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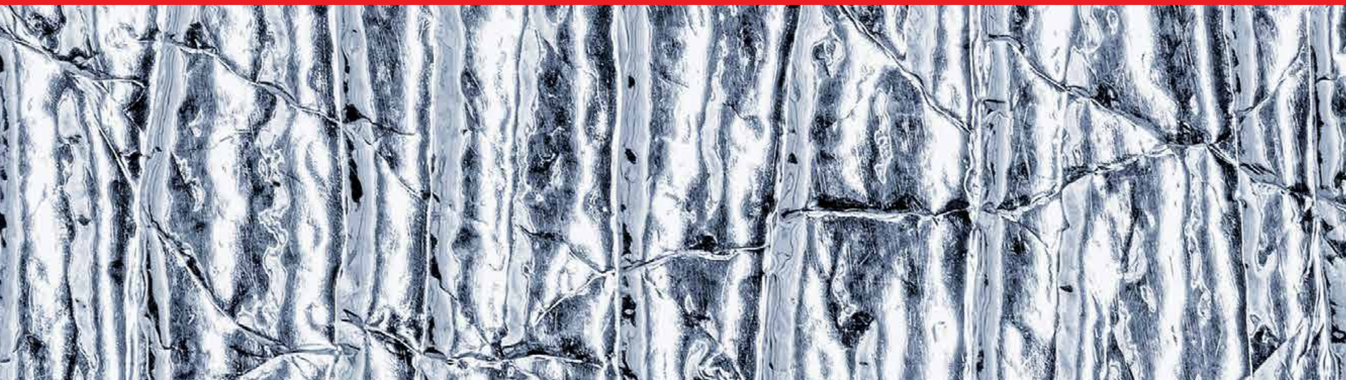
Trace Metals in the Environment

Edited by Daisy Joseph



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Meet the editor

Dr. Daisy Joseph is a scientist from the Bhabha Atomic Research Centre (BARC), Mumbai, India, and has represented the center at numerous conferences and workshops in Spain, Italy, New Zealand, and more. She obtained her Ph.D. in Physics from Mumbai University, India, in 2006. She is an expert in energy-dispersive X-ray fluorescence (EDXRF) and particle-induced X-ray emission (PIXE). Dr. Joseph has more than 150 publications in peer-reviewed journals to her credit and is on the editorial board of many international journals. She has also edited two books.

Contents

Preface

The environment is defined as the surroundings or conditions in which a person, animal, or plant lives or operates. It is composed of many elements, including water, air, plants, and so on. Unfortunately, the environment is becoming more polluted as time goes on by harmful chemicals, toxic elements, heavy metals, greenhouse gas emissions, and more. This book focuses on trace elements, the accumulation of which, especially heavy metals, can have negative effects on soil. This, in turn, can cause toxicity to plants and contaminate the food chain. The book includes two sections on trace elements in soil and trace elements in water. The chapters examine the harmful effects of trace elements and discuss microplastics, which frequently accumulate trace elements from the environment.

It is a global trend to focus on climate change and environmental pollution. This book is our contribution to highlighting the environmental challenges we face and inspiring students, experts, environmentalists, and researchers to continue developing ways of facing them.

Daisy Joseph
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Section 1

Trace Elements and Soil

Chapter 1

Demographical Identification of Trace Metals Found in Soil Samples from India

Sreelakshmi Krishna and Pooja Ahuja

Abstract

Soil has various trace metals, which help to identify the demographical origin of the soil. The formation of soil undergoes changes due to several external factors. However, certain trace metals are not affected by these external factors. This chapter considers two approaches for the detection of these trace elements; first, it highlights the usefulness of the trace elements present in the soil whose presence in deficiency or excess affects the soil quality; second, the analysis of soil transferred from various surfaces, to detect the presence of these trace elements. This chapter involves various instrumental techniques used to study its elemental composition and morphological characteristics. Due to the heterogeneous nature of the soil, the information from this chapter can be used as a database to narrow down the area of search and objects under study. It also provides insights into understanding the presence of trace metals in soil, their effects, and their role in forensic soil science. The use of soil in the search for trace evidence, which gives background knowledge on the importance of comprehending soil from the topographical scale to the crime scene, has been overviewed. This aids law enforcement agencies in investigations.

Keywords: soil, trace metals, trace elements, environmental factors, heavy metals, forensic science

1. Introduction

Formerly, all elements were believed to be trace metals, with the exception of the eight common rock-forming elements: O, Si, Al, Fe, Ca, Na, K, and Mg. Elements with concentrations of 0.1% and lower were categorized as trace elements. Therefore, “Any element having an average concentration of less than about 100 parts per million atoms” is defined as trace element as per the IUPAC Gold Book [1, 2]. Due to their occurrence in trace amounts (ppb range to less than 10 ppm) in a wide range of natural environments, heavy metals are also categorized as trace elements. Natural elements with a high atomic weight and a density at least five times greater than that of water are known as heavy metals. Arsenic, cadmium, chromium, lead, and mercury are among the priority metals of public health concern due to their high degree of toxicity. Even at modest exposure levels, these metallic elements are known to cause numerous organ damage and are regarded as systemic toxicants [3] (**Figure 1**).

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Figure 1.
Soil and its analysis play an important role in soil science and forensic soil science.

As a result of human activities such as mining, metal smelting, combustion agriculture, improper deposition of industrial waste, other metal-based industrial activities, and use of commercial fertilizers and pesticides, heavy metals such as cadmium (Cd), iron (Fe), lead (Pb), zinc (Zn), cobalt (Co), copper (Cu), nickel (Ni), etc., enter the soil. These heavy metals also occur in the soil as a consequence of natural processes. However, the presence of a few of these trace metals in the soil in high or low concentrations is beneficial for plant growth. Plants utilize the vital micronutrients present in the soil for their growth. For example, copper is a necessary heavy metal that actively contributes to photosynthesis, and several metabolic enzymes, like malic dehydrogenase and oxalosuccinic decarboxylase, have manganese as an essential component. This chapter aims to offer an overview of the various trace metals present in the soil, their origin, the extent of contamination, and their influence on plant growth and development [4].

2. Soil and its formation

Soil is primarily composed of mineral particles, organic materials, air, water, and living organisms, all of which interact slowly but consistently with one another as rocks gradually deteriorate *via* weathering resulting in soil formation. It takes hundreds to thousands of years for soil formation. However, the soil is destroyed more quickly than it is formed due to negligent land reclamation, man-made erosion, acidification, pollution of water, air, and other resources, and takeover of land for residence, construction, transportation, and setting up of industries. The spatial arrangement of numeric microscopic particles determines their physical properties. All terrestrial organisms depend on soil, as it is a unique and vital natural resource essential for living and sustaining an ecosystem. The topmost thin layer of the soil that makes up the earth's crust and where plant roots embed themselves to get water and essential nutrients for their growth is not the sole part. These are complex and sophisticated natural formations that emerge from their parent materials, such as sediments or solid rock, as a result of the interaction between soil organisms, water, air, plants, bacteria, and other soil-dwelling organisms. In terms of their physical, chemical, and mineralogical characteristics, they typically differ significantly from the parent material, which makes them best suited as a rooting media for plants. The hydrological cycling of water, carbon, nitrogen, and other components is significantly influenced by soils. In addition to acting as a foundation for plant growth, this affects the chemical composition of various materials found in the hydrosphere and the atmosphere [5].

3. Factors affecting soil formation

Soil formation is attributed to several factors. External environmental factors, including climate, biological factors, biota, time, parent material, temperature gradients, and variations, are some of the key physical processes affecting soil formation. The unique characteristics of soil are contributed by these factors (**Figure 2**).

3.1 Climate

The most crucial elements in the development of soil are temperature and rainfall, which influence how well the parent material weathers, how much water percolates through the soil, and what kinds of microorganisms are present. In the same type of climate, the same soil may form from two different parent materials. Similarly, two distinct soil types in two distinct climates can result from the same parent material. In moderately moist sections of the monsoonal zone, the crystalline granites generate laterite soil and non-laterite soil in drier places. Regardless of the parent rock, hot summer and low rainfall create black soil, as is the case in several areas of Tamil Nadu [6]. Sandstone and granite both produce sandy soil in Rajasthan's desert environment. In arid and semi-arid regions in India like Rajasthan, Gujarat and, Punjab, respectively, the evaporation rates are usually greater than precipitation due to which they lack much vegetation and are highly humus deficient which in turn gives a pale

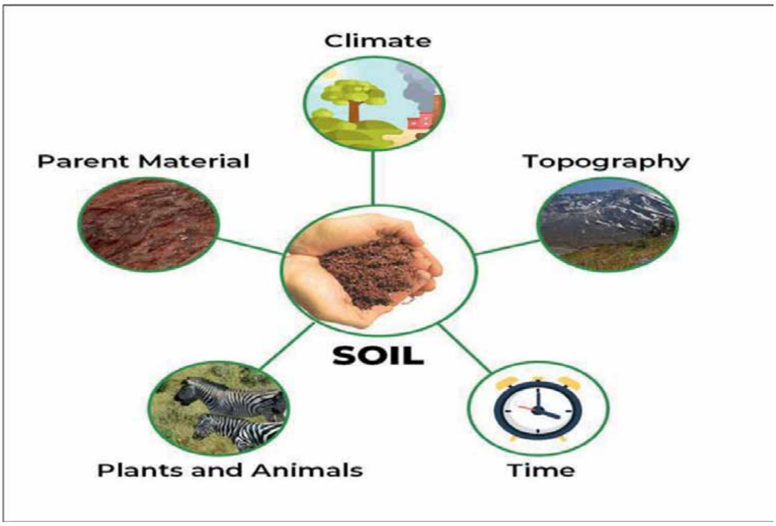


Figure 2.
Representation of various factors affecting the soil formation.

color to the soil. Excessive evaporation causes lime accumulation in soils in Rajasthan and the surrounding dry and semi-arid regions, making the soil pedocal in nature, which has minimal organic matter and is high in calcium carbonate. The deterioration of vegetation occurs slowly in the Himalayan region due to its frigid winters, and the soils are acidic in nature.

3.2 Temperature effects

As soils have a large heat capacity and a low heat conductivity, which significantly minimizes temperature variations, the magnitude of daily and seasonal temperature changes decreases dramatically with depth. The diversity and activity of the biota, chemical changes, the mechanical degradation of rocks, and the distribution of small and large particles are the four key factors that temperature has on soil formation processes.

3.3 Biological factors (biota)

The soil formation has been significantly influenced by biological agents present in the soil such as bacteria or gophers. These consist of flora and fauna. The expansion of vegetation has a significant impact on how soil forms and develops. The decomposed leaf matter enriches the soil with much-needed humus, enhancing its fertility. Some of India's finest soils are found in the densely forested areas, and there is a direct connection between the different types of vegetation and the soil. Soil erosion is lessened by vegetation. Through the action of carbon dioxide and other acidic substances, they stimulate percolation, drainage, and stronger mineral dissolution. Due to the continual mixing of the soil profile by the animals that dig underground, such as rats, earthworms, ants, and others which are crucial in the development of soil, the soil formation has enhanced [7].

3.4 Time

Numerous researches have been carried out regarding the type and degree of changes that the soil undergoes over time. These studies compare distinct properties of soils with various backgrounds but generated from the same type of parent material in the same environment. The outcome of these studies demonstrated a significant rise in the concentration of the organic components in the soil initially followed by its degradation with passage of time. Climate, the composition of the parent material, the prevalence of burrowing species, etc. are just a few of the many associated factors formation of various layers of the soil. Clay content in the soil rises when weathering progresses as a result of primary minerals being physically and chemically altered. The soil region containing the clay concentration may undergo transformations with additional chemical changes. The climatic factors and chemical environment of the soil determine the nature of the clay particles generated [8].

