Heavy Metal Air Pollution Study, Using A Moss Bio monitoring Technique.

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TO THE CHEMISTRY DEPARTMENT
Declaration
I declare that this research is my own, unaided work. It is being submitted for the Master of
Science Degree in Chemistry at the University of Zimbabwe, Harare. It has not been submitted
before for any degree or examination at any other University.

........................................

Signature of candidate
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Dedication
This study is dedicated to my Father, Nicholas Munyuki Gaza, a great man indeed. I say this is the fruit of your forever support and encouragement.
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Abstract

Air pollution is increasingly becoming a problem in developed and developing countries. As a corrective measure, constant air monitoring has been done using conventional techniques which are costly and time consuming hence the need for cheaper and affordable methods. Of recent, biomonitoring has emerged as an effective alternative method. The aim of this study was to investigate heavy metal air pollution in the environment using Moss. Moss are lower plants that can provide a surrogate and time-integrated means of measuring elemental depositions from the atmosphere to terrestrial systems. Atmospheric deposition of heavy metals Chromium (Cr), Copper (Cu), lead (Pb), and Zinc (Zn) was studied at the University of Zimbabwe. 17 samples of Moss were hung on sites selected by a systematic grid sampling method, during the summer of 2016. The concentrations of heavy metals were determined by Atomic Absorption Spectroscopy (AAS). The concentrations were expressed as Relative Accumulation Factors (RAFs). The results showed the concentration order of deposition as Cu > Cr > Zn > Pb and that Zn deposited uniformly. Although the distribution patterns of Cr and Cu were similar, Pb and Zn had their own patterns; these results suggested that the source of heavy metal could be from traffic related air pollutants.

Keywords: Air quality; Heavy Metals; Moss Biomonitoring; Relative Accumulation Factors; GIS technology; low-cost; equipment; time-consuming.
Chapter 1

1 Introduction

1.1 Background

Uncontaminated air is a fundamental requisite of human health and well-being [1]. Air pollution however continues to be a serious problem in many parts of the world, particularly in developing countries [2]. According to a WHO assessment of the burden of disease due to air pollution, more than two million premature deaths each year can be attributed to the effects of air pollution and more than half of this disease burden is borne by the populations in developing countries [3]. The considerable contribution of air pollution to the diminished health status of exposed human populations, compromised of integrity of ecosystems, forest decline, loss of agricultural productivity, and many others, has been a reason for increased public concern throughout the whole world. This makes, air pollution, to be a topic of intense scientific, governmental, and also industrial interest.

The environment is increasingly getting contaminated by a wide array of atmospheric pollutants which may either be natural or anthropogenic. They may occur as solid particles, liquid droplets, gasses or in various mixtures of these forms. Natural sources include volcanic emissions, accident and veld fires as well as soil particles. Anthropogenic sources include emissions from industry, power generation, mining activities, traffic emissions, waste incineration and many others [4]. The major components of these air pollutants include sulphur dioxide, airborne particulate matter (APM), carbon oxides, hydrocarbon compounds, nitrogen oxides and ozone. Amongst these are heavy metals and other toxic elements which usually exist in association with
APM. Once these pollutants are deposited into the atmosphere, they undergo, physical, chemical and photochemical transformations that will eventually decide their fate and atmospheric concentrations [2].

In developing countries, air pollution problems are fuelled by increased rural to urban migration, industrialisation and the rapid growth of fuelled transportation systems in-line with population growth. In Africa the problems are further compounded by poor urban planning and the importation of second hand vehicles. Evidence of air pollution is normally found around large uncontrolled point sources and in some instances at national or even regional scales. This is mainly because air pollutants, do not stay confined near the source of emission, but rather, disperse over distances, transcending natural and political boundaries, depending upon the terrain and meteorological conditions, in particular wind direction, speed, vertical and horizontal temperature gradients [2].

The necessary information on air pollutants can be obtained by either dispersion modelling or by taking actual measurements of the emissions in the field. Amongst the two, dispersion modelling is more appealing to most researchers as it a lot cheaper when compared to taking field measurements [5]. However, emission measurements taken from the field are still necessary and indispensable as they are used to provide physical evidence that validates dispersion models. In addition, data obtained from field measurements, may also indicate the presence of sources which were not previously known or registered [6].

From literature, there are two conceptual approaches for taking field measurements relevant for atmospheric deposition and air pollution related studies that clearly emerge. These are (1) the
direct collection of APM, precipitation, and total deposit, and (2) the use of suitable air pollution biomonitors. The first approach is aimed at quantitative surveys of local, short-range, medium-range or global transport of pollutants, including human health-related studies when collecting size fractionated APM. It requires long-term sampling on a continuous basis at a large number of sites, in order to ensure the temporal and spatial representativeness of measurements. The application of such direct measurements on a large scale is very expensive and person-power intensive [6]. Furthermore, it is not always feasible, due to logistic problems, to set up instrumental equipment at all the required locations. It is here that, the second approach is considered because it is non-expensive and yet provides a reliable way of carrying out air quality status assessment in a country or a region.

Biomonitoring is defined as the act of continuously observing a geographical area with the help of living organisms such as, plants, or animals, to obtain information on environmental quality over space and time, that is the response of living organisms to changes in their environment (e.g. by their elemental content). The following papers have, the definitions for the main terms that have been defined in the field of biomonitoring [7] [5] [8]. These organisms when employed, integrate pollution over time, thereby reducing the need for continuous chemical monitoring, thus avoiding the difficulty of interpreting “snapshot” measurements and presenting a potential for retrospective monitoring. Such organisms enrich the substance to be determined so that the analytical accessibility is improved and the measurement uncertainty reduced. By observing and measuring the changes in an appropriately selected organism, a conclusion as to the kind of pollution, its source, and its intensity can be drawn [2].
Two types of biomonitoring emerge distinctively from literature. These are passive and active biomonitoring. Passive biomonitoring employs the use of biomonitors that grow naturally (i.e. they are indigenous to a particular region) in the area under study. It is usually applied to extensive studies involving large areas such as national or even regional scales. For active biomonitoring, the biomonitor samples are collected from relatively unpolluted habitats, cleaned, and exposed in a standardized fashion in a different environment for a defined period of time. It is more useful for intensive studies in smaller areas such as urban or industrial areas [9].

When compared to animals, plants are not only more sensitive to most prevalent air pollutants but are also better at reflecting the local air condition status [10]. It is on this basis, that plants are more commonly employed as biomonitors in air quality biomonitoring studies [11]. Several types of plants, such as lichens, mosses, ferns, grass, tree bark, tree rings, tree leaves and pine needles have been applied in air monitoring programs before [12] [13]. Although both higher and lower plants have been used for biomonitoring, lower plants are the most preferred because they are resistant to many substances which are toxic higher plants. Lower plants are also able to survive in diverse and often extreme [4] [14] [15]. Of all biological species used in biomonitoring, lichens and mosses have the most common usage. 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 [12]. In this study, however mosses are used as the biomonitors.

Botanically, mosses are bryophytes. Two Swedish scientists Åke Rühling and Germund Tyler (1960) discovered that mosses are good biomonitors of heavy metal pollution in the atmosphere.
After this successful discovery many European countries have used mosses in national and multinational surveys of atmospheric-metal deposition. Mosses are cryptogams that thrive in a humid climate. They possess many properties that make them suitable for monitoring air pollutants [16]. These species obtain nutrients from wet and dry deposition because they do not have real roots so there is no uptake of mineral substrates from other sources except the atmosphere. Nutrient uptake from the atmosphere is promoted by their weakly developed cuticle (so metal ions easily penetrate the cell wall) and large surface to weight ratio. Other suitable properties include a slow growth rate, small size and easy to handle, undeveloped vascular bundles (so transport of minerals between segments is limited), minimal morphological changes during the mosses’ lifetime, perenniary, wide distribution (even in industrial and urban areas), an ability to survive in highly polluted environment, ease of sampling and the possibility to determine concentrations in the annual growth segments [15]

Air pollutants are deposited on mosses in aqueous solution, in gaseous form or attached to particles. The accumulation of pollutants in mosses occurs through a number of different mechanisms:

- As layers of particles or entrapment on the surface of the cells.
- Incorporation into the outer walls of the cells through ion exchange processes
- Metabolically controlled passage into the cells [17].

Ion exchange mechanism is a fast physiological-chemical process that is affected by several factors which include the number and type of free cation exchange sites, the age of the cells and their reaction to desiccation, growing conditions, temperature, precipitation pH, composition of
the pollutants and leaching [18]. In the ion exchange process, cations and anions become attached to functional organic groups in the cell walls among other things through chelation [19].

The cell walls have a high polyuronic acid content which makes moss a very good natural ion exchanger. The cell walls of bryophytes possess many negatively charged anionic sites to which cations are bound in exchangeable form. Studies with electron microscope have shown that the sorbed metal may be held in the extracellular region outside of the cytoplasm bound to the cell wall, and due to the highly reduced presence or absence of cuticle in the moss, ions have a direct access to the cell wall, mosses surfaces and rhizoids and thus do not perform any active heavy metal ion discrimination [20] [16].

The “moss bag technique” is the most common type of active biomonitoring with terrestrial mosses that is reported in literature. The technique, involves exposure of moss samples held within mesh bags in order to monitor the presence of contaminants in the air. The technique is mainly used to monitor levels of inorganic contaminants as metals, metalloids, nitrogen, sulphur, ozone, radionuclides and more recently polycyclic aromatic hydrocarbons (PAH).

1.2 Problem Statement

Several studies on air pollution have been carried out before in Zimbabwe by workers such as [21] [22] [23] [24] [25]. However in most existing studies, environmental measurements relied on either instrumental monitoring devices or passive samplers. Although, these devices provide high quality data, with low detection limits, monitoring is limited by several practical constraints. For instance, they require long-term sampling on a continuous basis at a large number of sites, in order to ensure the spatial representativeness of measurements. The application of such direct
measurements on a large scale would be very expensive and person-power intensive [6]. Furthermore, it is not always feasible, due to logistical problems, to set up instrumental equipment at all the required locations. They also require some sort of security to prevent them from being vandalized [26].

