HM

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.001	7	.000	5.703	.000
Within Groups	.001	40	.000		
Total	.002	47			

HM

Duncan

SPP	N	Subset for alpha = 0.05		
		1	2	3
1	6	.0100		
2	6	.0130	.0130	
4	6		.0190	.0190
5	6			.0200
3	6			.0203
6	6			.0217
8	6			.0233
7	6			.0250
Sig.		.326	.054	.087

Means for groups in homogeneous subsets are displayed.

Cr

Descriptives

Cr

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	6	.3030	.05215	.02129	.2483	.3577	.21	.36
2	6	.3270	.10600	.04327	.2158	.4382	.16	.45
3	6	.3155	.04432	.01810	.2690	.3620	.23	.35
4	6	.3293	.02448	.01000	.3036	.3550	.28	.35
5	6	.3230	.06595	.02692	.2538	.3922	.27	.45
6	6	.2302	.11776	.04808	.1066	.3537	.10	.43
7	6	.2107	.07271	.02968	.1344	.2870	.11	.31
8	6	.2078	.08643	.03528	.1171	.2985	.13	.35
Total	48	.2808	.08778	.01267	.2553	.3063	.10	.45

ANOVA

Cr

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.125	7	.018	2.999	.013
Within Groups	.237	40	.006		
Total	.362	47			

Cr

Duncan

Treatment	N	Subset for alpha = 0.05	
		1	2
8	6	.2078	
7	6	.2107	
6	6	.2302	.2302
1	6	.3030	.3030
3	6		.3155
5	6		.3230
2	6		.3270
4	6		.3293
Sig.		.056	.055

Means for groups in homogeneous subsets are displayed.

Descriptives

Zn

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	6	.4398	.26221	.10705	.1647	.7150	.20	.76
2	6	.3138	.15948	.06511	.1465	.4812	.06	.47
3	6	.1902	.05935	.02423	.1279	.2525	.11	.28
4	6	.0993	.03075	.01255	.0671	.1316	.07	.16
5	6	.1843	.14272	.05826	.0346	.3341	.03	.38
6	6	.1803	.17838	.07282	-.0069	.3675	.04	.45
7	6	.0685	.01854	.00757	.0490	.0880	.04	.09
8	6	.0903	.02871	.01172	.0602	.1205	.06	.12
Total	48	.1958	.17401	.02512	.1453	.2464	.03	.76

ANOVA

Zn

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	.663	7	.095	4.985	.000
Within Groups	.760	40	.019		
Total	1.423	47			

Zn

Duncan

Treatment	N	Subset for alpha = 0.05		
		1	2	3
7	6	.0685		
8	6	.0903		
4	6	.0993		
6	6	.1803	.1803	
5	6	.1843	.1843	
3	6	.1902	.1902	
2	6		.3138	.3138
1	6			.4398
Sig.		.189	.133	.121

Means for groups in homogeneous subsets are displayed.

Descriptives

SO2

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	6	1.2198E2	145.87417	59.55288	-31.1056	275.0656	30.19	415.00
2	6	90.5317	34.41759	14.05092	54.4126	126.6507	45.28	135.84
3	6	83.0150	24.80149	10.12516	56.9874	109.0426	45.28	120.75
4	6	62.8917	37.48017	15.30122	23.5586	102.2247	30.19	135.84
5	6	1.5849E2	73.17315	29.87281	81.6995	235.2805	60.38	241.52
6	6	2.1635E2	24.65085	10.06367	190.4789	242.2178	181.13	241.52
7	6	2.2389E2	25.99878	10.61396	196.6076	251.1757	196.22	271.69
8	6	2.0628E2	12.32420	5.03133	193.3482	219.2151	196.22	226.41
Total	48	1.4543E2	84.09139	12.13755	121.0112	169.8463	30.19	415.00

ANOVA

SO2

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	175986.422	7	25140.917	6.431	.000
Within Groups	156367.592	40	3909.190		
Total	332354.014	47			

SO2

Duncan

Treatment	N	Subset for alpha = 0.05		
		1	2	3
4	6	62.8917		
3	6	83.0150	83.0150	
2	6	90.5317	90.5317	
1	6	1.2198E2	1.2198E2	
5	6		1.5849E2	1.5849E2
8	6			2.0628E2
6	6			2.1635E2
7	6			2.2389E2
Sig.		.143	.062	.105

Means for groups in homogeneous subsets are displayed.

Descriptives

NO3

	N	Mean	Std. Deviation	Std. Error	95% Confidence Interval for Mean		Minimum	Maximum
					Lower Bound	Upper Bound		
1	6	.0935	.03049	.01245	.0615	.1255	.05	.14
2	6	.1108	.04092	.01670	.0679	.1538	.07	.18
3	6	.1287	.06529	.02666	.0601	.1972	.04	.23
4	6	.0513	.01164	.00475	.0391	.0635	.04	.07
5	6	.1257	.09236	.03770	.0287	.2226	.04	.30
6	6	.0937	.03599	.01469	.0559	.1314	.05	.14
7	6	.0790	.01831	.00747	.0598	.0982	.05	.10
8	6	.1402	.08728	.03563	.0486	.2318	.07	.31
Total	48	.1029	.05837	.00842	.0859	.1198	.04	.31

ANOVA

SO2

	Sum of Squares	Df	Mean Square	F	Sig.
Between Groups	.036	7	.005	1.671	.144
Within Groups	.124	40	.003		
Total	.160	47			

Duncan

Treatment	N	Subset for alpha = 0.05	
		1	2
4	6	.0513	
7	6	.0790	.0790
1	6	.0935	.0935
6	6	.0937	.0937
2	6	.1108	.1108
5	6		.1257
3	6		.1287
8	6		.1402
Sig.		.105	.106

Means for groups in homogeneous subsets are displayed.