3.5 Parent material

Parent materials are the bedrock that soils are created from. The parent material has a great influence on and governs the color, composition, texture, and properties of soil including physical and chemical properties. The soil that is created under varying climatic conditions may differ in its physical characteristics from the parent rock. Weathering that takes place at the surface layers of the rocks turns them into tiny granular particles that act as a foundation for the development of soil. For instance, in India, the red soils found in ancient crystalline and metamorphic rocks are caused by the presence of iron oxides. As the Gondwana rocks have immature sedimentary rocks, the soils evolved are less fertile, 2hereas the basalts from the Deccan region are known as "black soils" because they are rich in minerals like titanium, magnetite, aluminum, and magnesium [9, 10].

4. Constituents of soil

Solids, liquids, and gaseous phases all make up soils to form a complex medium. The important properties of soil comprise texture, density, structure, consistence, porosity, temperature, color, and aggregate stability. These parameters affect the properties of soil to a vast extend. The constituents of soil can be broadly classified as inorganic and organic components.

4.1 Inorganic components of soil

The majority of the soil's constituents are typically made up of inorganic material comprising aluminosilicates. The inorganic constituents of the soil can be further classified into crystalline and non-crystalline components. Primary minerals (formed from the weathering of rock) and secondary minerals (transformed as fine particles) are the two categories under which inorganic minerals fall. A significant amount of the sand and silt fraction is made up of primary minerals.

4.2 Organic components of soil

In accordance with the proportion of organic content they contain, soils are categorized as either organic or mineral. Mineral soils, which can have an organic matter content of only a trace to 30%, make up the vast portion of agricultural land on earth. Organic soils naturally contain a large amount of organic compounds, largely as a result of environmental factors. Non-humic and humic materials make up the organic matter of the soil. Polysaccharides, proteins, lipids, and low-molecular-weight organic acids are some of the non-humic compounds. Most of the organic matter in soil is made up of humic materials that play a vital role in improving the properties of the soil, growth of plants, etc. Humic compounds are divided into fluvic acids, humic acids, and humins based on how differently they dissolve in acid or base [11].

5. Trace elements present in the soil

Various databases obtained from previous literatures were surveyed and reviewed in an effort to evaluate the state of the soil pollutions caused by human activities and industrial processes. The findings show that pollution metal pollution in soils was particularly severe. Few elements that are often found in extremely minute concentrations in soils are necessary for the growth and development of flora and fauna. They are referred to as trace elements due to their low presence and minute quantity in naturally occurring geological formations or land surfaces [12]. As reported by Kabir *et al.,* Pb, Zn, Ni, Cu, Fe, and As were produced as a result of industrial activities such as metal manufacturing, Mn and Cd from textile manufacturing, and Cr from the leather manufacturing. The study also discovered that metal levels in the tested locations exceeded the standard regulation guideline values that are applied by several countries. To control and minimize this scenario, it is crucial to maintain regular and ongoing monitoring of heavy metals. Natural processes cannot break down metals, particularly when elemental metallic content is taken into account. In contrast, organic pollutants may undergo biological or chemical processes that cause them to breakdown into less harmful components. As a result, metal contamination may have significant and long-lasting effects on local habitats and other living species [13].

6. Contamination of soil with trace metals

All the possible sources of soil contamination arising from heavy metals include pain containing lead, residues from mine, the discarding and dumping of waste containing heavy metals, overuse of chemical fertilizers and pesticides, and spilling of petrochemicals containing metals such as cadmium (Cd), lead (Pb), nickel (Ni), zinc (Zn), chromium (Cr), arsenic (As), mercury (Hg), and copper (Cu) [14]. The aforementioned heavy metals are most frequently discovered in contaminated sites (**Figure 3**).

The major soil contaminants arise mostly from two factors, namely natural and man-made factors. The former includes soil erosion, volcanic eruption, etc., and the latter includes industrial development, hospital waste, etc. Metal contamination causes the metal concentration in the soil to rise above the acceptable threshold, making it harmful to plants and animals. Metals, in general, are a potential long-term source of soil contaminants. In a study conducted by Zhang *et al.,* they have calculated the average pesticide usage per year globally, between the years 2010–2014. The results of the study predicted that by 2020, the yearly global use of pesticides would reach 3.5 million tons [15].

As depicted in **Figure 4**, soil and plants are affected by the high concentrations of heavy metals. It is assumed that metals with high allowable limits are safe. Pb has the greatest acceptable levels in soil, followed by Zn and Cu, and Cd has the lowest permissible values. These data indicate that the accumulation of Cd in the soil is more hazardous than Cu, Zn, and Pb even at lower concentrations. However, Pb, Zn, Cd, and Cu have the greatest limits in plants, respectively. In contrast to soil, which has the safest limits for Cu, Pb, and Zn, buildup of Cd in plants poses the greatest threat. **Figure 5** shows the statistical representation of the results obtained in their study for pesticide-consuming countries.

These heavy metals cause adverse effects on human health as well as the environment. The risk of heavy metal contamination in the environment has recently been rapidly increasing and causing havoc, especially in the agricultural industry, as a result of the accumulation of heavy metals in the soil and their plant uptake. An array of elements in the ecosystem is what is referred to as heavy metal buildup. The primary site of interaction for heavy metal ions transported from the soil is plant roots. They frequently bind and link the contaminants in the soil, which lowers their bioavailability [16].

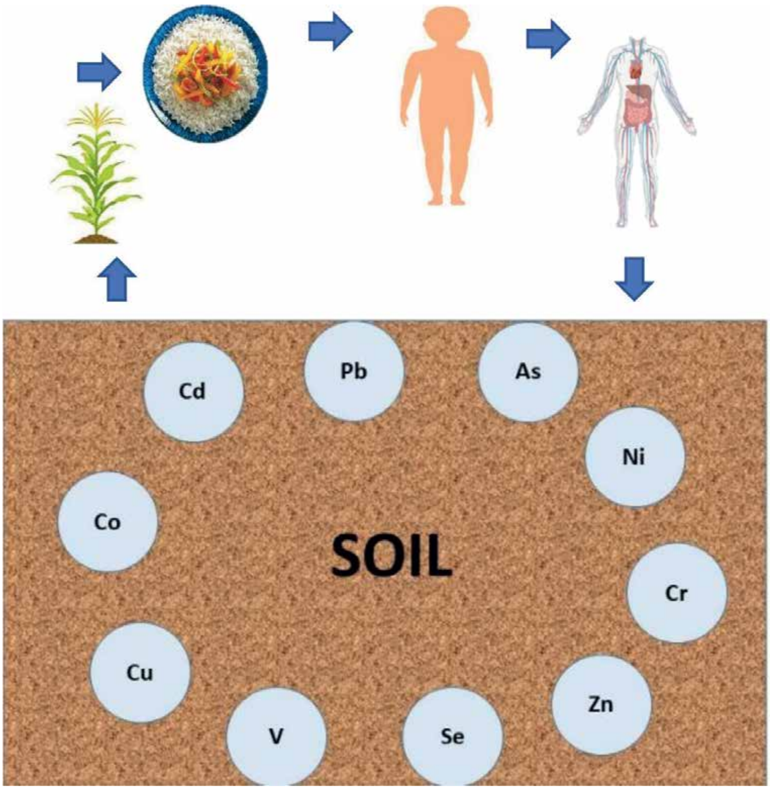


Figure 3.
Schematic representation showing the transfer of trace elements from soil to the human body and causing adverse effects like metabolic disorders which can be fatal.

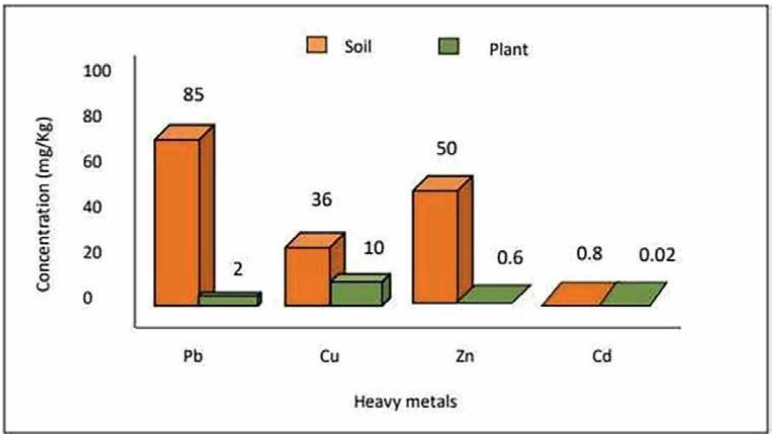


Figure 4.
Representation of the admissible upper limits for heavy metal concentrations in plants and soil as per WHO; reprinted from [16].

The trace metals present in the soil eventually turn into soil contaminants as their rates of transfer *via* artificial cycles are faster than natural ones and are easily transferred from mines to random environmental locations where there is

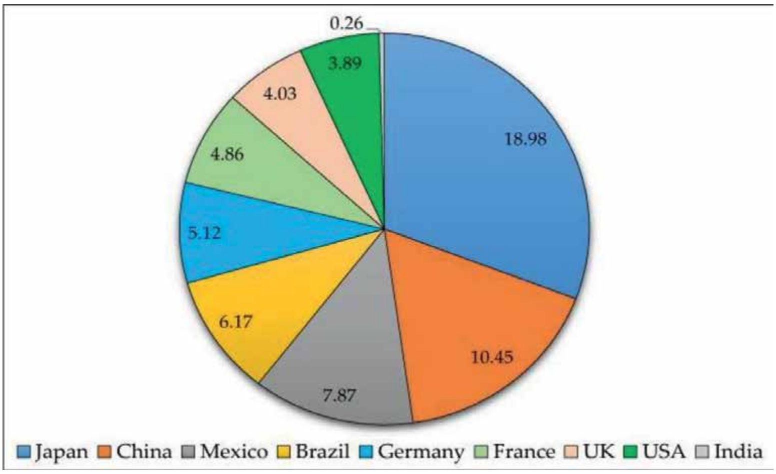


Figure 5.
Statistical representation of averaged pesticide use per year (kg/ha) in India and other countries between 2010 and 2014; reprinted from [16].

a higher risk of direct exposure. The higher rate of concentration of these trace metals in discarded products than in the surrounding environment is also a major factor contributing to soil contamination [17]. Trace elemental concentrations of heavy metals such as Pb, Zn, Mn, Ni, Cn, Cr, Fe, Cd, and As arising from various industries involving textiles, tannery, plastic, furniture, chemicals, dyes, paint, pharmaceuticals, batteries, and fertilizers from various parts of the country have been listed below in **Table 1**.

7. Methods used for analysis of soil samples for trace metal analysis

The most commonly used methods for preparation of soil samples for trace metal analysis are as follows:

1. **ISO 11466:** Air-dried soil of 1 gram is weighed precisely to the nearest 0.001 g. With 1 ml of water, it is moistened. About 21 ml of HCl and 7 ml of HNO_3 are added. The sample is allowed to stay at room temperature for around 16 hours. The sample is then annealed for a further 2 hours at 180 to 200°C. The remaining is filtered and transferred quantitatively to a 50-ml measuring flask.

2. **EPA Method 3051**: In polytetrafluoroethylene (PTFE) containers, 1 g of air-dry soil is precisely weighed to within 0.001 gram. HNO_3 (10 ml) is then added. The samples are processed by a microwave system before being analyzed.