In the light of these constraints, sampling ends up proceeding with only a few monitoring points, as representatives of very large spatial areas. Results from recent studies have also shown that data from such few monitoring stations may not accurately characterize the complexities of spatial dispersion of air pollutants in urban areas [27] [28]. For example concentrations of traffic related air pollutants such as heavy metals; demonstrate steep concentration gradients from on source to near source micro environments [29] [30]. So the spatial contrasts of these contaminants can be very large within the first hundred meters of source [31], reaching background levels after a 100 -200 m only [32]. A dense network of long-term measurements is thus needed to capture the spatial contrasts of these contaminants [33]

This could have been attempted by Mujuru [24] when he extensively studied NO₂ and SO₂ with passive samplers. But due to the saturation of samplers, repeated deployment of passive samplers for a few (often two) weeks is needed to describe long-term average conditions [33]. Also measurement of particle bound toxicants including metals is even more demanding and costly, and thus long-term monitoring at a high spatial resolution is prohibitive. Therefore with low density air quality sampling, assessment of phenomena such as atmospheric deposition, hot spot and source identification might not be possible.
The above-mentioned implies the need for development of other alternative monitoring techniques such as bio-monitoring that can be operated at a high spatial resolution, over longer periods of time without the need for power and can be operated at low costs and robust monitoring of air quality.

1.3 Justification

Air pollution is one of the most pressing problems facing the world at present. Its effects can be felt at the local, national and global levels, impacting on human health and well-being, vegetation and crops, buildings and outdoor monuments, integrity of ecosystems and world climate. In Zimbabwe the foremost drivers of change in atmospheric composition have been identified as urbanization; motorization; economic activity; power generation using fossil fuels; use of biomass for energy, especially for domestic cooking and heating and open burning including vegetation fires and waste burning [34]. Given the above, there is increasing need to determine the state of air quality in Zimbabwe and the challenges it presents so as to mitigate them and identify the most effective measures to protect human health and the environment.

The emission of contaminants into the atmosphere has been increasing ever since the industrial revolution and even accelerated during the Second World War as a result of the technological advances made during that period. Although the quality of life did improve considerably since these times, other basic aspects such as the integrity of ecosystems and human health have been seriously and perhaps even irreversibly affected [35]. Not only is air pollution detrimental to our health but it is also expensive. According to a study Rana [36], in Africa air pollution is causing more premature deaths (about 712 000 people per year) than unsafe water or childhood malnutrition. He estimates that the total economic cost of these premature air pollution deaths in
2013 was around $215bn. Thus as a first step towards combating this air pollution, it is critical to ascertain the status of the air quality in our settlements and one of the ways to do that is via high density air monitoring networks.

Although the current conventional techniques used, for air quality assessments have all the benefits as explained before, their demands are so crippling to poor nation such as Zimbabwe. As a result, there is only limited or no spatial coverage of human environs by air quality monitoring. Therefore either baseline data does not exist in most areas or they are of limited spatial representatively in the areas where monitoring is performed. Such data is important in assessment of longtime exposure to air contaminants such as heavy metals. These contaminants have serious damaging effects on human health and ecosystems, as recognised by diverse international agencies such as the United States Environmental Protection Agency (USEPA) and the Agency for Toxic Substances and Disease Registry (ATSDR).

Lack of availability of data on the concentrations of specific contaminants such as heavy metals, impedes on the implementation of corrective measures for improving environmental health. Therefore, taking into account all of the above, there is currently a need to develop new tools, specifically bio-tools, which would enable the simple, economic and robust monitoring of air quality. Of the biomonitors available, terrestrial bryophytes (specifically mosses) are the most suitable because of their characteristics [7]. Their properties confer mosses with a high cation exchange capacity and suitable morphology for fixing and accumulating contaminants that are present in gaseous or particulate form, and of both organic and inorganic nature, which are derived from atmospheric deposition.
The use of mosses can enable the establishment of large scale networks for extensive-type studies (e.g. regional or national studies) and also the establishment of small scale networks for more intensive-type studies (e.g. in urban or industrial areas). Active biomonitoring studies have been successfully carried out in cities such as Belgrade [37], Budapest [38], Naples [39] and Oporto [40], among others, and in industrial facilities such as aluminium smelters [41], electricity power stations [42] [43], chloro-alkali plants [44] [45], and copper smelters, among others.

Extensive studies on the characterization of spatial dispersion of air pollutants in areas near micro-environments such as major roads, cross roads, vicinities of industrial complexes and mines, commuter omnibus stations and tollgates would be enabled. Data generated from such studies would allow for the assessment and examination of long-term on-road exposure of pedestrians, commuters, cyclists and workers (e.g. drivers and policemen) to mining activities, industrial and traffic-related air pollutants. It can also be useful in epidemiological studies focusing on the impact of such micro environments that are in close proximity to social public places such as shopping malls, schools, hospitals and suburban areas etc. Micro-scale specific urban topology has been shown to contribute to the creation of poor air dispersion conditions. This may give rise to contamination hotspots [27] [28]. At low density data collection regimes, these hotspots would be difficult or even impossible to detect.

With biomonitoring networks, air-pollution monitoring is possible even in remote and rural areas as samples can be collected and measurements of pollutants done at laboratories many kilometers away from the site. In addition, data obtained from field measurements, may also indicate the presence of sources which were not previously known or registered. The technique
also fits well into the Zimbabwe Agenda for Socio-Economic Transformation (Zim Asset), which is the current national economic programme that seeks to tackle national problems using home grown solutions.

This study seeks to contribute to the knowledge regarding the monitoring and the measurement of air pollution levels in Zimbabwe in a way that is simple, reliable, cost-effective and does not need electricity to be operational.

1.4 Aim and Objectives

1.4.1 Aim

To assess heavy metal air pollution in urban environments, using a moss bag, bio-monitoring technique.

1.4.2 Objectives

1. To quantitatively characterise atmospheric deposition of heavy metals namely Cr, Cu, Pb and Zn.
2. To produce maps that show the spatial distribution patterns of the heavy metals determined.
3. To identify and indicate the spatial extent of different regions of atmospheric heavy metal deposition.
4. To deduce the sources of these heavy metals.
Chapter 2

2 Literature Review

2.1 The Atmosphere

The word atmosphere is literally translated as a "sphere of vapours". In planetary science, it is generally described as a gaseous envelope that surrounds a solid body of a planet. Although its thickness can extend for more than 1100 km about half its mass is concentrated in the lower 5.6 km [46]. Thus the Earth’s atmosphere can be described as a layer of gases (or a "sphere of vapours") that surrounds the Earth and retained by its gravity. It contains roughly 78% nitrogen, 21% oxygen, 0.93% argon, 0.04% carbon dioxide, and trace amounts of other gases, in addition to water vapour [47]. A more detailed composition is given in Table 2.1.

Table 2.1: The gaseous composition of air on a wet basis [46].

<table>
<thead>
<tr>
<th></th>
<th>ppm (vol.)</th>
<th>μg m⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen</td>
<td>756500</td>
<td>8.67 \times 10^8</td>
</tr>
<tr>
<td>Oxygen</td>
<td>202900</td>
<td>2.65 \times 10^8</td>
</tr>
<tr>
<td>Water</td>
<td>31200</td>
<td>2.30 \times 10^7</td>
</tr>
<tr>
<td>Argon</td>
<td>9000</td>
<td>1.47 \times 10^7</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>305</td>
<td>5.49 \times 10^5</td>
</tr>
<tr>
<td>Neon</td>
<td>17.4</td>
<td>1.44 \times 10^4</td>
</tr>
<tr>
<td>Helium</td>
<td>5.0</td>
<td>8.25 \times 10^2</td>
</tr>
<tr>
<td>Methane</td>
<td>0.97–1.16</td>
<td>6.35–7.63 \times 10^2</td>
</tr>
<tr>
<td>Krypton</td>
<td>0.97</td>
<td>3.32 \times 10^3</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>0.49</td>
<td>8.73 \times 10^2</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>0.49</td>
<td>4.00 \times 10^1</td>
</tr>
<tr>
<td>Xenon</td>
<td>0.08</td>
<td>4.17 \times 10^2</td>
</tr>
<tr>
<td>Organic vapors</td>
<td>ca. 0.02</td>
<td>—</td>
</tr>
</tbody>
</table>
This mixture of gases is what is more commonly known as air. The atmosphere protects life on earth by absorbing solar UV radiation and reducing temperature extremes between day and night. The atmosphere slowly becomes thinner and fades away into space. Therefore, there is no definite boundary between the atmosphere and outer space. About 75% of the atmosphere’s mass is within 11 km of the planetary surface [47].

The atmosphere is composed of four major regions, each with a unique chemical composition and temperature. These are the troposphere, stratosphere, mesosphere and thermosphere, as is shown in Figure 2.1. The troposphere is the region of interest in this study.

![Diagram of atmospheric regions]

Figure 2.1 Variation of temperature and chemical composition with altitude [47].

### 2.2 Concept of air Pollution
The composition and chemistry of the atmosphere is of paramount importance for several reasons, but primarily because of the interactions between the atmosphere and living organisms.
The composition of the Earth’s atmosphere has been evolving since the birth of the planet [46]. In the beginning, the Earth's composition was very different what it is today. Its atmosphere was very similar to today's Venus and Mars's atmosphere. It had about 95% carbon dioxide, 2-3% nitrogen, and very little, less than 1% oxygen. Today the Earth contains 79% nitrogen, 21% oxygen, and 3% water vapour [48].

It is evident that over billions of years the Earth's atmosphere evolved mainly due to natural processes to a composition that could sustain life. Then another era began with the emergence of the human being where the atmosphere composition changed due to natural processes and the contribution of man. This contribution by man is mainly due to anthropogenic activities. For centuries the anthropogenic contribution was by far less than the natural. Thus it was the natural processes that were responsible for the general outlook of the atmosphere. This was so, until recently in the 17 century with the emergency of the industrial revolution. Now it is evident that modernization and progress have led to air getting more and more polluted over the years. Industries, vehicles, increase in the population, and urbanization are some of the major factors responsible for air pollution. The following industries are among those that emit a great deal of pollutants into the air: thermal power plants, cement, steel, refineries, petro-chemicals, and mines [47]. Although the quality of life did improve considerably since these times, other basic aspects such as the integrity of ecosystems and human health have been seriously and perhaps even irreversibly affected [49].

It is in the light of the above that Air pollution can be defined as the introduction of contaminants such as chemicals, particulates, or biological materials/substances into the atmosphere that cause discomfort, disease, or death to humans, damage other living organisms such as food crops, or
damage the natural or built environment [50]. It is important to note that these contaminants are not necessarily pollutants. A contaminant can only become a pollutant when its concentration in the atmosphere goes beyond a certain threshold value [51].

Anthropogenic air pollution commenced with human's systematic use of fire. Its historical development has been characterized by steadily increasing amounts of total emissions, the invention of new sources of pollution emission as well as the emission of pollutants that had not formerly been emitted by man-made sources. So far, this development has had the greatest impact on the air quality of so-called mega-cities (cities with over 10,000,000 inhabitants). Today the major sources of man-made air pollution are motorized street traffic (especially exhaust gases and tire abrasion), the burning of fuels, and larger factory emissions. Depending on the pollutant particles' size, they can be carried for distances of several thousand miles. With decreasing diameter, they are able to infiltrate finer lung structures [52].

The major components of anthropogenic air pollutants include sulphur dioxide, Airborne Particulate Matter (APM), carbon oxides, hydrocarbon compounds, nitrogen oxides and ozone. Amongst these are heavy metals which form an important group of pollutants to be considered [2]. For some time now the term “heavy metals” has been used increasingly in various publications and in legislation related to chemical hazards and the safe use of chemicals. It is often used as a collective term for metals and semi-metals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity [53].
2.3 Heavy metal air pollution

2.3.1 Ecosystem Performance

Longest standing attention for widespread air pollution stems from concern over its ecological effects. The environmental impact of atmospheric deposition has been studied for more than a century; probably the first effect that was described on a scientific basis was the decline of epiphytic lichens in areas with high levels of atmospheric pollution. Ever since Nylander’s classical report on the epiphytic lichens of Paris and its surroundings, extensive studies have been performed in many areas [51]. The decline of forest tree vitality caused by atmospheric pollution has been known for a long time [48], and the occurrence of forest decline over large parts of Europe is now well known [55]. In comparison to the lake and stream water acidification, first described for Scandinavia [52], widespread effects of atmospheric deposition (‘‘acid-rain”’) were described for ecosystems such as freshwater bodies, forest tree layers, heathland, chalk, grass and moorlands [56], and for the decline of many plant species [57].

2.3.2 Human health

In addition to the ongoing concern for ecosystem performance as such, attention has been and becomes increasingly more directly focused on human health. This may be ascribed to the generally recognized impact of ecosystem performance on human well-being; furthermore, health-care has also been progressively developing towards approaches which include our nutrition and our social and environmental surroundings [58].

As a result, throughout the world, epidemiological studies were set up on air pollution and mortality rates and respiratory health effects, initially mostly on air particulates, ozone, acid rain, NOx and Sulphur oxides [59] [60]. For The Netherlands, the latter may be illustrated by the
steady increase in clinical epidemiological medical services from the 1980s onwards [58], and by current Dutch epidemiological studies, which also focus on the relationships between atmospheric black smoke (diesel engines) and nitrogen dioxide (all motorized vehicles) on one hand and both total mortality and cancer incidence on the other [61].

2.4 Heavy metals

Heavy metals represent a large group of chemical elements (> 40) whose density is about five times the density of water [53]. Most heavy metals may be important trace elements in the nutrition of plants, animals or humans (e.g. Zn, Cu, Mn, Cr, Ni, V), while others are not known to have any positive nutritional effects (e.g. Pb, Cd, Hg). However they can all cause toxic effects (some at a very low content level) if they occur excessively [62]. The toxicity of heavy metal depends a great deal on their chemical form, concentration, residence time, etc. [63]. Because these elements do not decay with time, their emission to the environment is a serious problem which is increasing worldwide due to the rapid growth of population, increasing combustion of fossil fuels, and the expansion of industrial activities [2].

2.5 Origin of heavy metals in the environment

There are two different sources for heavy metals in the environment. These sources can be both of natural or anthropogenic origin.

2.5.1 Natural

The principal natural source of heavy metals in the environment is from crustal material that is either weathered on (dissolved) and eroded from (particulate) the Earth’s surface or injected into the Earth’s atmosphere by volcanic activity. These two sources account for 80% of all the natural
sources; forest fires and biogenic sources account for 10% each. Particles released by erosion appear in the atmosphere as wind blown dust. In addition, some particles are released by vegetation. [64].

2.5.2 Anthropogenic

There are a multitude of anthropogenic emissions in the environment. Generally heavy metals enter the environment mainly via three routes:

(I) deposition of atmospheric particulates (e.g. mining, smelting, fossil fuel combustion, municipal waste incineration, cement production and phosphate mining).

(II) disposal of metal enriched sewage sludge and sewage effluents, commercial Fertilizers and pesticides and animal waste specially to the terrestrial and aquatic environment

(III) by-products from metal mining processes [65] [2].

Among them, the major source of metals is from mining and smelting. Mining releases metals to the fluvial environment as tailings and to the atmosphere as metal-enriched dust, whereas smelting releases metals to the atmosphere as a result of high-temperature refining processes [66]. The estimation of metal input into environment from the two latter sources (II & III) is relatively easy to measure, but atmospheric input is difficult to quantify accurately because of after emission, the pollutants are subjected to physical, chemical and photochemical transformations, which ultimately decide their fate depending upon the atmospheric concentrations [65] [2]. Air pollutants do not remain confined near the source of emission, but spread over distances, transcending natural and political boundaries depending upon topography.
and meteorological conditions, especially wind direction, wind speed and vertical and horizontal thermal gradients [2]. Among the various species present in the particulate matter, a great attention has been devoted since many years to the study of the elements with elevated toxicity and great diffusion in the environment (As, Cd, Cr, Hg, Ni, Pb, etc.) because of both anthropogenic and natural pollutant emissions [67]. The contributions of natural and anthropogenic sources in atmospheric heavy metal pollution are shown in Table 2.2.

Table 2.2: Natural and Anthropogenic elements fluxes (value x 10^8 g per year) [68].

<table>
<thead>
<tr>
<th>Element</th>
<th>Fluxes from crustal origin</th>
<th>Fluxes from volcanic origin</th>
<th>Fluxes in gas of volcanic origin</th>
<th>PM emission of industrial origin</th>
<th>Element flux from fossil fuel</th>
<th>Total Emission</th>
<th>Atmospheric Alteration Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.5</td>
<td>0.1</td>
<td>0.0006</td>
<td>40</td>
<td>16</td>
<td>50</td>
<td>8333</td>
</tr>
<tr>
<td>Al</td>
<td>356,500</td>
<td>132,750</td>
<td>8.4</td>
<td>40,000</td>
<td>32,000</td>
<td>72,000</td>
<td>15</td>
</tr>
<tr>
<td>As</td>
<td>25</td>
<td>3</td>
<td>0.1</td>
<td>620</td>
<td>160</td>
<td>780</td>
<td>2786</td>
</tr>
<tr>
<td>Cd</td>
<td>2.5</td>
<td>0.4</td>
<td>0.001</td>
<td>40</td>
<td>15</td>
<td>55</td>
<td>1897</td>
</tr>
<tr>
<td>Co</td>
<td>40</td>
<td>30</td>
<td>0.04</td>
<td>24</td>
<td>20</td>
<td>44</td>
<td>63</td>
</tr>
<tr>
<td>Cr</td>
<td>500</td>
<td>84</td>
<td>0.005</td>
<td>650</td>
<td>290</td>
<td>940</td>
<td>161</td>
</tr>
<tr>
<td>Cu</td>
<td>100</td>
<td>93</td>
<td>0.012</td>
<td>2200</td>
<td>430</td>
<td>2630</td>
<td>1363</td>
</tr>
<tr>
<td>Fe</td>
<td>190,000</td>
<td>87,750</td>
<td>3.7</td>
<td>75,000</td>
<td>32,000</td>
<td>107,000</td>
<td>39</td>
</tr>
<tr>
<td>Hg</td>
<td>0.3</td>
<td>0.1</td>
<td>0.001</td>
<td>50</td>
<td>60</td>
<td>110</td>
<td>27,500</td>
</tr>
<tr>
<td>Mn</td>
<td>4250</td>
<td>1800</td>
<td>2.1</td>
<td>3000</td>
<td>160</td>
<td>3160</td>
<td>52</td>
</tr>
<tr>
<td>Mo</td>
<td>10</td>
<td>1.4</td>
<td>0.02</td>
<td>100</td>
<td>410</td>
<td>510</td>
<td>4474</td>
</tr>
<tr>
<td>Ni</td>
<td>200</td>
<td>83</td>
<td>0.0009</td>
<td>600</td>
<td>380</td>
<td>980</td>
<td>348</td>
</tr>
<tr>
<td>Pb</td>
<td>30</td>
<td>8.7</td>
<td>0.012</td>
<td>16,000</td>
<td>4300</td>
<td>20,300</td>
<td>34583</td>
</tr>
<tr>
<td>Sb</td>
<td>9.5</td>
<td>0.3</td>
<td>0.013</td>
<td>200</td>
<td>180</td>
<td>380</td>
<td>3878</td>
</tr>
<tr>
<td>Se</td>
<td>9.5</td>
<td>1</td>
<td>0.13</td>
<td>50</td>
<td>90</td>
<td>140</td>
<td>3390</td>
</tr>
<tr>
<td>Sm</td>
<td>32</td>
<td>9</td>
<td>-</td>
<td>7</td>
<td>5</td>
<td>12</td>
<td>29</td>
</tr>
<tr>
<td>Sn</td>
<td>50</td>
<td>2.4</td>
<td>0.005</td>
<td>400</td>
<td>30</td>
<td>430</td>
<td>821</td>
</tr>
<tr>
<td>Ti</td>
<td>23000</td>
<td>12,000</td>
<td>-</td>
<td>3600</td>
<td>1600</td>
<td>5200</td>
<td>15</td>
</tr>
<tr>
<td>V</td>
<td>500</td>
<td>150</td>
<td>0.05</td>
<td>1000</td>
<td>1100</td>
<td>2100</td>
<td>323</td>
</tr>
<tr>
<td>Zn</td>
<td>250</td>
<td>108</td>
<td>0.14</td>
<td>7000</td>
<td>1400</td>
<td>8400</td>
<td>2346</td>
</tr>
</tbody>
</table>
2.6 Mechanisms of heavy metal deposition

The aerosols, which have a very small falling velocity, are easily transferred by the wind and it is possible to be deposited through the rain at long distances from the point of their emission [69]. Therefore, it is expected that chemical components in the rainwater (acid components, anions, cations and heavy metals) damage significantly the environment (surface waters, plants, animals, human beings). These metals even if deposited constantly in small rates over long periods of time, accumulate in the environment and will probably pose an increasing major environmental and human health hazard in future. The transfer of airborne particles to land or water surfaces by dry, wet and occult deposition constitutes the first stage of accumulation of atmospheric heavy metals. The predominant path depends upon the type of chemical species and upon meteorological factors such as the intensity and distribution of rain fall.