3. **BDS ISO 14869-1**: A platinum pot containing 0.250 g of air-dry soil is weighed, and then it is heated in an electric oven. The oven's temperature is progressively raised to 450°C for an hour before being maintained for 3.5 hours before being lowered to room temperature. The cooled sample is mixed with 5.0 ml HF and 1.0 ml $HClO_4$, and it is then heated on a hotplate for 30 to 40 minutes until the steams from the $HClO_4$ and SiFa vanish. After the melting pot has cooled, 1.0 ml

Sl No.	Type of industry	City	Trace element concentration (mg kg^{-1})								
			Pb	**Zn**	**Mn**	**Ni**	**Cn**	**Cr**	**Fe**	**Cd**	**As**
1.	Textile	Haridwar	191	_	668	_	109	568	308	83.6	_
2.	Tannery	Haridwar	_	_	097	_	0.04	744	37.7	0.04	_
3.	Textile, plastic, furniture, industries	Thane-Belapur	—	191	—	184	105	521	—	—	—
4.	Chemicals, dyes, textile, paint industries	Rajasthan	293	—	—	136	298	240	—	—	_
5.	Chemicals, pharmaceutical, batteries	Hyderabad	65.0	313	—	45.0	193	433	—	0.70	33.0
6.	Tannery, textile, fertilizer, rerolling and casting, chemicals paints plastics	Jajmau, Unnao	38.3	159.9	—	—	42.9	265	—	—	—

Table 1.
Representation of trace element concentrations in soils impacted by diverse industrial operations in several cities across the nation; reprinted from [13].

of nitric acid and 5.0 ml of water are added. Careful heating can assist in the sediment's disintegration [18].

To determine the heavy metal content in the soil samples, the samples prepared using any of these above-mentioned methods must be introduced to desired instrumental techniques.

8. Forensic soil science

Soil science or pedology involves the study of soil as a naturally occurring resource material which enables farming and building and provides structural support. The term pedology has been coined from a Greek word "pedon" which means soil, whereas forensic soil science can be used to address legal interrogations by studying the morphological features of the soil, soil mapping, and its chemical and biological composition. The biological, chemical, physical, mineralogical, and hydrological aspects of soils are intricate and dynamic. Forensic interpretations and comparisons can be made by the determination of the origin of the soil and its characterization. Understanding crime scene protocols, evidential requirements for forensic personnel, and the different types of legal bounds that pertain to forensic work are all crucial steps in the move from conventional soil research to forensic soil science. Understanding the wide variety of naturally occurring and artificial soils, their formation and thorough analysis are crucial since it enables precise forensic interpretations [19]. This chapter discusses the standardized procedures including the conventional as well as modern methodologies used for the forensic testing of soils.

9. Role of soil in forensic science

The use of soil as trace evidence is crucial in forensic investigations. These trace pieces of evidence are strong proof or corroborative evidence when they clearly link one or more individuals to the crime. Soil, which is a physically transferable material, has a tendency to be carried away from one place to another by wind or objects such as shoes, textiles, tools. In forensic crime scene investigations, it can be used to link particular crime scenes to criminal suspects by determining the nature and point of contact (**Figure 6**).

The presence of foreign material, such as trace elements and paint chips, may provide a degree of individuality to soil collected from a crime scene and may provide vital information to forensic soil investigations in addition to the study of rocks and minerals [20].

The importance of soil as forensic trace evidence in allied cases has been listed below:

1. It provides additional information in criminal cases involving

    a. Hit and run cases

    b. Sexual abuse and sexual assaults

Figure 6.
Collection of soil samples from a crime scene for forensic analysis.

   c. Abduction

   d. Murder

   e. Wildlife crimes

   f. Illegal mining of land

   g. Theft.

2. It provides additional information in civil cases involving

   a. Drug shipment pathway

   b. Construction.

3. It provides additional information for intelligence work involving

   a. Identification of geographical location of the crime scene

   b. Narrowing down the area of search

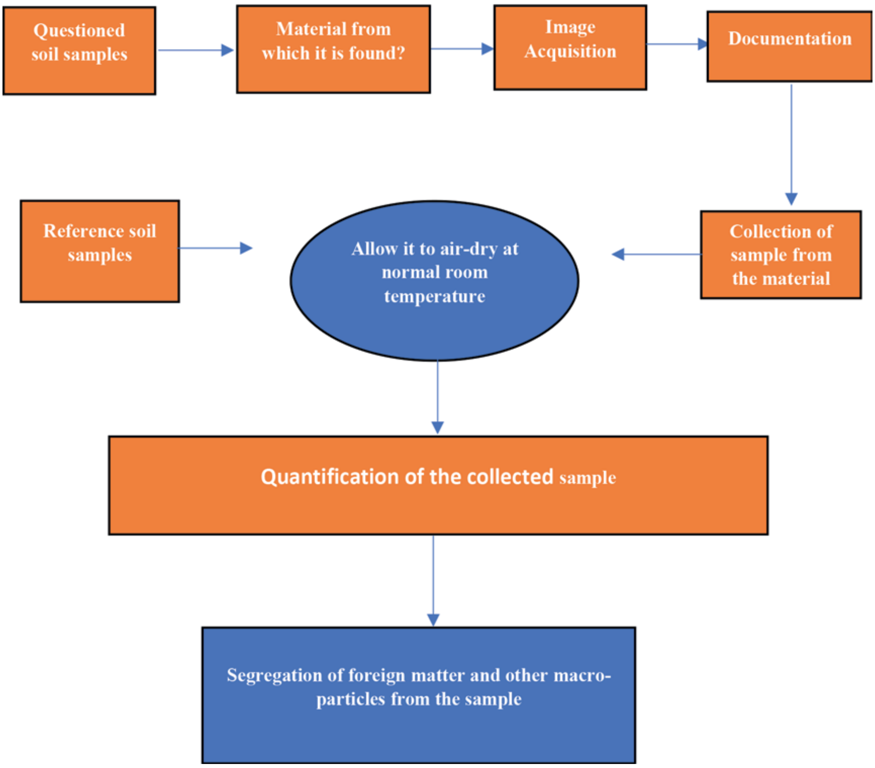
   c. Determination of the presence or absence of a suspect or a vehicle at a particular location.

10. Trace evidential value of soil transferred from one surface to the other

As Dr. Edmond Locard in the early twentieth century stated that "Every contact leaves a trace" which later came to be known as Locard's principle of exchange, which holds that when two surfaces make physical contact with one another, there is a possibility of mutual material transfer. Trace evidence is used to link persons or things to places, other people, or things, and it frequently serves as the initial point for a search or as a lead for a specific path of inquiry. Forensic experts often spot soil components on the surface of objects such as vehicle tires, shoes, tools, clothing, carpets. Such soil samples must be first spotted and identified on the enquiry-related objects followed by the systematic documentation, collection, and preservation of the soil samples in order to safeguard the integrity of the evidence for reanalysis and characterization. The soil samples collected from questioned objects, such as vehicles and shoes, are then matched with the control samples [21].

11. Forensic protocol and methods for comparison of soil traces

This chapter offers guidance on systematic approaches to be used in particular examinations but does not include any standard procedures followed universally. It offers a summary of the essential criteria and suggestions for choosing the most suitable analytical methods and the optimal sequence in which they should be used in forensic cases. A flowchart describing the steps involved in the analysis of forensic soil samples and presence of trace metals in them is depicted below [22] (**Figure** 7).



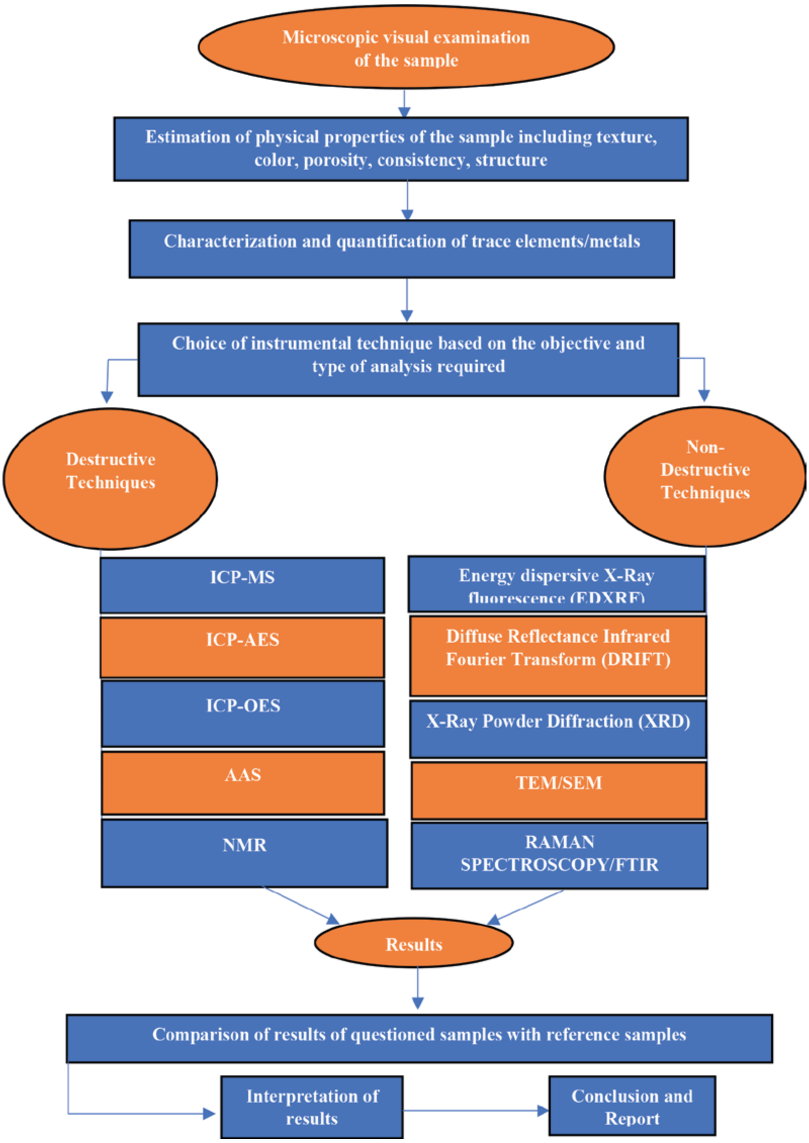


Figure 7.
Flowchart describing the steps involved in the analysis of forensic soil samples and presence of trace metals in them.

12. Instrumental techniques used for the soil sample analysis

Particularly soil found on polluted sites is a very complex material to analyze. Sand, limestone, clay, microorganisms, trace metals, etc., or a combination of several minerals may make up the actual soil matrix. From hazardous waste to highly toxic medical waste, mercury, explosives, etc., to comparatively safe construction materials, the variety of pollutants is likewise wide. Significant innovations in trace evidence have been made possible by improvements in microscopy, chemical analysis, improved instrumental procedures, and database technology for evidence comparison. The increase in accessibility and availability of these techniques has made it easy to compare trace evidence samples like soil against established standards to produce reliable results with compatible classification rates. The World Reference Base (WRB) and Soil Taxonomy are the two most extensively used international soil classification standards. Various facets of granular soils or soil samples such as their color, texture, consistency, moisture content, and the structural arrangement of each particle vary for soil samples from different geographical regions. These soil samples are complex and have varying mineralogy, composition, and quantity of organic and inorganic components. The soil material or earth material is often subjected to change with the passage of time and exposure to external environmental conditions due to which they exhibit variation at different time intervals. There is a need to monitor these variations for effective forensic soil analysis which is achieved by the use of various characterization techniques that are often performed in the laboratory. To distinguish soil from various geographical places and to assess its color, texture, particle size, etc., a range of methodologies can be utilized, a few of which are discussed in this chapter [23].

12.1 Microscopic examination

The main mineral components of soil specimens are frequently identified and quantified *via* microscopic inspection. A forensic expert may be able to positively identify a plant that produced the pollen grains, for instance, if a soil sample under investigation contains pollen grains or seeds. If the obtained plant mixture seems to be unusual, it may be possible to signify with high confidence level that the questioned specimen originated from the same location. This can be done by comparing it to known or control soil samples collected from an area where those plants are present (**Figure 8**).

A stereo microscope is often used for the preliminary visual examination of the specimens at low magnification ranging from 10X to 40X. A forensic expert can get a general sense of the soil sample from this visual inspection and record the existence and abundance of several foreign material such as metal fragments, glass particles, and pollen grains. Particles ranging from a size of down to 10 micrometers to large as the physical limits of the microscope stage can be seen under the stereo microscope. The grid features often built in the eyepieces make it easier to count individual particles in the sample and provide information regarding the particle size distribution.