2.6.1 Dry Deposition

Dry deposition involves four distinct processes: gravitational settling, impaction, turbulent transfer and transfer by Brownian motion. The relative importance of these processes depends primarily on the size of particles [65]. Dry deposition is more likely to remove particulate forms. Two major categories of particulate matter are fine particles and coarse particles. Fine particulate matter (FPM) comprises particles with aerodynamic diameters of 2.5 μm or less. They are emitted from fossil fuel combustion, motor vehicle exhausts (including diesel) and wood burning. Several toxic metals, including arsenic, cadmium, lead, zinc, antimony and their compounds are associated with FPM in ambient air This is important from a public health perspective since these fine particles are irrespirable and can be transported over very long distances. Coarse particulate matter or PM10 is the mass concentration of particulate matter having aerodynamic diameters less than 10 μm (USEPA, 1996). Anthropogenically added
particulates and aerosols in atmosphere show a broad size distribution from 0.001 μm to 50 μm and are strongly influenced by atmospheric transport processes. In rural regions anthropogenic particles > 5μm are absent [35] and in Polar Regions heavy metals are mostly associated with small aggregated particles in the range of 0.1-10 μm. Dry deposition of heavy metals in rural and remote regions is therefore, through impaction and turbulent transfer [70]. Dry deposition represents a major removal pathway for many pollutants from the atmosphere, and it is especially important in arid and semiarid regions where removal by wet deposition (i.e., rainfall scavenging) is greatly diminished because of limited precipitation [71].

2.6.2 Wet deposition

In wet deposition, there are always some atmospheric hydrometeors which scavenge aerosol particles. This means that wet deposition is gravitational, Brownian and/or turbulent coagulation with water droplets. Wet deposition involves two major processes: nucleation and within and below cloud scavenging, whereby the wet aerosol particles are collected by falling raindrops [70]. Wet deposition (via rain another types of precipitation) is most efficient at removing soluble form of heavy metals from the air. A great percentage of metals fall through the rain at the place of their production [72]. For example, dry deposition can remove gaseous mercury forms (particulate forms), while wet deposition is responsible for removing divalent mercury form (soluble form) [72].

2.6.3 Occult Deposition

Generally, this route is considered as one of the wet deposition processes. In occult deposition, wetted particles (fog and mist) are deposited by impaction or turbulent transfer [70]. However, heavy metals are principally dispersed by atmospheric transportation [73], but it is necessary to
consider that most atmospherically dispersed heavy metals enter the soil surface and the above
ground plant tissues very rapidly. In the soil, they are sorbed by the absorption complex and
redistributed through the soil profile. A proportion of heavy metals is taken up by plants and
leached by surface and subterranean runoff. The need to control atmospheric contamination of
soils by heavy metals and take preventive and remediation measures is dictated by the serious
ecological consequences of this contamination, as observed in different regions of the world
[74].

2.7 Urgency of monitoring air contamination

The degree and extent of environmental changes over the last decades has given a new urgency
and relevance to the detection and understanding of environmental change, due to human
activities, which have altered global biogeochemical cycling of heavy metals and other
pollutants. Approximately 5 million chemicals are presently known and 80,000 in use; 500 -
1,000 are added per year resulting in a progressive increase in the flux of bioavailable chemical
forms to the atmosphere. Therefore air pollution has been one of the major threats to human
health and the environment since the last century [75] [76] [77].

2.8 Approaches for monitoring air contamination

There are two conceptual approaches for collecting samples relevant to air and atmospheric
deposition related pollution studies. The first approach involves the direct collection of airborne
particulate matter, precipitation and total deposit whereas the second approach uses air pollution
biomonitors. The first approach is aimed at quantitative surveys at local, short-range, medium-
range or global transport of pollutants, including health-related studies when collecting size
fractionated airborne particulate matter. It requires continuous sampling on a long-term basis at a
large number of sites, in order to ensure the temporal and spatial representativeness of measurements. The application of such direct measurements on a large scale is extremely costly and person-power intensive. Furthermore, it is not possible, due to logistic problems, to install instrumental equipment at all needed locations. Therefore, the second approach is considered as a non-expensive, yet reliable means of air quality status assessment in a country or a region. Certain types of biological organisms provide a measure of integrated exposure over a certain amount of time and enrich the substance to be determined so that the analytical accessibility is improved and the measurement uncertainty reduced. Sampling is relatively simple (even in remote areas and areas with difficult access) because of no expensive technical equipment is needed [78]. Furthermore, the sample treatment and analysis steps in the laboratory are facilitated [5]. Also, this method avoids the need for deploying large numbers of precipitation collectors with an associated long-term program of routine sample collection and analysis [79]. Therefore, a much higher sampling density can be achieved than with conventional precipitation analysis and increases the possibility of monitoring many sites simultaneously [80]. Also bioindicators may be very useful due to their high sensitivity towards a broad spectrum of substances or because of their tolerance to high levels of a substance, accumulated in their tissues over an extended period of time or to integrate its influence in an area of known and relevant size [81]. Biomonitoring data are being compared with precipitation, particulate matter fractionation, and speciation data and also with medical statistics to evaluate the correlation between the amount of pollutants in the atmosphere and the human reaction to it [12].

2.9 Definition of biomonitoring and related terms

The term bioindicator or biomonitor is used to refer to an organism, or a part of it, that depicts the occurrence of pollutants on the basis of specific symptoms, reactions, morphological changes
or concentrations [8]. There is considerable variation in the use of the terms bioindicator and biomonitor: A bioindicator is an organism (or part of an organism or a community of organisms) that contains information on the quality of the environment (or a part of the environment). A biomonitor, on the other hand, is an organism (or part of an organism or a community of organisms) that contains information on the quantitative aspects of the quality of the environment. The clear differentiation between bioindication and biomonitoring using the qualitative/quantitative approach makes it comparable to instrumental measuring systems [8]. Therefore biomonitoring, in the general sense, may be defined as the use of organisms and biomaterials to obtain information on certain characteristics of the biosphere. With proper selection of organisms, the general advantage of the biomonitoring approach is related primarily to the permanent and common occurrence of the organism in the field, even in remote areas, the ease of sampling, and the absence of any necessary expensive technical equipment [5].

### 2.10 Classification of biomonitors

Organisms can be classified according to the way in which the reaction is manifested:

(I) reaction indicators, which have a sensitive reaction to air pollutants and which are used especially in studying the effects of pollutants on species composition, and on physiological and ecological functioning, and

(II) accumulation indicators that readily accumulate a range of pollutants and are therefore used especially when monitoring the amount of pollutants and their distribution [8].

Bioaccumulation monitoring methods can be divided into two groups as is shown in: Figure 2.2
2.10.1 Active biomonitoring

Active biomonitoring includes the exposure of well-defined species under controlled conditions and can be divided into transplantation, test plant, and test chamber methods [83]. In the transplantation procedure, suitable organisms (mainly mosses and lichens) are transplanted from unpolluted areas to the polluted site under consideration. The exposure time thus is well defined, but the change in uptake efficiency due to climatic change is usually applied to testing either synergistic or single species effects of pollutants on sensitive biomonitors. Transplant techniques appear to be useful, in particular at relatively high pollutant levels. One distinct advantage, compared to the use of indigenous species, is that of well-defined exposure time, but the reproducibility of this technique appears not to be very satisfactory for parameters such as air concentration and deposition rate [83].
2.10.2 Passive biomonitoring

Passive biomonitoring refers to the observation or chemical analysis of indigenous plants. In general, the passive biomonitoring method has one major disadvantage; all processes and all sources act at the same time and there is no possibility of separating them and looking for a particular one [83]. Natural variabilities in ambient macro and microclimate conditions, such as acidity, temperature, humidity, light, and altitude [84], or ambient elemental (nutritional) occurrences may cause the biomonitors to exhibit variable behaviour. Part of this variance is local [5], but it may be clear that this variable behaviour becomes a problem when it seriously affects the biomonitors in its accumulative exposure [5].

2.11 Principles of bioaccumulation monitoring

Biomonitoring is regarded as a means to assess trace element concentrations in aerosols and deposition. This implies that the monitor should concentrate the element of interest and quantitatively reflect its ambient conditions [5]. In general, a good accumulation indicator of air pollutants should:

- Accumulate pollutants from the air in the same way and to the same degree under different conditions [85].

- The pollutants should be easily measured and the measurements should provide information about the level of pollutant deposition.

- It should also indicate the risk limits caused by increasing levels of pollutants.

- The species of organism used should be common enough and be available for collection throughout the year in the same area.
• Its use should be based on standard sampling and analysis methods.

• In order to determine the state of the ecosystem in relation to the pollutant under study, the state of the ecosystem in the background area should also be known [86].

The background level is usually considered to be the “natural” level at which emissions have as small an effect as possible [43]. The background level of different pollutants varies between plant species.

2.12 Type of biomonitors

As plants are immobile and more sensitive in terms of physiological reaction to the most prevalent air pollutants than humans and animals, they better reflect local conditions [10]. For these reasons, plants are the most common used bioindicators in air quality biomonitoring studies [11]. Types of plant and their different parts have been applied in trace element air monitoring programs, such as lichens, mosses, ferns, grass, tree bark, tree rings, tree leaves and pine needles [12] [13]. For all biomonitors used, the mechanisms of trace element uptake and retention are still not sufficiently known. For grass, tree rings, and ferns, substantial element contributions from other sources than atmospheric, such as the soil or the tree bole, have to be taken into account [12] [87] reported that the accumulation pattern in the different parts of Pinuspinea L. and Neriumoleander L. was the following: wood < bark ≤ leaves, because of metals are taken up by wood stem from the soil and soil water, while the outer part (leaves and bark) intercept metals also by deposition from the atmosphere [87].