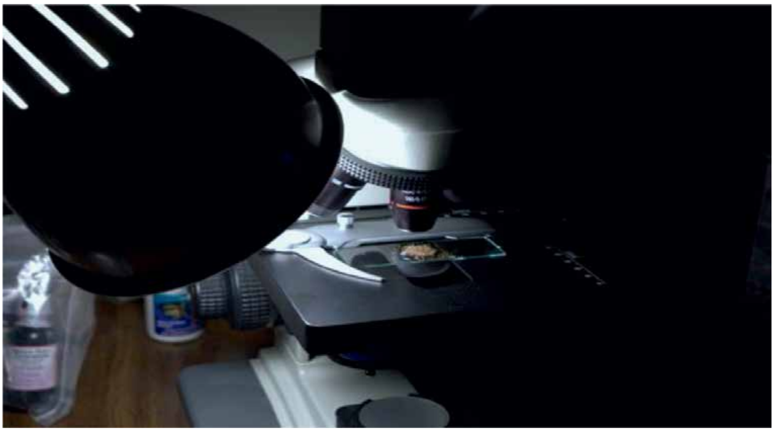


Figure 8.
Microscopic set up for the examine soil specimens.

12.2 X-ray fluorescence (XRF)

The extend of soil degradation or weathering is obtained by assessing the elemental composition of the soils. XRF, which is a non-destructive technique, enables the rapid analysis of elemental composition of the soil consisting of heavy metals and other trace elements (**Figure 9**).

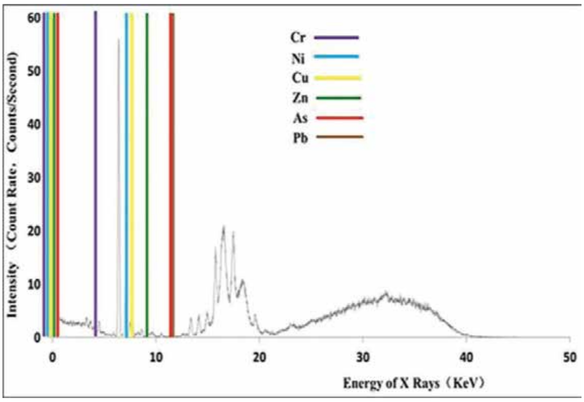


Figure 9.
Graphical representation of soil spectrum obtained using XRF showing the ranges of heavy metals present in the soil; reprinted from [24].

For heavy metals present in the soil, XRF offers multi-elemental analysis with good sensitivity [25]. However, due to insufficient sensitivity for some trace elements, X-ray fluorescence spectrometry has been restricted in its application for trace element identification.

12.3 XRD

Over the past two decades, there has been a significant advancement in X-ray-based techniques for elemental analysis. There are now many different scientific fields that utilize X-ray-based methodologies. As these techniques can quantify trace components *in situ*, they are among the most potent analytical techniques available. Unlike many other analytical techniques, there is no requirement for chemical extraction for this technique. Moreover, secondary minerals created by weathering processes could have crystallographic properties that have a significant impact on the chemical and physical properties of soils. Certain soil minerals, such as phyllosilicates, are referred to as expansible because they adsorb water and cations on internal surfaces within the crystal structure itself. The method that is most frequently used in soil mineralogical analysis and study of the crystal structure is X-ray diffraction (XRD) [26, 27].

12.4 SEM-EDX

SEM-EDX is a rapid surface analysis method that gives surface morphological features in the form of photos in high resolution showing the topography of the sample analyzed. The macro-elements present in the soil such as nitrogen, carbon, phosphorous, oxygen, sulfur, potassium, chlorine, sodium, magnesium, aluminum, silicon, calcium, titanium, iron, manganese, and nickel can be detected and quantified using this instrumental technique (**Table 2**).

S. No.	Na	Mg	Al	Si	P	K	Ca	Ti	Fe	Mn	Ni
1	0.39	0.33	6.09	19.16	0.34	1.27	1.87	0.57	4.81	0.17	0.07
2	0.13	0.24	5.61	16.45	0.25	0.99	1.53	0.46	4.31	0.11	0.04
3	0.11	0.31	4.43	12.78	0.2	1.02	0.86	0.25	2.32	0.08	0.06
4	0.25	0.36	6.22	19.09	0.39	2.13	1.63	0.41	4.75	0.18	0.08
5	0.37	0.48	6.79	24.42	0.46	2.57	2.34	0.61	6.4	0.21	0.14
6	0.21	0.28	5.96	17.37	0.33	2.01	1.87	0.5	4.71	0.18	0.07
7	0.24	0.25	5.23	15.53	0.18	0.92	0.84	0.38	2.77	0.09	0.04
8	0.12	0.26	5.9	13.77	0.26	0.74	0.9	0.44	4.05	0.08	0.05
9	0.26	0.17	5.42	16.4	0.12	0.82	0.84	0.35	3.88	0.10	0.12
10	0.17	0.23	5.14	14.04	0.28	1.77	1.48	0.48	4.74	0.21	0.06
11	0.33	0.27	5.36	18.4	0.26	1.49	0.83	0.45	4.77	0.16	0.05
12	0.14	0.44	6.09	15.99	0.29	1.29	1.41	0.34	3.02	0.12	0.04
13	0.16	0.33	5.09	17.26	0.21	1.7	1.57	0.37	3.95	0.09	0.05
14	0.35	0.38	9.5	16.15	0.23	1.37	1.64	0.48	5.78	0.16	0.06
15	0.36	0.49	7.36	17.66	0.37	2.18	1.57	0.58	5.15	0.21	0.12
16	0.18	0.27	5.98	17.37	0.16	1.41	1.33	0.25	3.81	0.12	0.08
17	0.25	0.33	8.49	15.42	0.18	1.24	1.26	0.33	3.04	0.11	0.07
18	0.11	0.28	5.21	17.57	0.17	1.69	1.39	0.36	3.44	0.12	0.05
19	0.26	0.38	4.53	12.86	0.29	1.95	1.65	0.56	4.06	0.19	0.09
20	0.13	0.35	3.68	19.15	0.16	1.71	1.58	0.32	3.96	0.17	0.06
21	0.19	0.32	4.76	13.97	0.11	0.68	1.65	0.36	3.25	0.18	0.06
22	0.27	0.28	7.59	14.59	0.21	1.26	1.47	0.31	5.94	0.11	0.07
23	0.17	0.29	5.27	16.2	0.29	2.17	1.01	0.41	5.91	0.09	0.07
24	0.1	0.26	5.85	17.86	0.35	1.06	1.63	0.41	4.41	0.22	0.16
25	0.24	0.35	6.19	17.09	0.26	1.84	1.11	0.36	4.99	0.1	0.05
26	0.27	0.12	4.56	12.19	0.16	1.35	1.27	0.31	2.42	0.12	0.04
27	0.31	0.31	9.85	17.61	0.34	1.6	2.3	0.46	5.63	0.18	0.16
28	0.19	0.33	5.44	17.88	0.30	1.86	0.85	0.32	4.53	0.11	0.05
29	0.21	0.32	6.19	20.34	0.60	1.62	2.17	0.35	4.26	0.12	0.10
30	0.36	0.48	10.31	22.31	0.49	3.22	2.72	0.53	5.22	0.21	0.15

Table 2.
Concentration of trace elements in soil, percentage of soil samples from Korba; reprinted from [28].

The table above depicts the various trace metals present in soil samples from Korba along with their concentration in percentage. The elemental composition, size, and morphology of soil minerals are all highly variable due to which they vary in metal concentration from region to region depending upon the activities occurring in that region. For example, due to extensive coal mining and burning, the soil found at the surface of the Korba basin was discovered to have a higher metal concentration than other parts of the nation [28].

12.5 IR spectroscopy

The physicochemical characteristics of soil can be analyzed using this spectroscopic technique. As reported in the literature [29], the total carbon, total nitrogen, their ratio, etc., can all be investigated using infrared spectroscopy. Highly detailed spectrum information may be a benefit of the high-resolution data. For more precise object recognition and identification, the sensing capabilities of visible and near-infrared spectral imaging systems can be utilized. These techniques have significantly increased in recent years. The complex optical features from the sample can be captured with higher spectral and spatial resolution using this spectroscopic technique [30].

12.6 Atomic absorption spectrometry

Atomic absorption spectrometry developed is an analytical technique widely used to identify metals in materials. It is incredibly dependable and easy to use. The quantity of trace metals present in the soil samples is also measured. It is the most common method used to analyze metals in soil. The solvent is vaporized, and the sample is broken up into its constituent atoms using an acetylene flame. Light from a hollow cathode lamp passes through the cloud of atoms created by the atomization process and is absorbed by the target atoms. In a study conducted by Senthamilselvi P *et al.,* they collected and analyzed soil samples from three regions of a steel plant in Tamil Nadu state, using this technique, the results of which are listed below in **Table 3**.

The findings of the study demonstrated that the amount of Cr in the soil sample was within the WHO-permitted level. All three samples have levels of Cd, Mn, and Pb that are less than the acceptable limit and lower than those of Cr. Assessing the concentration of heavy metals in soil samples helps to identify if they are present in amounts that may cause a threat to human health [31].

12.7 ICP-OES/MS

There is a need for predictive soil extraction techniques for pollutants including lead, mercury, arsenic, and other toxic elements due to the rise in toxic heavy metal that leads to pollution of soils from industrial sources, mining, disposal of waste on fields or bare land, etc. There is no such extraction process for several of these components. The plant uptake of these trace metals such as lead and cadmium in trace concentration beyond the detection limit of some instruments can be analyzed using mass spectroscopic

Sample No.	Lead (Pb) concentration range ppm	Chromium(Cr) concentration range ppm	Cadmium (Cd) concentration range ppm x10–4	Manganese (Mn) concentration range ppm
Sample 1	0.00438	0.00401	4.33	0.247
Sample 2	0.00168	0.00591	3.17	0.221
Sample 3	0.00129	0.00592	3.04	0.272

Table 3.
Heavy metal concentration in soil samples from three regions of Tamil Nadu; reprinted from [31].

techniques such as ICP-MS or ICP-OES [32]. The device employs temperatures as high as 10,000°C to effectively atomize even the most refractory materials for ICP/ICP-AES analysis. As a result, the limits of detection of the system can be in orders of magnitude lower than FAAS methods (usually at the 1–10 parts-per-billion level). In a single sample run of less than a minute, the ICP method may simultaneously screen for up to 60 elements without any loss of precision or detection limits [13].

13. Conclusion

It is vital to understand how trace metals affect the environment and living organisms. A well-established area of forensic science that is crucial to both criminal and environmental forensics is soil science, which analyzes trace metals found in soil. In sophisticated criminal investigations where traditional forensic techniques fall short of providing sufficient evidence, soil samples are often used as a physical evidence. The obtained soil data can be utilized for intelligence work or as an important evidence in the court. In order to locate and stop environmental crimes, environmental forensics is essential. In order to locate and prevent environmental crimes, environmental forensics is essential. In order to identify and locate the crime scene, experts working in the field of environmental forensics compare the questioned soil samples with the existing soil databases, control samples, or natural soil samples from the scene of occurrence. In the majority of the crime scenes, soil samples and controlled samples are collected from the crime scene and control sites, respectively, since these are the locations from which dirt or soil can be transferred to footwear, tools, clothes, tires, etc. The chapter highlights the significance of trace metals present in the soil found at a crime scene, the analysis of which helps; to narrow down the area of search, to locate the crime scene, to determine the origin of soil, aids in intelligence work and can be produced as an evidence in court. To validate the testimony of soil as proof, a comparative analysis of soil samples taken from several sites around a crime scene will be beneficial.

Conflict of interest

The authors declare no conflict of interest.