It is important to note that a unique species that can be a suitable bioindicator for biomonitoring of toxic metal pollution all over the world has not been found yet. But lower and higher plants
use as suitable biomonitors world-wide. Plants accumulate metals due to many factors, such as element availability, the characteristics of the plants (such as species, age), state of health, and type of reproduction, temperature, available moisture, substratum characteristics, etc. [43].

2.13 Biomonitoring by lower plants

Lower plants are resistant to many substances which are toxic to other plants species. They are able to survive in such diverse and often extreme environment; these sedentary organisms possess an equally diverse set of physiological adaptations [4] [15]. Of all biological species used in biomonitoring, lichens and mosses have the most common occurrence. 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 [12].

2.14 Factors affecting efficiency of heavy metal uptake by mosses

The chemical composition of deposition has a large effect on the accumulation of pollutants, because the uptake efficiency of mosses for individual elements varies considerably [88]. A high proportion of the pollutant load accumulates in mosses through wet deposition. The amount, duration and intensity of precipitation affect accumulation and leaching [88]. Ross [89] and Berg et al [88] found the best correlation between the concentrations in mosses and in wet deposition for elements such as Pb, Cd, Co and Cu that have high uptake efficiency from wet deposition. The contribution of dry deposition increases on moving from humid to arid climates [43]. Uptake efficiency is also affected by competition for free cation exchange sites; for instance, the presence of sea salts and acidic deposition has been found to have an effect on the absorption of metals by mosses [90]. The types of vegetation and soil dust have also been
reported to cause regional differences in uptake efficiency [12]. Other factors affecting the concentrations include stand through fall and leaching from vegetation layers located above the mosses [91], the nutrient status of the site [92] and snowmelt water [37]. The altitude may also have an effect [84] for example due to changes in the amount of precipitation, dust or biomass production. The sampling measuring methods employed can also have a considerable influence on the analytical results in biomonitoring studies [93] [5].

Table 2.3: Comparison of indogenous samplers and transplants in heavy metal deposition monitoring [94].

<table>
<thead>
<tr>
<th>Indigenous</th>
<th>Transplants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Results of pollution patterns can be obtained within a few days.</td>
<td>A survey period of a year is required to allow for effects of seasonal variation.</td>
</tr>
<tr>
<td>Results demonstrate pollution in previous years.</td>
<td>Results illustrate pollution only over the sampling period.</td>
</tr>
<tr>
<td>Accumulation levels are usually above detectable levels due to longer exposure time.</td>
<td>Concentrations of accumulated levels may be undetectable over shorter sampling period.</td>
</tr>
<tr>
<td>Minimal supervision and risk from vandalism.</td>
<td>Potential risk from vandalism.</td>
</tr>
<tr>
<td>Costs acquired from transport to sites and chemical analyses.</td>
<td>Additional costs from materials, increased transport and more sampler preparation.</td>
</tr>
<tr>
<td>Potential shortage of indigenous samples.</td>
<td>Density of sampling sites, samplers and their position under the control of investigators.</td>
</tr>
<tr>
<td>Pollution deposition rates difficult to estimate.</td>
<td>Deposition rates calculated from controlled exposure time.</td>
</tr>
<tr>
<td>Metal concentrations reflect influences from other factors such as age of plant, metal content of substrate and local contamination.</td>
<td>Pollutant concentrations in plants can be more directly related to airborne pollution.</td>
</tr>
<tr>
<td>Plants may be stressed or undergo morphological/physiological changes, which affect uptake, by long-term exposure to certain pollutants.</td>
<td></td>
</tr>
</tbody>
</table>

It must be noted that the high concentrations of atmospheric pollutants such as Sulphur dioxide and heavy metal particulates are harmful to the full development of mosses, and mosses do not thrive well around locations of such very high pollution levels [16].
2.15 Moss to lichens comparison

Mosses and lichens do not have root systems like higher plants therefore their contaminant content depend on surface absorption. These organisms have been shown to concentrate particulates and dissolve chemical species from dry and wet deposition. Differences in substrata result in differences in lichen metal content. For mosses, relatively high contribution of crustal elements such as Al, Sc, La and lanthanides is observed. The increase in cation exchange capacity from moss apex to base is a part of its natural balance of elements, which in turn is affected by the proximity of the soil.

Lichen identification and collecting turns out to be very complicated, whereas for mosses it is much easier. The annual growth increment is easier to distinguish for mosses than for lichens; therefore they are considered superior to lichens, if any time resolution in the measurement is required. Older parts of lichens carry fruiting bodies rich in metals. Mosses build carpets during a period of 3–5 years, and their metal content is generally considered to reflect the atmospheric deposition during that period [12]. Ares [49] showed that lichens and mosses can be used indifferently as accumulators of As, Cd, Cu, Mo, and S. Differences in concentrations between lichens and mosses were statistically significant (P<0.05) for Al, B, Fe, Hg, Pb, Sb and Zn, with mosses retaining higher values than lichens except for Hg and Zn. The elements found in higher concentrations in mosses were associated with particulate matter [12]. Bargagli [7] found higher concentrations of lithophile elements (Al, Cr, Fe, Mn, Ni, and Ti) in moss and atmophile elements (Hg, Cd, Pb, Cu, V, and Zn) in lichen [7]. According to studies by, Kansanen and Venetvaara [95] mosses and lichens as the most effective indicators for low and moderate level of metal deposition in polluted areas.
2.16 Biomonitoring by higher plants

However mosses and lichens most frequently used for monitoring metal pollution, but these lower plants are characterized by irregular and patchy distribution and their sampling should be done by specialists who can differentiate between similar-looking species. These limitations become more pronounced in industrial and densely populated areas, where severe anthropogenic pressure may cause scarcity or even lack of indicator species at some sampling points. For instance lichens are characterized by slow regeneration and relatively weak tolerance to the complex influence of myco phytotoxic pollutants; therefore intensive sampling may lead to their reduced availability and even disappearance [96]

The use of higher plants, especially different parts of trees (leaves and barks), for air monitoring purposes is becoming more and more widespread. The main advantages are greater availability of the biological material, simplicity of species identification, sampling and treatment, harmless sampling and ubiquity of some genera, which makes it possible to cover large areas. Higher plants also exhibit greater tolerance to environmental changes which is especially important for monitoring areas with elevated anthropogenic influence [96], therefore higher plants have appeal as indicators in air pollution monitoring in highly polluted areas where lichens and mosses are often absent.

Higher plants not only intercept pollutants from atmospheric deposition but also accumulate aerial metals from the soil. Aerial heavy metal depositions are taken up from the soil by plants via their root system and translocated them to other parts of the plant [97]. An otherwise in the industrial and urban areas, higher plant scan give better quantifications for pollutant concentrations and atmospheric deposition than non-biological samples [8].
Some plant species are sensitive to single pollutants or to mixtures of pollutants. Those species or cultivars are likely to be used in order to monitor the effects of air pollutants as bioindicator plants [81].

In general, it can be assumed two separated groups of higher plants for biomonitoring purposes including herbs/grasses and trees/shrubs on both groups, above ground plant tissues (leaf and bark) contribute in airborne heavy metal accumulation.

### 2.17 Herbs and grasses as biomonitor

Kovács [98] recommended the use of ruderal plants as bioaccumulative indicators due to their ability to accumulate metals in high quantities without visible injury. Some plant species may be more efficient in retaining atmospheric metal particles than others. A measure of this efficiency can be resolved by calculating air accumulation factors (AAF) according to the following equation:

\[
\text{AAF (m}^3\cdot \text{g}^{-1}) = \frac{\text{PAc (mg. g}^{-1} \text{ dry weight)/CA (mg. m}^{-3})}{\text{}}
\]

\[
\text{PAc} = \text{atmospheric contribution of the metal in plants and CA = concentration of the metal in the atmosphere [97].}
\]

### 2.18 Analytical method

The choice of analytical method for heavy metal detection in all plant materials depends on the purpose of the respective survey. Some analytical methods are non-destructive (e.g. Neutron
Activation Analysis: N.A.A.) and are useful for repetitive surveys such as baseline studies. Samples can also be archived and used at a later date for additional analysis. Destructive techniques include atomic absorption spectrometry (AAS) and inductively coupled plasma (ICP) analysis [97].

On consideration of the methods available for moss, biomonitoring in Norway, Steinnes. [91] concluded that ICP-ES works well for Fe, Zn, Pb and Cu, to a lesser extent for V and Ni and but is not satisfactory for Cr, Cd and As. ICP-MS analysis proves a good method for all of the above except As and Cd where less satisfactory results were observed [91].

2.19 Indices of atmospheric heavy metal contamination.

Several integrated environmental indices reflecting the quality of environment and life have begun to appear in recent years. On the other hand, quantitative information can be obtained by calculating different indices to estimate air quality [77].

2.19.1 Index of Atmospheric Purity (IAP)

DeSloover (1964) and DeSloover and LeBlanc (1968) suggested the IAP method for mapping air pollution on the basis of epiphytic lichen and bryophyte sensitivity for mapping aerial pollution [99]. This method is based on the fact that the epiphytic lichen and mosses diversity is impaired by air pollution and environmental stress. Therefore the frequency of occurrence of species on a defined portion of a tree trunk is used as a parameter to estimate the degree of environmental stress. This index gives an evaluation of the level of atmospheric pollution, which is based on the number, frequency, and tolerance of the epiphytic species present in an area.
\[ IAP = \sum_{i=1}^{n} (Q_i \times f_i) \]

n, the number of epiphytic species per site; Qi, the resistance factor or ecological index of each species, thus representing the sensibility of a species against pollutants; fi, the frequency or coverage score of each species per site (Max. 10; 1\(\leq f \leq 10\)). The IAP-index was calculated separately for each sampling site [100].

The frequency method makes it possible to predict pollution levels with a certainty of over 97% [43]. After calculation of IAP, pollution intensity will be determined by IAP classification is shown in Table 4.

Table 2.4: Quality levels of index of atmospheric purity [12].

<table>
<thead>
<tr>
<th>Level</th>
<th>IAP Interval</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level A</td>
<td>0(\leq IAP \leq 12.5)</td>
<td>Very high level of pollution</td>
</tr>
<tr>
<td>Level B</td>
<td>12.5(\leq IAP \leq 25)</td>
<td>High level of pollution</td>
</tr>
<tr>
<td>Level C</td>
<td>25(\leq IAP \leq 37.5)</td>
<td>Moderate level of pollution</td>
</tr>
<tr>
<td>Level D</td>
<td>37.5(\leq IAP \leq 50)</td>
<td>Low level of pollution</td>
</tr>
<tr>
<td>Level E</td>
<td>IAP(&gt; 50)</td>
<td>Very low level of pollution</td>
</tr>
</tbody>
</table>

Quality levels may somewhat differ in various studies. As Dymytrova [73] studied a total of 1730 trees and 272 sampling plots in different parts of Kyiv (Ukraine) including industrial areas, residential areas, roads and inner parks and investigated epiphytic bryophytes and lichens on isolated trees. Results showed the highest and lowest epiphytic richness in the inner parks and industrial area respectively. Consequently based on IAP, four zones with different air pollution were distinguished: highly polluted (0-8.5) moderately polluted (8.6- 20.2) slightly polluted (20.3-31.9) and unpolluted (32-88.8). In these studies, heavy metal concentrations in epiphytic vegetation and quality levels of IAP are correlated.
2.19.2 Enrichment factor

One approach used to characterize airborne particulate matter in terms of chemical composition is to calculate so called ‘enrichment factors’ (EF), relating the concentration of an anthropogenic ‘pollutant’ element (X), such as Pb, to that of a crustal element (typically Al, Ti, Sc or Fe) in air, normalized to the ratio of these elements in the average continental crust:

$$EF = \frac{X_{\text{air}}/A_{\text{air}}}{X_{\text{crust}}/A_{\text{crust}}}$$

Enrichment factors close to unity thus indicate that windblown dusts are the dominant airborne source, whilst values in excess of unity indicate that analyte concentrations have been elevated as a result of anthropogenic inputs. The calculation assumes that the anthropogenic contribution of the normalizing element (i.e. Al) is insignificant [86] [101].
Chapter 3

3 Materials and Methods

3.1 Study area

The study was conducted at the University of Zimbabwe main campus in Mt pleasant suburb of Harare (-17.7790--17.7920N and 31.0430–31.0650E) as is shown in Figure 3.1. Harare is the capital city of Zimbabwe and it has a sub-tropical climate. The year-round average temperature is 18.40C, the hottest month is October, with an average temperature of 28.80C; the average annual rainfall is about 865 mm. The University of Zimbabwe main campus is a community with a population of approximately 16 000 people composed of students, staff and service providers. The choice of this study site was based on the fact that, it is a closed environment that has all the components of a major city and therefore can be used as a pilot study which can later be up scaled for extensive city wide (e.g. Harare, Bulawayo etc.) air pollution studies in future. The bio-monitoring survey was conducted from the 1st of March to the 29th April, 2016. During the experimental period, the average daily air temperature was 22.50C, the prevailing wind direction was NW, the average daily wind speed was 2 m s−1 and the average relative air humidity and total rainfall were 78% and 15 mm, respectively (UZ Dept of Geography and Environmental sciences, 2016).
Figure 3.1: Location of the study area

Figure 3.2. Stand-alone map of the study area
Figure 3.3 Location of study sites

3.2 Sampling

3.2.1 Moss Bag Preparation.

At the beginning of February 2016, mosses were collected from a presumed pristine, rocky area located in the Mukuvisi Woodlands, in Harare Zimbabwe. The logic behind the use of moss collected from Mukuvisi Woodlands was that, the woodland is nature reverse and thus would be less influenced by anthropogenic air contamination which is known to be prevalent outside its boundaries. The moss species was identified (with the help of the Zimbabwe National Herbarium & Botanic Garden and the University of Zimbabwe, Biological Science Dept. as the species Grimmia dissimulate (Figure 3.5). Its botanical classification is as follows:
Kingdom: Plantae

Division: Bryophyta

Class: Bryopsida

Subclass: Bryidae

Order: Grimimiales

Family: Grimiaeeae

Genus: Grimmaea

Species: Dissimulate

Figure 3.4: Botanical classification of the moss species

Figure 3.5 Moss species Grimmia Dissimulata
In the laboratory, the green apical portion of the mosses was separated from the rest and carefully manually cleaned of soil particles, plant remains and epiphytes [102] [9]. Subsequently, it was rinsed three times with double distilled water (approximately 10 L water per 100g of moss dry weight and 10 min of shaking). The moss material was then, air-dried and gently hand-mixed to obtain homogeneous samples. Approximately 5.0 g of the moss was packed loosely in 13 × 13 cm polythene net bags with a 5-mm mesh size, resulting in a surface area of approximately 30 mg cm−2, which was suggested by Ares, et al., [9] to be the most suitable for maximum uptake. To avoid contamination of the moss material, the entire process of moss sampling and bag preparation was conducted while wearing polyethylene powder-free gloves. Several moss bags were stored at room temperature in laboratory conditions as a control sample for the determination of the initial pollutant concentrations. The moss bags were mounted on wooden poles, and this enabled the covering of any microenvironment of interest, such roads, residential-housing areas, sports fields, etc. The moss bags were placed at a representative height of 2–3 m [9] in open spaces far from tree canopies, roofs and electric cables. The sites were uniformly positioned across the study area to represent all land use classes. The remaining moss samples were divided into three equal portions, for further treatment. Two-thirds of each sample was air dried, and kept at room temperature, and the remaining one-third was stored in a refrigerator at 4 °C.

3.2.2 Moss Bags Bio-Monitoring Network

To identify spatial variations in air pollution throughout the study area, 17 sampling sites were chosen to uniformly cover the study area (Figure 3.3). The entire territory was divided into a regular grid of 450m × 350 m with sampling sites located at the corners of each rectangle and their geographical coordinates determined by a GPS devise. Each site was formed by collecting
three sub samples located within an area of 20 x 20 m$^2$. In the field, certain sampling sites were relocated to avoid unusable locations, such as buildings, construction sites, sport fields, tree plantations and rivers. The moss samples were collected using polyethylene gloves how to prevent any further sample contamination. The collected material was stored in plastic bags. All of the collected samples were cleaned from extraneous material (litter and dead leaves) and dried to constant weight for 48 h at 40 °C. Unwashed green and green-brown parts of the moss stems corresponding to 3 years of the moss growth were prepared for analysis [103].

### 3.3 Sample Preparation

Each of the three sub samples were combined to come up with one composite sample. The composite sample was then ground to fine powder in a mortar and pestle. About 5.0 g of each composite sample were transferred into Kjeldahl flasks. Concentrated HNO$_3$ and HCl were added to each flask in the ratio 3:1 and the mixture heated (Figure 3.6). After digestion, the solution was allowed to cool and then filtered through Whatman filter paper and the volume of the filtrate was made up to 20 ml with deionised water [104]; [20]. The metal contents in the filtrates (Cr, Cu, Pb and Zn) were determined using Absorption Spectrophotometry shown in Figure 3.7.
3.4 Reagents and Standards

For this study, reagents of analytical grade (or better) were used and deionized water was used for the preparation of all solutions.

3.5 Preparation of Standard solution

1000 ppm Stock solutions were prepared as follows:

Chromium stock solution was prepared by dissolving 1.421 g of potassium dichromate in 5 ml of concentrated HCl, deionized water and diluted to 500 ml with deionized water.

Copper stock solution was prepared by dissolving 0.502 g of copper metal in 5 ml of HNO₃ and diluted to 500mls with deionized water.
Lead stock solution was prepared by dissolving 0.824 g of lead nitrate in 5 ml deionized water, 1 ml concentrated HCl and then diluted to 500 ml.

Zinc stock solution was prepared by dissolving 0.506 g of Zinc metal in 5 ml concentrated HCl and then diluted to 500 ml with deionized water.

3.6 Instrumentation

The instrument used for the analysis of the heavy metals the Atomic Absorption Spectrophotometer (Shimadzu, AA-6701F) shown in Figure 3.7.

Figure 3.7 Shimadzu AA-6701F Atomic absorption Spectrophotometer
Table 3.1: Instrumentation and operating conditions for the Atomic absorption System.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength /nm</td>
<td>358.0</td>
<td>324.8</td>
<td>283.3</td>
<td>213.7</td>
</tr>
<tr>
<td>Spectral Width slit /nm</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Lamp current /mA</td>
<td>10</td>
<td>6</td>
<td>10</td>
<td>8</td>
</tr>
</tbody>
</table>

3.7 Data Processing

To assess the element accumulation of the studied moss species, Relative Accumulation Factors (RAFs) were calculated based on the moss content of each element after exposure (Cexposed) subtracted and then divided by the element content before exposure (Cinitial) as is shown below:

\[ \text{RAF} = \frac{C_{\text{exposed}} - C_{\text{initial}}}{C_{\text{initial}}} \]

The data were processed using Microsoft Office 2007 and all maps were made using ArcGIS 9.3. Universal kriging with the linear variogram interpolation method was applied for the construction of maps showing the spatial distribution of heavy metals in moss samples. IBM SPSS version 21 was used for statistical calculations.
Table 3.2 Location of study sites

<table>
<thead>
<tr>
<th>Sampling site</th>
<th>Type of Sampling site</th>
<th>Geographic coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1.</td>
<td>Major Road</td>
<td>-17.7810N, 31.0570E</td>
</tr>
<tr>
<td>S2</td>
<td>Commuter Omnibus Station</td>
<td>-17.7810N, 31.0570E</td>
</tr>
<tr>
<td>S3</td>
<td>Car Park</td>
<td>-17.7810N, 31.0530E</td>
</tr>
<tr>
<td>S4</td>
<td>Close To Car A Park</td>
<td>-17.7810N, 31.0490E</td>
</tr>
<tr>
<td>S5</td>
<td>Minor Road</td>
<td>-17.7830N, 31.0620E</td>
</tr>
<tr>
<td>S6</td>
<td>In Between Buildings</td>
<td>-17.7830N, 31.0570E</td>
</tr>
<tr>
<td>S7</td>
<td>Car Park</td>
<td>-17.7830N, 31.0530E</td>
</tr>
<tr>
<td>S8</td>
<td>In Between Buildings</td>
<td>-17.7830N, 31.0490E</td>
</tr>
<tr>
<td>S9</td>
<td>Close To A Major Road</td>
<td>-17.7860N, 31.0620E</td>
</tr>
<tr>
<td>S10</td>
<td>Open Field</td>
<td>-17.7860N, 31.0570E</td>
</tr>
<tr>
<td>S11</td>
<td>Sports Arena</td>
<td>-17.7860N, 31.0530E</td>
</tr>
<tr>
<td>S12</td>
<td>In Between Buildings</td>
<td>-17.7860N, 31.0490E</td>
</tr>
<tr>
<td>S13</td>
<td>Close To A Major Cross Road</td>
<td>-17.7890N, 31.0620E</td>
</tr>
<tr>
<td>S14</td>
<td>Open Field</td>
<td>-17.7890N, 31.0570E</td>
</tr>
<tr>
<td>S15</td>
<td>Major Road</td>
<td>-17.7890N, 31.0530E</td>
</tr>
<tr>
<td>S16</td>
<td>Minor Road</td>
<td>-17.7890N, 31.0490E</td>
</tr>
<tr>
<td>S17</td>
<td>Close To A Major Road</td>
<td>-17.7890N, 31.0450E</td>
</tr>
</tbody>
</table>
4 Results