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Chapter 2

E-Waste and Metal Contamination in the Environment: Health Effects

Mark E.C. Dockrell, Diane Purchase and Robert G. Price

Abstract

It is predicted that electronic waste (e-waste) derived principally from discarded electronic equipment will reach 74 million metric tonnes by 2030. In addition, urbanization and industrialization have contributed to metal contamination in the environments. E-waste is often deposed of in low-income countries adversely affecting the health of the working population. The main sources of e-contamination are soil, dust, and food matrices. Drinking water can also be contaminated with heavy metals such as arsenic (As), cadmium (Cd), mercury (Hg), and lead (Pb) causing a major health concern. Exposure to pollutants present in waste has a significant detrimental impact on human health; children in developing countries are often particularly susceptible. Sensitive monitoring procedures are needed to improve the rate of detection and monitoring of the possible adverse effects on the population exposed to significant quantities of e-waste.

Keywords: air quality, biomarkers, contamination pathways, biomarkers of effect, biomarkers of exposure, metals, electronic waste

1. Introduction

Electronic and electrical waste (e-waste) is the fastest growing domestic waste stream in the world [1]. E-waste is a broad category; the term is used to cover all items of electrical and electronic equipment and its parts that have been discarded as waste without the intention of reuse. It particularly affects impoverished city dwellers who work in or near informal dumps and landfills. Many of these sites are in low- and middle-income countries. E-waste can contain valuable material, for example, gold but it can also be harmful to human health if it is not disposed of correctly or preferably recycled under the correct conditions and procedures. Workers often use primitive recycling techniques such as acid leaching and cable burning to recover, gold, copper, and other valuable metals and are, therefore, directly exposed to contaminants arising from these processes [2]. Other hazardous by-products are also released into the environment with unknown effects. According to the global e-waste statistics partnership (GESP), 53.6 million tonnes of e-waste are produced worldwide, but only 17.4% of this was recorded as collected and appropriately recycled [3]. In addition to the risk from exposure to the original constituents of, for example, electronic equipment, substances added in the recovery process, as well as those resulting from the recycling process is also health threats. The residents of the local area, as well as those working, are likely to be exposed to a complex mixture with currently unknown toxicity [4]. Airborne contaminants had an immediate effect on the respiratory system but have longer-term effects on the kidney and liver function of Chinese e-waste dismantling workers exposed to high levels of heavy metals [5]. Biomarkers of kidney and liver function should, therefore, provide valuable indicators of early damage to these organs. The waste stream of obsolete electronic equipment grows exponentially with the result that the ecological impact of e-waste is growing exponentially [6].

2. E-waste chemical composition and exposure pathways

The nature of e-waste is highly heterogeneous (from temperature exchange equipment to small IT and telecommunication equipment with external dimensions less than 50 cm); the chemical composition of e-wastes is extremely complex, featuring a mix of metals (e.g., precious, ferrous, and nonferrous metals), metalloids, rare earth elements, glass, plastics, flame retardants, and other additives. Heavy metals are naturally occurring elements that have a high atomic weight and a density at least five times greater than that of water. **Table 1** presents the key transition metals, and metalloids found in e-waste and their usage in electrical and electronic equipment. Many of the raw materials in e-waste are valuable commodities, for example, copper (Cu) and gold (Au), they exist in high purity and quality that can be recovered. The recoverable value of e-waste was estimated to be US$ 57 billion [7]. E-waste is a valuable resource; many formal and informal activities have evolved to reclaim these materials around the world. Such activities have a direct impact on human health and the environment.

Many developed countries have strict regulations for recycling their e-waste. For example, in the EU, the WEEE Directive 2012/19/EU stipulated the requirements for e-waste disposal and require the producers to manage their product’s life cycle, from cradle to grave including end-of-life recycling. In the formal sector, the recycling process mainly involves four key stages: collection, sorting, mechanical size reduction and physical separation, and metal recovery (**Figure 1**). The mechanical process entails dismantling, shredding, or crushing the e-waste, and a number of techniques are available to separate the particles after size reduction such as sieving, gravity, magnetic and electrostatic separation, and particle flotation. Metal recovery can be achieved by pyrometallurgy involving high-temperature smelters, hydrometallurgy (using various aqueous solutions and solvents), and bio metallurgy (employing microorganisms to leach or extract metals. The size reduction stage has the highest potential in releasing dust particles containing toxic metals into the environment. Workers can be exposed to these compounds *via* inhalation and skin contact. Studies carried out in formal recycling factory around the world have shown the high levels of metal present in the dust (**Table 2**). For example, a study in five sheltered e-waste facilities disassembling flat-screen and tube displays showed the presence of Al, As, Be, Cd, Cr, Co, Ni, and Hg in the inhalable fraction of air samples, although the level was below German and international occupational limit [12]. Another study of three e-waste recycling companies in Sweden of varying sizes showed that recycling workers are exposed to elevated levels of metals and rare earth elements, around 10–30 times higher than the control of office workers [13].

It was estimated 80% of the e-waste worldwide is processed by the informal sector in low or lower-middle income countries [7, 18] where legislations on environmental protection and workers’ right are less strong than in developed countries, and they

	Usage
V	Used in rechargeable flow battery. VO_2 is used as semiconductors and in transistors.
Cr*	Cr^{6+} is widely used as a corrosion inhibitor in corrosion protection in metal housing. Cr is a crucial component of stainless steel (where it is present at least at 10.5%) which is widely employed for EEE production. It can be also used in form of NiCr alloy, in multilayer metallisations in printed circuit boards, smart card chips and microdevices for ensuring adherence between metallic layers and between Au finishing and the device surface.
Mn	As an alloy with steel, Al or Cu, it has important metallurgical applications. As manganese oxides, they are used as a depolarizer in batteries, sensors and super capacitors.
Fe	There are numerous uses *e.g.*, as electrical steel used in magnetic cores for transformers, generators and motors. AsFe_2O_3 it is used in hard drive and printed circuit boards. Widely recycled.
Co	As a magnetic alloy with Fe, Ni, Al, Nd, Sm (*e.g.*, AlNiCo, SmCo, etc. magnets). It is widely used in Li-ion batteries. Often found in CRT, printed circuit boards and hard drives. It is often recovered due to its economic value.
Ni	As an alloy with steel, Cr, Mn or Fe for corrosion protection in housing. Ni is widely used in batteries and CRT. It is employed as a coating in preserving NdFeB magnets from oxidation. It is often recovered due to its economic value.
Cu	Commonly used in electrical wiring. Copper wire is found in most electrical equipment and electronic circuitry. It is used for printed circuit board pathways and as bulky material in multilayer connections where Au is the external finishing (*e.g.*, smart card chips, printer cartridge connections and pathways). It represents the most abundant non-ferrous metal in de-manufactured printed circuit boards and small electronic equipment. Also forms important alloy with Al and Ti. It is often recovered due to its economic value.
Zn	Used in die-castings in electrical industries. As alloys such as Ni, Ag and Al solder. ZnO is widely used in the manufacture of rubber, plastics, inks, batteries and electrical equipment. ZnS is used in making luminous paints, fluorescent lights and x-ray screens. It is often recovered due to its economic value.
Ga	HHigh-purityGa is used in the manufacturing of semiconductors. GaAs and GaN are used in electronic components *e.g.*, integrated circuit, hhigh-speed logic chips, diode lasers and light-emitting diodes (LEDs)
Ge	Commonly used in fluorescent lamps, LEDs, and transistors (historically). Si-Ge alloy, it is used in the manufacturing of ssemiconductors for high-speed integrated circuits.
As	As alloys with Pb or Ga. GaAs is a semiconductor material used in printed circuits boards and laser diodes.
Se	Used in Li-Se battery and ZnSe has been used in the manufacturing of LEDs and laser diodes.
Sr	Primarily used in the manufacturing of glass for CRT.
Pd	Often used as soldering materials and as electrodes in multilayer ceramic capacitors in laptops and mobile phones. It is often recovered due to its economic value.
Ag	Widely used in membrane switches and pathways, it is often present in printed circuit boards, plasma display panels and photovoltaic panels (PVPs). Powdered Ag and its alloys are used in paste preparations for conductor layers and electrodes, ceramic capacitors, and other ceramic components. It is often recovered due to its economic value.
Cd**	Commonly used in contacts, switches and rechargeable Ni-Cd batteries. CdS is used in CRT.
In	Extensively used in liquid crystal display (LCD) as transparent electrodes (indium tin oxide) and thin-film transistors in the production of flat screen monitors, TVs and solar panels. GaInN and GaInP are used in LEDs and laser diodes.
Sn	Used in alloys with Pb as solder for electric circuits in historic electric and electronic equipment. Nb_3Sn is used in coils of superconducting magnets. Also used as electrode in Li-ion batteries. Stannate aqueous solutions are used to produce electrically conductive and corrosion-resistant coatings on glass by electroplating and Zn_2SnO_4 is a fire-retardant used in plastics housing.

	Usage
Sb	Used in antifriction alloys in electrical cable sheathing, as lead-free solder as well as fining agent in glass for TV screens. As semiconductor material, it is used in infrared detectors and diodes.
Te	Used in the manufacturing of solar panels. It is often doped with Ag, Au, Cu or Sn in semiconductor applications.
Pt	It is a component of the Co-Cr-Pt alloy used for hard drive platters coating; also found in fiberglass, liquid-crystal and flat-panel displays, and CRT. It is often recovered due to its economic value.
Au	Widely used in the production of corrosion-free connectors in electronic devices, cables and integrated circuits. It is often recovered due to its economic value.
Hg*	Historically used in mercury-vapor lamps and cold-cathode fluorescent lamps. It has also been used in switches, relays of older mainframe computers, LCD and batteries.
Tl	Used by the electronic industry in photoelectric cells.
Pb*	Historically used in electrical solder with Sn on printed circuit boards and PbO is used in CRTs.

*EU Restriction of Hazardous Substances (RoHS) regulation restricted concentration in new equipment since 2006: *: ≤0.1% by weight; ** ≤0.01% by weight.*

Table 1.
Key transition metals and metalloids and their use in electric and electronic equipment. (adapted from Purchase [6] et al., 2020).

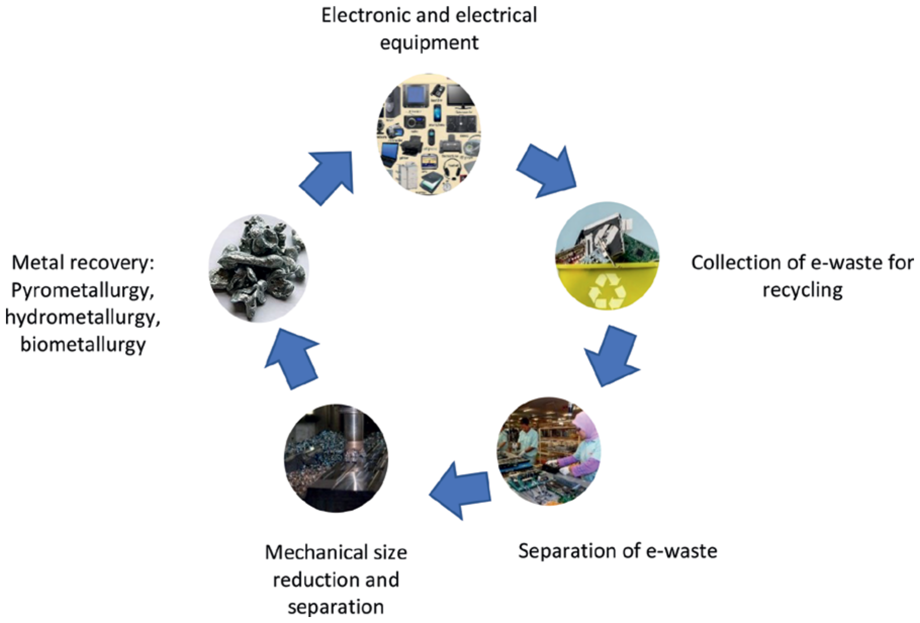

Figure 1.
Different stages of formal recycle of e-waste and its potential in circular economy.

are also difficult to enforce due to the informal nature of the operation. The recycling practice generally uses simple and crude methods to recover the precious metals in an informal environment where the workers and their kin have little protection against the hazardous materials generated. In comparison to the highly automated processes in the formal sector, informal recycling of e-waste normally involves three stages: (i) manual dismantling, (ii) recovery of valuable materials via open burning and/or acid stripping, and (iii) disposal of unsalvageable waste. E-waste is dismantled with

Region & Country	Comments	References
North America:		
US	Lead and Cd in electronics recycling facilities.	Ceballos [8]
	Hg detected in a battery recovery facility.	Reh [9]
Europe:		
France	Inhalation exposure to Pb, Cd, Y in CRT processing plant	Lecler [10]
	Pb and Y were detected in dust and skin of workers in fluorescent lamp recycling facilities	Zimmermann [11]
Germany	Al, As, Be, Cd, Cr, Co, Ni and Hg detected in an inhalable fraction of air samples in flat screen and tube display dismantling area	Gerding [12]
Sweden	High levels of Cr, Pb, In and Hg in CRT recycling facilities.	Julander [13]
Asia:		
China	Pb, Ni, Fe, Mn, Zn, Cu and Cd were detected from formal e-waste dismantling parks from 18 cities are distributed in indoor workshops	Wu [14]
	Pb and Cu detected in waste electronic and electrical equipment recycling plants	Deng [15]; Lau [16]

Table 2.
Examples f metal exposure of e-waste recycling workers in air samples.

rudimentary tools such as hammers, chisels, and screwdrivers into smaller fragments or valuable components, which can then be melted down on open fires. For example, valuable metals and chips can be recovered after burning waste printed circuit boards; similarly, cable wires are burnt to extract copper and resell (**Figure 2**). Hazardous solvents or acids may also be used to strip and clean the metals. Any residual materials of no immediate economic value will be discarded on land or burnt.

As a result of the proximity of the workers, their kin, and livestock to the informal recycling activities, they are exposed to high levels of hazardous chemicals from e-waste combustion and acid and waste disposed on the site through different routes (**Figure 3**). Metals and metalloids are among some of the chemicals released into the air from manual dismantling in dust particles, which can be deposited to the ground or water body *via* dry and wet deposition, soil particle transport, or runoffs. As air borne particles, they can be inhaled and as deposit, they can be taken up by direct human contact e.g., by children who live in the vicinity. This can be by drinking contaminated water or by consumption of crops and local livestock. A number of studies have reported elevated levels of metals in the dismantling area compared to other areas in an informal recycling site [19, 20]. Disposal of the acid from metal stripping into a water body or directly into the soil also affects the soil health and may leach into groundwater. Elevated levels of metals in e-waste recycling sites have been reported to impact soil microbial diversity, population, and functional activities of the microbial communities [17, 21]. A systematic review carried out by [22] on electronic waste recycling activities between 2005 and 2017 around the world showed that the levels of As, Cd, Cr, Hg, and Cd in soil, water, and sediments are generally higher than international standards, and the risk associated with their exposure for both human health

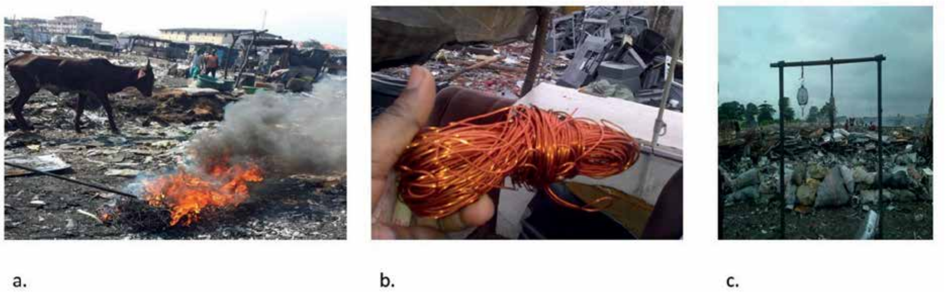

Figure 2.
Scenes from an e-waste informal recycling site in Alaba Lagos, Nigeria: A – E-waste was burned to recover the metal in the site where livestock and workers also resided; b – Copper wires were recovered from burnt cables; and c – Scales used to measure the weight of the recovered metals to be resold. (photos source: Khadijah Isimekhai©).

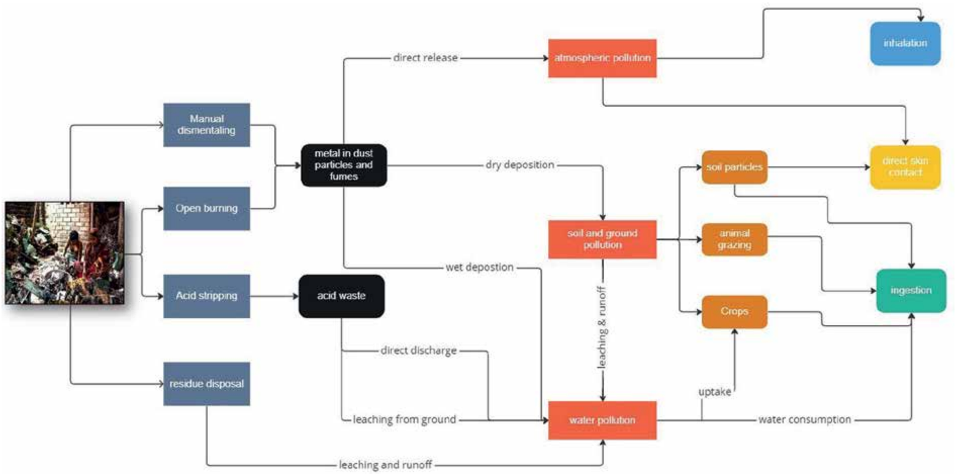

Figure 3.
Different pathways of metal exposure from informal e-waste recycling. (photo source: Debashish Chatterjee).

and the environment are not well characterized. The latter is not surprising given the complexity of the living conditions and varying practices and traditions in dietary intake.

3. Biomarkers

A study of biomarkers for disease caused by all the chemical composites of e-waste would be of great value for monitoring people who may be exposed in formal or informal recycling environments. However, this would be a substantial piece of work and is beyond the remit of this chapter. The following focuses specifically on some of the important potentially toxic metals present in e-waste.

Biomarkers can be subcategorized into biomarkers of effect and biomarkers of exposure. A biomarker of effect is used in the assessment of health risk and can give an assessment of absorbed dose in industrial workers and populations exposed to waste recycling. Both have their uses. Biomarkers of effect can directly relate a potentially harmful substance to a pathological process, demonstrating cause and effect. As such, it can also indicate possible remedial treatment. Biomarkers of exposure give an assessment of a worker's current exposure to a hazard. However, when there is pathological damage caused by chronic exposure to the hazard this type of biomarker may be less useful. This is not always the case. Deciduous teeth have been shown to provide retrospective information on timing of early-life metals exposure [23]. In addition, chronic lead exposure affects bone turnover and, consequently, can be identified by studying markers of bone formation and bone turnover [24]. Some biomarkers of exposure may also be predictors of subsequent adverse health effects.

4. Biomarkers of effect

4.1 Arsenic

Arsenic (As) is a common component of e-waste found in circuit boards, semiconductors, LCD displays, and computer chips. When dumped in landfill, As can leach into the soil and the groundwater, and when recycled, As can be released exposing workers by inhalation [25].

Serum matrix metalloproteinase-9 (MMP-9) has been suggested as a biomarker for As inhalation. Serum MMP-9 is associated with chronic respiratory disease and lung inflammation [26]. Although it did correlate with estimated exposure levels, it was not significantly associated with urinary As levels. Serum MMP-9 is also a potential biomarker for other conditions including tick-borne encephalitis [27], brain tumors [28], and alcohol intoxication in adolescents [29]. The specificity of these biomarkers needs to be considered.

As can cause both liver and kidney damage. Peripheral blood mitochondrial DNA copy number (mtDNAcn) is a potential biomarker of arsenic-induced liver damage [30]. As exposure has been shown to be associated with renal tubular injury [31]. Studies of As nephrotoxicity have used a combination of biomarkers of tubular toxicity including N-acetyl-beta-D-glucosaminidase (NAG), β2-microglobulin (β2-MG), α1-microglobulin (α1-MG), as well as retinol-binding protein (RBP) [32]. Urinary levels of four putative cancer-related proteins, FASLG, SEZ6L, LYPD3, and TFPI2, were associated with blood As levels in a study of Bolivian women [33].

4.2 Cadmium

Cadmium (Cd) is stored in the kidney and liver with a biological half-life of 10–30 years [34]. Cd is primarily toxic to the kidney. Prolonged or high exposure to Cd may result in a reduced glomerular filtration rate (GFR) and ultimately in renal failure. Prolonged urinary levels of >4 μg Cd/g creatinine are associated with renal tubular dysfunction. Biomarkers of tubule function, such as RBP, β2MG, and NAG, have been used in the identification of Cd induce tubular function [34].

Cd can also cause bone demineralization in children [35, 36] and increase the risk of osteoporosis and fracture in pregnant, postmenopausal women, and the elderly [37, 38]. Urinary calcium (uCa) excretion is a determinant of bone mineral density. Deoxypyridinoline (DPD) represents a specific degradation product of mature collagen found in bones. It is excreted unmetabolized in urine and is a specific marker of bone resorption and osteoclastic activity. Two studies found urinary Cd concentrations associated with β2-MG, U-Ca, and DPD levels [36, 39]. Bone mass density has also been proposed as a marker of Cd exposure [40].

4.3 Chromium

Hexavalent chromium [Cr(VI)] is a known carcinogen and is increasingly being recognized as a neurotoxicant 8-hydroxy-2′-deoxyguanosine is a marker of DNA damage, and urinary 8-hydroxy-2′-deoxyguanosine/creatinine ratio has been shown to correlate with Cr(VI)] exposure [41]. Positive dose-response associations were also found between chromium levels in erythrocytes and olive tail movement, tail length, and tail DNA%. The comet is a very widely used assay to microscopically detect DNA damage at the level of a single cell. In exposed workers, Cr(VI) markers of genotoxicity and oxidative stress have been measured. These included micronucleus analysis in lymphocytes and reticulocytes, the comet assay in whole blood, and malondialdehyde and 8-oxo-20-deoxyguanosine in urine [42].

Exposure to Cr and Cr compounds through dermal contact mainly induces DNA damage, metastasis, and immune system disorders. mRNA expression of IL-4, IL-6, and IFN-Q was increased in skin tissues exposed to chromate [43]. A correlation was reported between urinary levels of Cr(III) and the renal damage biomarker KIM-1in tannery workers [44].

4.4 Copper

In a 2001, paper copper (Cu) was said to make up 20% of "typical electronic scrap," which was more than any other metal [45]. An occupational exposure study of workers in e-waste recycling in Sweden found that dismantling workers had a significantly higher exposure to copper by inhalation than outdoor workers [13]. However, there is little evidence of long-term Cu-induced toxicity due to inhalation, possibly due to the tightly regulated homeostasis that prevents Cu toxicity. The development of chronic Cu toxicity is dependent on Cu homeostasis and its tissue retention. This homeostatic control is disturbed in Wilson's disease. Wilson disease is a rare genetic condition typified by Cu retention in the liver. There is some evidence from animal studies that Cu ions are involved in the development of type 2 diabetes [46], this needs further investigation.