4.1 Descriptive Statistics

Table 4.1: Descriptive statistics of the RAUs

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>14.38</td>
<td>18.14</td>
<td>9.63</td>
<td>10.78</td>
</tr>
<tr>
<td>Standard Error</td>
<td>2.36</td>
<td>2.52</td>
<td>1.35</td>
<td>0.33</td>
</tr>
<tr>
<td>Median</td>
<td>13.95</td>
<td>15.59</td>
<td>9.42</td>
<td>11.30</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>9.73</td>
<td>10.37</td>
<td>5.57</td>
<td>1.34</td>
</tr>
<tr>
<td>Sample Variance</td>
<td>94.70</td>
<td>107.54</td>
<td>31.07</td>
<td>1.80</td>
</tr>
<tr>
<td>Kurtosis</td>
<td>-0.68</td>
<td>-1.30</td>
<td>0.73</td>
<td>-0.13</td>
</tr>
<tr>
<td>Skewness</td>
<td>0.50</td>
<td>0.29</td>
<td>0.67</td>
<td>-1.17</td>
</tr>
<tr>
<td>Range</td>
<td>31.90</td>
<td>31.62</td>
<td>21.34</td>
<td>4.07</td>
</tr>
<tr>
<td>Minimum</td>
<td>0.78</td>
<td>4.75</td>
<td>1.55</td>
<td>7.93</td>
</tr>
<tr>
<td>Maximum</td>
<td>32.68</td>
<td>36.37</td>
<td>22.89</td>
<td>12.00</td>
</tr>
<tr>
<td>Sum</td>
<td>244.43</td>
<td>308.32</td>
<td>163.64</td>
<td>183.22</td>
</tr>
<tr>
<td>Count</td>
<td>17</td>
<td>17</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>Confidence Level (95.0%)</td>
<td>5.00</td>
<td>5.33</td>
<td>2.87</td>
<td>0.69</td>
</tr>
</tbody>
</table>
Figure 4.1: The mean and median values of the RAFs

Figure 4.2 Comparison of heavy metal moss content at each sampling site.
Figure 4.3 Line chart showing the variation of each metal’s moss content.

Figure 4.4 Chromium moss content at each sampling point
Figure 4.5 Sampling points arranged according to increasing Chromium content

Figure 4.6 Copper, moss content at each sampling site.
Figure 4.7 Sampling points arranged in increasing order of Copper content.

Figure 4.8 Lead, moss content at each sampling site.
Figure 4.9 Sampling points arranged in order of increasing Lead moss content.

Figure 4.10 Zinc moss content at each sampling point.
Figure 4.11 Sampling points arranged in increasing order of Zinc content.

Figure 4.12 Total Heavy Metal Content At Each Sampling site.
Figure 4.13 Spatial distribution map Chromium deposition based on moss content.

Figure 4.14 Spatial distribution map of Copper deposition based on moss content.
Figure 4.15 Spatial distribution map of Lead deposition based on mass content.

Figure 4.16 Spatial distribution map of Zinc deposition based on moss content.
Figure 4.17 Spatial distribution map of Total Heavy Metal deposition based on moss content.

Table 4.2 Correlation coefficient (r) between element content in mosses derived from un-normalised data.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.87</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.55</td>
<td>0.80</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.78</td>
<td>0.83</td>
<td>0.76</td>
<td>1.00</td>
</tr>
</tbody>
</table>

**. Correlation is significant at the 0.01 level (2-tailed).
Table 4.3 Correlation coefficient (r) between element content in mosses derived from normalised (log transformed) data.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>1.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.89</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.79</td>
<td>0.87</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.80</td>
<td>0.91</td>
<td>0.90</td>
<td>1.00</td>
</tr>
</tbody>
</table>

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

Figure 4.18. Dendrogram showing clustering of the Heavy Metal distributions
Figure 4.19. Dendrogram showing clustering of analysed chromium sampling sites.

Figure 4.20. Dendrogram showing clustering of analysed Copper sampling sites.
Figure 4.21. Dendrogram showing clustering of analysed Lead sampling sites.

Figure 4.22. Dendrogram showing clustering of analysed Zinc sampling sites.
Figure 4.23. Dendrogram showing clustering of analysed Total Heavy Metal sampling sites
Chapter 5

5 Discussion

5.1 Quantitative Descriptions

5.1.1 Descriptive statistics

A total of 4 elements were analysed by application of Atomic Absorption Spectrophotometry. According to McGarigal [105] environmental data sets are usually skewed to the right and would need to be normalised. To test for the normality of the data, comparison of the means and the medians was done as is shown in Figure 4.1. It can be noted from the chart, that for Cr, Cu and Pb, the mean was higher than the median and for Zn the median was higher. However the means and the medians were approximately the same for all the heavy metals. This property of the mean being equal to the median is characteristic of normal distributions. Hence the data set was preliminary assumed to be normal. One of the criteria used for checking for normality of a data set is when its skewness is in the range of −0.8 to 0.8 and its kurtosis in the range of −3.0 to 3 [106]. Since the skewness and kurtosis for this data set were within the limits specified above, it was concluded that the data was normal and hence no data transformations were necessary.

The bar chart in Figure 4.2 compares the RAFs of heavy metals at each sampling point. Just by visual inspection, it can be noted that the RAFs of Cu and Cr were generally higher than those of Zn and Pb. This implies that Cu and Cr had higher depositions than Zn and Pb. Unfortunately the chart cannot clearly differentiate between the depositions of Cu and Cr. The same applies for the depositions of Zn and Pb. Using the means and medians shown in Figure 4.1, as an alternative way for differentiating the distributions; a clear order emerges in which Cu is the highest,
followed by Cr, Zn and then Pb. Thus it can be concluded that the order of deposition was as follows, Cu > Cr > Zn > Pb. Therefore Cu can be described as having been the most polluting and Pb the least polluting.

Figure 4.4 shows the distribution of Cr throughout the study area. When the same bar chart is rearranged, in order of increasing moss content, Figure 4.5 would result. It shows that point S12 has the least RAF (0.78) and S7 has the highest (32.68). Subtracting the value of S12 from that of S7, would give the range (31.90). These values confirm the minimum, the maximum and the range values for Cr given by descriptive statistics shown in Table 4.1. Doing the same for Cu, Zn and Pb matching results would be found in the descriptive statistics table. In all the charts for the metals it is interesting to note that point S11 features as either the lowest value, or the second lowest and the same applies for S12 with the exception for Zn.

5.1.2 Distributions of Heavy Metals

The distributions of Cr, Cu, Zn and Pb are shown in Figure 4.4, Figure 4.6, Figure 4.8 and Figure 4.10 respectively. Again just by visual inspection they all have a similar distribution pattern and hence no differentiation can be done based on that alone. The line chart in Figure 4.3, also confirms the same distribution pattern but here it becomes clearer. However one aspect that emerges from the line chart and can be used to distinguish between the distributions is the spread. All the other metals, Cr, Cu and Pb have similar spread but the one for Zn is so small that it approximates a straight line. The same trend can be picked up by analysing the sample variances shown in Table 4.1. The sample variances of Cr and Cu are almost the same (94.70 ≈ 107.54) and hence can be treated as one. The variance of Pb (31.07) is about 3 times smaller than that of Cr and Cu. But that of Zn is about 15 times than that of Pb. So it can
be concluded that Zn deposited in almost equal amounts throughout the study area hence the low spread.

In an effort to further distinguish between the 4 distributions, cluster analysis using the hierarchical method was applied. The results are shown in a tree diagram otherwise known as a dendrogram in Figure 4.18. The results show that the distribution of Cr and Cu are almost the same and hence similar. The distribution of Pb is different from that of Zn and those of Cr and Cu. However the distribution of Pb shows a resemblance to those of Cr and Cu more that it does to that of Zn. Thus it can be concluded that the distribution patterns of Cr and Cu are almost a similar while Pb and Zn have their own patterns, though that of Pb was somewhat similar to that of Cr and Cu.

5.2 Spatial Distribution Maps

Spatial Distribution Maps (SDMs) convey instant visual information on how the heavy metals are distributed in actual physical spatial space. They work by plotting the values from the sampling points on a map. The SDMs for Cr, Cu, Pb and Zn are shown in Figure 4.13, Figure 4.14, Figure 4.15 and Figure 4.16 respectively. Basically they yield the same data as obtained in the distribution charts, but these go a step further in that they show quantitative depositions and their respective exact spatial extends. As a result they show different zones or regions of heavy metal concentrations (expressed by RAFs) and hence a spatial distribution pattern.
5.2.1 Different Clusters of Heavy Metal Air Pollution

From the SDMs it can be seen that different zones of deposition and hence heavy metal air pollution emerge. Zones of similar attributes (i.e. concentration, depositions) can be classified into clusters. As a way of determining how many clusters of such zones exist per each spatial distribution and to classify the zones into clusters, cluster analysis was carried out. The resulting dendrograms for Cr, Cu, Pb and Zn are shown in Figure 4.19, Figure 4.20, Figure 4.21 and Figure 4.22 respectively. The results suggest that for Cr, Cu, and Pb, 3 clusters exist and for Zn only 2 clusters exist. It further classifies each sampling point into an appropriate cluster, based on similar concentration and hence the clusters or regions of different pollution emerge. The three clusters that emerge from the Cr, Cu, and Pb dendrograms were termed as cold spots, mild spots and hot spots. The SDM for Zn appear to have two predominant Clusters. This is in strong agreement with regions that appear in the SDM for Zn. Thus the clusters were simply termed as polluted and unpolluted.