4.5 Mercury

The main adverse health effects of Mercury (Hg) include neurotoxicity, teratogenicity, nephrotoxicity, and immunotoxicity [47]. After consumption of methylmercury (MeHg)-contaminated food, the gastrointestinal tract absorbs approximately 95% of ingested MeHg, although it should be noted that MeHg can also be readily absorbed through the skin and lungs. Once absorbed into the bloodstream, the majority of MeHg enters the red blood cells or is transported by plasma proteins. Serum albumin (Alb) is the most abundant plasma protein to which MeHg covalently binds through sulfhydryl groups, forming a reversible MeHg-Alb conjugate. Circulatory distribution of MeHg conjugates to several organs, mainly to kidneys and the brain. All mercurial forms have known deleterious effects on human health at high doses; recent evidence indicates an association between chronic low doses of MeHg and cytotoxic effects, mainly in the central nervous system [48]. Neuron-specific enolase (NSE), a pro-inflammatory cytokine secreted by astrocytes S100B, and glutamate receptor (GRIA 1) levels were increased with mercury exposure. GRIA 1 and S100B levels discriminated between neurological symptoms in positive and negative groups [49].

The majority of plasmatic MeHg-Alb is transferred to the kidneys through a non-filtrating peritubular mechanism [48]. Several markers of tubule damage and dysfunction have been used to identify Hg-induced renal damage including RBP and NAG [47]. These, however, would not be able to discriminate between Hg- and Cd-induced renal damage. A more recent study offers the potential of greater discrimination. Medina Perez and colleagues identified single nucleotide polymorphisms (SNPs) in glutathione-related genes that could modulate the pathogenesis of Hg nephrotoxicity [50].

4.6 Lead

Lead (Pb) is an important component of e-waste due to its well-known toxicity. The nervous system is the mostly affected target in lead toxicity. Positive correlations between blood lead and ADHD scores (inattentive, hyperactive/impulsive, and total scores, $\beta = 0{\cdot}22\text{–}0{\cdot}28$; $p < 0{\cdot}001$) have been demonstrated [51]. However, a score of behavioral abnormalities may not prove a useful biomarker. In a study looking at plasma metabolite in two groups of adults, those with low plasma Pb level and high cognition vs. those with high plasma Pb level and low cognition, a significant reduction in docosahexaenoic acid, glycoursodeoxycholic acid, and arachidonic acid, and significant induction of p-cresol sulfate and phenyl acetyl-l-glutamine were observed [52]. Markers of tubule dysfunction, such as NAG [53] and kidney injury molecule 1(KIM-1) [54], have been associated with Pb-induced nephrotoxicity.

Biomarkers of Exposure.

4.7 Arsenic

Levels of both As and Pb in the hair, fingernails, and urine of shallow groundwater-consuming residents were greater than those in the hair, fingernails, and urine of tap water-consuming residents. Interestingly, the As level in urine showed a linear relationship with the As concentration in groundwater ($R2 = 0.91$) [55]. Urinary porphyrins have also been proposed as an arsenic biomarker of exposure. After chronic ingestion of As, dermatologic lesions have been used as a long-term biomarker of cumulative arsenic exposure [56] (Hughes FM, 2006). A study investigating novel biomarker sampling methods found a significant association between groundwater and fingernail arsenic concentration [57].

4.8 Cadmium

Blood cadmium levels are indicative of recent exposure rather than whole-body burdens. Urine cadmium levels primarily reflect total body burden. A biokinetic model can estimate intake based on urinary levels.

4.9 Chromium

Cr exposure determined by blood and hair analysis correlated with calculated exposure [58]. Exposure to Cr(VI) can cause serious adverse health effects such as lung cancer and irritation of the skin and airways. Although assessment of Cr in urine is not specific for Cr(VI) exposure, the total amount of Cr in urine is the most used marker of exposure for biomonitoring of Cr(VI) [59]. The half-life of Cr in the body is approximately 2 days; however, incomplete reduction of Cr (VI) to Cr (III) may cause longer Cr (VI) retention in tissues. For biomonitoring, urinary chromium has been widely used to assess recent total chromium exposure in the general population, whereas blood chromium is measured to assess Cr (VI) exposure, and hair chromium is used to assess chronic occupational exposure [60]. Specific exposure to Cr(VI) can be determined in erythrocytes [41]. Cr(VI) induced renal damage was found to correlate with Interleukin 18 (IL-18) in animal studies [60] (Tsai1T-L 2017). A study by Hegazy [61] revealed that lactoferrin protected against Cr-induced acute renal failure in rats and significantly showed antioxidant, anti-inflammatory and antiproliferative properties, and down-regulated IL-18 and IGF-1.

4.10 Copper

Copper can be measured in blood, urine, hair, and nails to indicate exposure [62].

4.11 Mercury

The most common biomarkers of exposure to mercurials are internal dose markers that encompass measurements of total Hg levels in hair, urine, and blood [47]. Hair MeHg and Tissue Hg (THg) correlations are reported to be high [63]. Urinary total Hg levels are suitable to assess long-term exposure to both elemental and inorganic Hg [64].

4.12 Lead

Humans are exposed to Pb through inhalation, ingestion, and skin contact *via* food, water, tobacco smoke, air, dust, and soil. Pb accumulates in bones, brain, liver, and kidney [65]. For example, lead inhaled in dust could be retained in the lungs, removed from the lungs by protective mechanisms and ingested, stored in bone, or eliminated from the body *via* the kidneys. Toxicity can be observed in the kidneys, blood, nervous system, or other organs and tissues. At any step after exposure, biological markers of exposure to lead can be detected.

Blood lead (Pb-B), mainly red cell lead, is a representative of soft tissue lead, and most widely used as a measure of body burden and absorbed doses of lead. Urine lead (Pb-U), as well as plasma lead (Pb-P), increases exponentially with increasing Pb-B under a steady-state situation and reflects recent exposure [66]. Pb-B can not differentiate between low-level chronic Pb exposure and a high-level short Pb exposure when based on a single B-Pb measurement. The toxicokinetic of Pb within various body compartments (i.e., cycling of Pb between bone, blood, and soft tissues) is complex. The determination of Pb in urine (U-Pb) is considered to reflect Pb that has diffused from plasma and is excreted through the kidneys. Nail-Pb is considered to reflect long-term exposure because this compartment remains isolated from other metabolic activities in the body. However, high variability in Pb levels measured in the same fingernails and toenails of various subjects, even after rigorous washing procedures have been reported; such lack of reproducibility suggests that nail specimens offer only limited scope in assessing exposure to Pb but teeth accumulate Pb over the long term and may provide a better source [67].

5. Conclusion

The world demand for electronic equipment has increased exponentially in the last decade resulting in a significant problem of how the resulting waste is handled. During the same period, the supply of key metals has been compromised by the limitation of the world supply. As a result, the requirement for recycling has become apparent. The policy of sending waste materials to poorer countries with few facilities has led to the realization that there is considerable health risks in the methods currently used to recycle waste materials. The need for monitoring increased with the realization that chronic exposure is as serious as acute exposure. There is a requirement for simple-to-use monitoring tests, which could be used on-site and checked if required in the nearest laboratory. This would require the use biomarkers of exposure and effect. Exposure should include air monitoring. Most biomarkers of effect are excreted in the urine, which provides a readily available source for monitoring. A prior requirement would be to establish normal ranges and acceptable limits for the biomarkers in the nonexposed population. If possible, these should be point-of-care tests, which could be utilized on-site. The current guidelines would need to be reviewed in the light of these findings. Only about 20% of the world's electronic waste is currently recycled and this needs to be increased for both economic and health reasons. More local recycling plants need to be set up and recycling procedures standardized. The supervision of the recovery of metals from dump needs to improve and formalized, particularly in sites located in the developing world. Increasing pressure on the producers of electronic equipment to demonstrate tracking the waste could help facilitate appropriate testing.

Methodology used for data searching

The data included in this review was obtained from searches of a number of resources including but not exclusively, The National Library of Medicine, PubMed; The World Health Organization, www.who.int; The European Commission, www.environment.ec.europa.eu; Web of Science, and The UN environment programme, www.UNEP.org/ietc. The search terms included e-waste, e-waste plus biomarker, and e-waste plus metal biomarker."

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Chapter 3

Non-Invasive Samples for Biomonitoring Heavy Metals in Terrestrial Ecosystems

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Abstract

As highly relevant environmental contaminants, metals and metalloids have been extensively evaluated for decades in biomonitoring programs, due to their potential toxicity at low levels and high persistence in many ecosystems. When considering chemical analysis, metal quantification has been carried out through conventional methods, based on the determination of their levels in internal organs, such as the liver and kidneys. Nevertheless, non-invasive methods constitute an alternative response regarding trace elements biomonitoring studies. Specifically, keratinized tissue from terrestrial mammals (such as hair, nails, or spines) presents a high accumulation rate, giving relevant information about heavy metal dynamics at internal levels and, most particularly, a chronic exposure. This critical review focuses on the use of non-invasive tissues, mainly hair and spines, as adequate tools on heavy metals assessment, specifically mercury (Hg) and lead (Pb), in biomonitoring studies performed in terrestrial wild mammals.

Keywords: biomonitoring, non-invasive, mammals, heavy metals, hair, spine, lead, mercury

1. Introduction

1.1 Wild terrestrial mammals as sentinel species

The presence of a broad spectrum of contaminants in the environment has led to the need to seek methods for the early detection of environmental disturbances that endanger biodiversity. One of the most relevant pollutants is inorganic elements such as heavy metals, and according to Ali & Khan [1], "Heavy metals are naturally occurring metals having atomic number greater than 20 and an elemental density greater than 5 g cm^{-3}." Their potential toxic effects at low concentrations and high persistence in the environment give them importance from a toxicological perspective. Systematic measurements of physical or chemical parameters carried out in the abiotic environment (water, air, soil, or sediment) are not enough, as they do not provide information and do not guarantee the representativeness of the data as far as the concentrations of toxicants in wildlife are concerned.

Over the past decades, the use of biomonitoring species has been established as a methodology for the determination of inorganic and organic contaminants. Biomonitoring includes bioindicator organisms, whose presence/abundance or absence provides a qualitative response on the availability of pollutants in the environment in which they develop. Besides, biomarkers are tools that consist of measuring biological responses of an organism exposed to any agent, providing in this case quantitative information [2]. In most of these programs, organisms from different taxonomic groups have been used, such as mammals, birds, and/or fish, whose physiological system is very complex, being potential bioindicators for metal pollution [3]. This is favored because these organisms have a high potential for accumulation and resistance to those, and a great sensitivity to environmental conditions, as well as constant weight and size, wide abundance and distribution, easily interpretable results, and can be extrapolated to the field of human health [1, 3, 4].

On terrestrial ecosystems, wild mammals are mainly chosen as potential sentinels of environmental pollutants loading because they are extremely linked to the environment [5]. Therefore, they are highly exposed to heavy metals through food intake, inhalation, and/or skin absorption, further contributed to by behavioral habits, such as grooming and burrowing, or physiological process, such as placental transfer during pregnancy [4]. In addition to the level of exposure on mammals, there are other intrinsic biological variables, which can influence metal uptake and retention in an individual, such as sex, age, species, tissue sampled, dietary habit, and season of sample collection [6]. Moreover, mammals are also commonly used in toxicological studies as experimental models to assess the risk of toxic exposure in humans [6, 7]. In general, the use of animals implies a number of advantages, which provides us temporal and spatial information on the presence of the pollutants. These animals are considered to be appropriate sentinel organisms since they can accumulate high levels of inorganic elements. Therefore, mammalian body burdens and responses are uniquely realistic indicators of mammalian exposure to chemicals [5].

1.2 The use of non-invasive tissues

Heavy metals are stored in different animal tissues at different rates and amounts. In most biomonitoring programs, the analysis and quantification of heavy metals in mammals are mainly performed in internal tissues, where they exert their main mechanism of action or bioaccumulate, such as liver, kidneys, brain, muscle, or bone [8–11]. Liver and kidneys are more frequently analyzed because they have a high affinity for metals, and therefore, both reach the highest concentrations in the body [8, 10]. In addition, the use of internal tissues provides information on toxicokinetics, metal-specific organic lesions, or diagnosis. These organs reveal information about exposure to the toxicant in a short period of time (poisoning cases) but also can reflect long-term metal exposure to low doses [12]. However, the sample collection of these tissues requires the sacrifice of the animals, which can be due to various causes such as traffic accidents, diseases, hunting, poisoning, or trapping the animals and killing them for the study purpose [12–15]. But it is evident that the sacrifice of the specimen carries strong ethical implication, even more so when focusing ecotoxicological studies on protected or endangered species. Faced with this situation, non-invasive methods constitute an alternative response to biomonitoring studies of inorganic elements.