5.2.2 Chromium Heavy Metal Air Pollution Clusters

The first cluster to emerge from the Cr dendrogram in Figure 4.19 consists of points S14, S16, S5, S10, S8, S17, S11 and S12. When read with reference to the SDM of Cr in Figure 4.13, it can be noted that this group consists of points with the lowest RAFs of Cr and hence denote the Cr cold spots. This cluster can be further subdivided into two other sub clusters. These were termed the high cold spots, consisting of points S14, S16, S5 and S10 and the other cluster the low cold spots consisting of points S8, S17, S11, and S12. This low cold spot cluster can be described as the pristine region for Cr.
Second cluster to emerge consists of points S2, S13, S9, S1, S6 and S15. This was termed the mild cluster. It can further be sub divided into to two sub groups one with points S2, S13 and S9, which are on the high side of mild and the other with points S1, S6 and S15 which are on the lower side of mild.

The third cluster to emerge consists of points S3, S7 and S4. These are the hot spots for Cr. Points S3 and S7 are red hot spots on the high side while point S4 is a hot spot on the low side.

5.2.3 Copper Heavy Metal Air Pollution Clusters

Applying the same analysis used for Cr above, for Cu the first cluster to emerge consists of points S8, S11, S12, S10 and S17. This cluster denotes the cold spots. It can be further sub divided into two subgroups one consisting of points S8, S11 and S12 and the other group of points S10 and S17. The first sub group consisting of points S8, S11 and S12 can be described as the pristine regions for copper.

The second group to emerge consists of points S1, S6, S5, S16, S14 and S15. This is the mild cluster for copper air pollution. However for this group, all the other points seem to cluster in one group except for point S15 which seem to be in its own sub group of being on the high side of being mild.

The last cluster to emerge consists of points S3, S4, S7, S13, S9 and S2. This cluster denotes the hot spots for Cu. Further analysis of this cluster shows that the hot spots can further be categorised into 3 sub clusters. The first sub cluster consists of points S3, S4, S7 and S13. This is
the lowest of the hot spots. The next sub cluster consists of point S9 which is a mild hot spot.

The third sub group consists of point S2 which is a high red hot spot.

5.2.4 Lead Heavy Metal Air Pollution Clusters

For Lead the first cluster to emerge consists of points S4, S16, S1, S3, S6, S7, and S14 and S15. These are the cold spots for Lead. Like in all the other cases encountered before, this cluster can be further sub divided into the low cold spots or the high cod spots. The high cold spots consists of points S7, S14 and S15 and the low cold spots consisted of points S4, S16, S1, S3 and S6. This lower cold spot cluster denotes the pristine region for Lead.

The second group consists of points S11, S12, S10, S5, S17, and S8. This is the mild cluster for Pb Lead air pollution. This cluster can be further sub divided into two groups, the high mild spot and the low mild spot. The high mild spots consist of points S5, S17, and S8. The low mild spot cluster consists of points S11, S12 and S10.

The third group consists of points S9, S13 and S2. These are the hot spots from Lead. These hot spots can further be split into two groups the lower side consisting of S9, S13 and S2 the

5.2.5 Zinc Heavy Metal Air Pollution Clusters

For Zn the first of the two clusters that emerges consist points S3, S13, S7, S2, S4, S9, S14, S16, S15, S1, S6, S17, and S5. This cluster is denotes the polluted cluster. This cluster can be further sub divided into two sub groups. One group consists of points S3, S13, S7, S2, S4, S9, S14, S16, and S15 which can be noted as the hot spots and the other consists of points, S1, S6, S17, and S5
which can be described as the mild spots. The second cluster consists of points S8, S10, S12, and S11. These can be described as the unpolluted clusters.

Even though these clusters were successfully classified, looking back at the variance it shows that the RAFs of Zn do not vary that much throughout the study area. So theoretically the classes do exist as is shown by the SDM and the dendrogram but in practical terms, the differences are insignificant can just be considered as one class.

### 5.3 Sources of the Heavy Metals

The question of sources is of paramount importance in air pollution studies. This is because, once the source has been identified, appropriate measures can be taken so that the integrity of the environment within its footprint is preserved. So in this study a fair question to be asked would be, where are these heavy metals coming from? In trying to answer this question, it was noted from previous studies by [29] [30] concentrations of air pollutants such as heavy metals; demonstrate steep concentration gradients from on source to near source micro environments. With that understanding, it was assumed that for heavy metal deposition from air, the sources would have to be somewhere close to the hot spots. So to accomplish this, the search for the sources was conducted in and around the vicinities of the hotspots.

Before searching for the source another prudent question to ask would be how many sources are to looking for? Since we are looking at 4 different heavy metals, each one can have one or more sources. So the first step would be to determine the number of sources to be considered. According to Sun, et al., [107] strong correlations among metals, indicate that they may have the
same source. So correlation coefficients were used as the criteria for the determination of the number of sources to be considered. Thus strong correlation coefficients between metals would imply they have the same source and weak correlation coefficients would imply different sources. Table 4.2 shows a matrix of correlation coefficients for all the metals analyzed. Based on their correlations, the metals all showed positive correlations but concern was raised by the value between Cr and Pb. This raised questions as to whether Pb had some other source different from all the other metals or some other phenomenon could be influencing its source. But its strong correlation to Zn and Cu proved that they may have the same source. To decide on this, the correlation coefficients were recalculated using log transformed data, in an effort to get the data to be more normalized. The results of this recalculation are shown in Table 4.3 and they all show strong positive correlation coefficients. Hence it was concluded that the heavy metals all had one source.

The SDM for the total heavy metals was used for this search of the source, since all the metals had similar spatial distributions. Looking at the SDM (Figure 4.17) it can be seen that the hot spots occurred at points S2, S3, S4, S7, S9 and S13. So by asking the question, what feature is common to all these points that can be a possible source of heavy metals, no answer could be arrived at a realization that points S2, S3, S4, and S7 are either close to or are within a car park. So the initial assumption was that these heavy metals were as a result of traffic related emissions. But this assumption could not explain points S9 and S13. On closer analysis of vicinities of points S9 and S13 it was realized that point S9 is close to the university’s site and transport department which is a high traffic zone. The point S13 is adjacent to a City of Harare, major road junction between Churchill Avenue and College Rd. Thus it can be concluded that the source of these heavy metals are traffic related emissions.
At crossroads, a pattern of braking and accelerating driving mode, so called “stop and go”, is especially increased [68]. So this can explain why we have these car parks and cross roads as the source of Heavy metals. With reference to the table Table 5.1, the exact sources of the heavy metals can be identified as follows:

- Chromium: Fuel, lubricating oil and Brakes emissions.
- Copper: Fuel, lubricating oil and Brakes emissions.
- Lead: Lubricating oil and brakes emissions.
- Zinc: Fuel, lubricating oil and Brakes emissions.

Table 5.1. Major and trace elements that originate from natural anthropogenic sources [108].

<table>
<thead>
<tr>
<th>Source Type</th>
<th>Associated elements</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exhaust traffic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diesel emissions</td>
<td>Al, Cu, Cr, Fe, Mn, V, Zn</td>
<td>EMEP/EEA, 2013</td>
</tr>
<tr>
<td>Gasoline Emissions</td>
<td>Br, Ba, Sb, V</td>
<td>Pulles et al., 2012</td>
</tr>
<tr>
<td>Lubricating Oil Emissions</td>
<td>Cd, Cr, Cu, Ni, Pb, Zn</td>
<td>Pulles et al., 2012</td>
</tr>
<tr>
<td>Non exhaust Traffic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brakes</td>
<td>Fe, Cu, Sn, Sb, Zn</td>
<td>Gietl et al., 2010</td>
</tr>
<tr>
<td>Tyres</td>
<td>Co, Cr, Fe, Mn, Pb</td>
<td>Thorpe and Harisson, 2009</td>
</tr>
<tr>
<td>Road dust</td>
<td>Al, Si, Ca, Fe, K</td>
<td>Viana et al., 2008</td>
</tr>
<tr>
<td>Industrial</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Metal working</td>
<td>Fe, K, Na, Pb, Zn</td>
<td>Sanderson et al., 2014</td>
</tr>
<tr>
<td>Power generation</td>
<td>Ce, Fe, La, Na, K, V</td>
<td></td>
</tr>
<tr>
<td>Incinerators</td>
<td>Cd, Pb, Sb, Zn</td>
<td></td>
</tr>
<tr>
<td>Natural</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Marine aerosol</td>
<td>Cl, Na, Mg</td>
<td>Viana et al., 2008</td>
</tr>
</tbody>
</table>
Chapter 6

6 Conclusion

6.1 From the descriptive statistics
It can be concluded that the:

- the order of deposition is as follows Cu > Cr > Zn > Pb.
- the deposition of Zn was almost uniform throughout the study area.
- the distribution patterns of Cr and Cu are similar while Pb and Zn have their own patterns, though that of Pb was somewhat similar to that of Cr and Cu.

6.2 From spatial distributions
It can be concluded that the different clusters of heavy metal depositions, hence heavy metal air pollution were identified and their spatial extends mapped. The points S2, S3, S4, S7, S9 and S13 were identified as being the hotspots, S1, S6, S14 and S15 as the mild spots and points S5, S17, S8, S10, S11 and 12 are the cold spots.

6.3 From sources
It was concluded that the heavy metals were as a result of traffic related emissions.
Chapter 7

7 Recommendations
The standard solutions used in this study were not standardised. As a way of improving accuracy, the analyses can be repeated using commercial standard stock solution whose potencies are actually known.
Chapter 8

8 References


review of land-use regression models to assess spatial variation of outdoor air pollution.,"  


[49] Á. Ares, "Active biomonitoring of the air quality with terrestrial mosses: standardization and optimization of the technique," PHD Thesis, Faculty of biology, University of Santiago,
Spain, 2014.


Hylocomium splendens: Variation Associated with Altitude, Net Primary Production and Soil Chemistry.," *Environmental Pollution*, vol. 116, no. 1, 2002.