A part of metal which is not subject to bioaccumulation in the internal organs is removed to a small extent through sweat, respiration, tears, or saliva [12, 16] and mainly through feces, urine, nails, feathers, hair, and spines [12, 17–19]. In the past decades, the use of these non-invasive samples has been approved as a helpful tool to monitor wildlife when compared to conventional methods because they do not induce pain or involve minimal stress for the individual, and as mentioned above, samples are taken without sacrificing the animal [12, 20, 21]. Moreover, the use of those matrix gives us some advantages; for examples, they are easy to obtain, transport, and store and allow successive measurements and assessing metal levels of the same individuals or population during a long period. For this reason, the use of non-invasive matrices is becoming increasingly important, especially when dealing with endangered, threatened, or sensitive species [20, 22].

1.3 Hair and spines

Hair samples have been shown to be promising for minimally invasive biomonitoring of global ecosystems pollution using sentinel species. This tissue provides relevant metal concentrations, resulting in the fact that it is able to incorporate and retain chemicals through the hair follicle, and constitute an elimination pathway from the body when it grows [20, 23–26]. It is composed of keratin, protein rich in cysteine, whose structure is composed of sulfur and thiol (sulfhydryl, SH-) groups, and thus constituting a suitable matrix, which allows the affinity binding of metals such as Hg, Pb, Cd, or As [27]. Moreover, it is worth mentioning that hair contains up to 30% of cysteine [27–29]. This hard tissue, due to its chemical composition, is metabolically and biologically inactive. In addition, hair is an epidermal appendage that contains three layers. First, the medulla is the most internal layer composed of columns of keratinized cells and is covered by the cortex, which is the second layer composed of pigments, and at last, this structure is protected by the cuticle; this third layer consists of species-specific cell plates [30]. Therefore, these layers have affinities for different chemicals; the two internal layers are engaged in pigments that provide the properties to link metals; meanwhile, the external layer is made up of sulfur group and, as mentioned above, has a special affinity for bonding with metal [18, 30]. In this stance, the metal's absorption ability could vary in relation to the hair morphology, differing among mammalian species [18, 27]. As a result of the fact that the hair, specifically the hair follicle, is in close contact with the bloodstream, it constitutes one of the major pathways for the excretion of metals that are incorporated into the matrix as it grows. Besides internal metal accumulation by blood, the external assimilation by the soil or air of metals that are continuously incorporated into the hair shaft during growth must be considered too [31–33]. It is noteworthy that according to the United Nations Environmental Program [34], hair is chosen as one of the most important materials for biological monitoring worldwide in the Global Environmental Monitoring System.

Spines are strong and durable structures, which play a defensive role [21, 35]. This kind of keratinized tissue is altered hair that has suffered a process of keratinization. Thus, it is expected to have a similar potential as hair in heavy metal assessment. These structures are composed of a porous core and dense shells. The solid columns evolve into a hollow for reducing weight or into a foam structure for preventing ellipticity. This kind of structure can develop in a longitudinal or transversal way [36]. Moreover, both are extremely in contact and may reflect long-term exposure to toxic metals because of their relatively slow rate of growth [37]. In this context, both inert matrices, hair and spines, are solid and durable in nature and are often used in ecotoxicological studies as alternative tools in order to minimize the employment of lethal techniques.

Hence, heavy metals are partly eliminated and sequestered by these keratinized tissues, but molting should be considered as a relevant factor on excretion pathways [38]. Some authors have observed that before molting, the hair contains higher amounts of metals than during, or just after molting [39, 40]. So molting could have a key role as an influencing factor on the metal accumulation in the hair.

2. Methodology

This systematic review was performed in different databases including Web of Science, Scopus, and PubMed, and using different combinations of the following keywords: "biomonitoring," "mammals," "trace elements," "heavy metals," "mercury," "lead," "hair," "spines." All data were selected when literature on hair and spines as measurement tools for mercury and lead exposure was available.

3. Results and discussion

In this review, 63 studies from 24 different countries have been reviewed. Mercury and lead have been quantified in 41 and 31 studies, respectively. Both metal data appear in 9 different studies. This review would be the first report that presents data on these heavy metals in hair and spines from 69 different terrestrial mammal species. **Figure 1** shows the methodology and distribution of the studies reviewed.

Table 1 compiles data regarding Hg levels in spines and hair of different mammal species. The average Hg concentration in the hair of terrestrial mammals is 40.91 ± 32.27 ppm from 0.022 to 2010 ppm. However, unique data of Hg on spines have been carried.

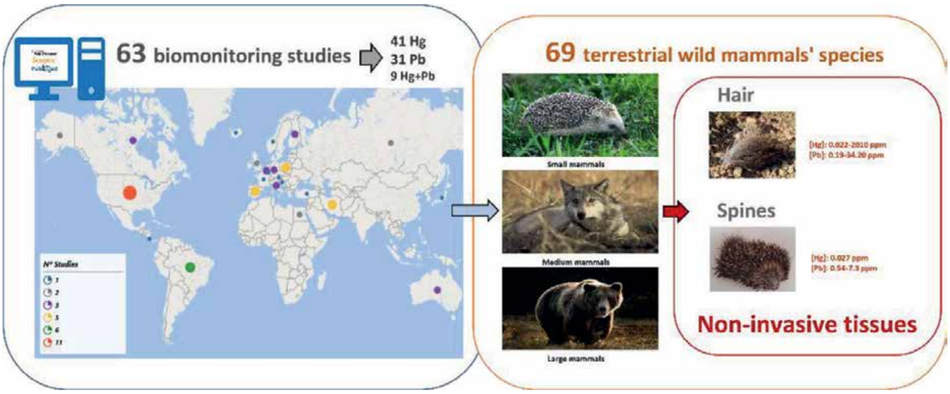

Figure 1.
Summary of the methodology and distribution of the studies reviewed: Use of non-invasive tissues for biomonitoring of Hg and Pb in terrestrial ecosystems.

	Species	Hg levels		Ref.
Small mammals				
Hair	*Apodemus sylvaticus* (n = 6)	0.78* (0.50–1.36)	ppm	[32]
	Clethrionomys glareolus (n = 7)	0.91* (0.40–2.15)		
	Miniopterus schreibersii (n = 24)	1.13* (0.41–2.27)	ppm	[41]
	Myotis lucifugus (n = 26)	132 (1.39–274)	ppm	[42]
	P. alecto (n = 281)	20.1* (4.84–416)	ppb	[43]
	Pteropus conspicillatus (n = 45)	40.3 (3.91–262)		
	Pteropus policephalus (n = 315)	27.1 (5.67–552)		
Spines	*Paraechinus hypomelas* (n = 50)	27 (2–94)	ppb	[35]
Medium mammals				
Hair	*Acinonyx jubatus* (n = 4)	1256 (229–3670)	ppb	[44]
	Caracal caracal (n = 7)	1139 (444–3416)		
	Canis aureus (n = 21)	187.3 (33.2–417.5)	ppb	[45]
	Canis lupus (n = 34)	0.044	ppm	[27]
	Chrysocyon brachyurus	0.62–9.8	ppm	[46]
	Didelphis virginiana (n = 24)	228–288	ppb	[47]
	Eptesicus fuscus (n = 14)	28.05 (4.8–65.4)	ppm	[48]
	Felis pardalis (n = 32)	0.70	ppm	[49]
	Felis silvestris (n = 19)	0.897 (0.035–3.669)	ppm	[44, 50]
	Felis chaus (n = 7)	531 (62–1751)	ppb	[44]
	Felis manul (n = 2)	339 (213–465)		
	Felis margarita (n = 1)	429		
	Leopardus pardalis (n = 8)	24.5 (7.65–38.6)	ppm	[51]
	Leopardus wiedii (n = 1)	0.53		
	Lutra canadienses (n = 264)	4–20.7	ppm	[52–55]
	Lutra lutra (n = 30)	5.9–29.5	ppm	[38]
	Lynx lynx (n = 4)	983 (498–1702)	ppb	[44]
	Martes americana (n = 40)	1.228 (0.290–2.228)	ppm	[56]
	Meles meles (n = 10)	0.52	ppm	[27]
	Mephitis mephitis (n = 87)	4.85 (1.53–27.02)	ppm	[57]
	Mustela vison (n = 77)	2.34–30.1	ppm	[52, 54, 55]
	Myrmecophaga tridactyla (n = 141)	1.54 (0.27–4.77)	ppm	[58]
	Panthera onca (n = 23)	11.3–2010.4	ppm	[51, 59]
	Panthera pardus (n = 11)	442 (134–1112)	ppb	[44]
	Proycon lotor (n = 144)	0.3–28.94	ppm	[50, 57, 60–63]
	Pteronura brasiliensis (n = 2)	2.94–3.68	ppm	[64]
	Puma concolor (n = 45)	1.64–2.45	ppm	[51, 65]
	Vulpes lagopus (n = 75)	3.55–10.58	ppm	[66, 67]
	Vulpes vulpes (n = 78)	0.28–2.794	ppm	[27, 68]

	Species	Hg levels		Ref.
Large mammals				
	Alces alces (n = 48)	0.042* (<0.001–0.311)	ppm	[69]
Hair	*Capreolus capreolus* (n = 5)	0.036 (n.d.-0.106)	ppm	[70]
	Capricornis crispus (n = 77)	350–444*	ppb	[71]
	Cervus elaphus (n = 26)	0.022 (n.d.-0.079)	ppm	[70]
	Rangifer tarandus (n = 59)	0.05–0.34	ppm	[72–74]
	Rupicapra rupicapra (n = 19)	0.024 (n.d.-0.099)	ppm	[70]
	Sus scrofa (n = 99)	0.066–0.136	ppm	[27, 69, 75]
	Ursus arctos (n = 85)	128–193.39	ppb	[76, 77]

**Wet weight (ww).*
n.d. (non-detected).

Table 1.
Concentration of mercury in hair and spine of small, medium, and large terrestrial wild mammals. Levels are expressed as mean (dry weight). Ranges are given when data were available.

Considering a potential chronic exposure of terrestrial wild mammals, at low Hg concentrations *via* food, water, and ambient air, Hg toxicokinetic is well described [78–80]. Emphasizing on Hg excretion pathways, one of the most relevant is through the feces (85–90%) and to a lesser extent urine (5%) [79]. On the other hand, an appreciable Hg amount present in the blood stream is distributed and incorporated into the hair follicles [81–83]. Several studies have established that hair is another main route of excretion, even representing more than 80% of the total burden [78]. In the past decade, hair has been established as an elemental tool for biomonitoring studies concerning Hg in humans [84–86], associated with the fact that the composition of such keratinized matrices is suitable for Hg accumulation. Multiple studies have demonstrated the high affinity of Hg to hair, which can be reached during the growth period of the coat and bioaccumulate over time [18, 47]. The mercury-containing moiety binds to thiol groups in membrane proteins and enzymes, thereby interfering with the membrane structure and function, and with enzyme activity. This affinity is one of the main factors underlying the biochemical properties of Hg and its compounds. Some authors have observed under laboratory and field conditions that this hard tissue is able to accumulate environmentally relevant Hg residues in comparison with internal organs from mammals [45, 56, 87, 88]. It should also be considered that the biological half-life of Hg is higher in hair when compared to those. Therefore, levels of Hg in hair are a manifestation of chronic exposure [5]. Various studies have observed the hair as a good indicator of the Hg amount in the body, showing high correlation between metal concentrations in hair and internal organs, where biotransformation and bioaccumulation occur, such as liver, kidneys, or brain [52, 89–93]. Therefore, this allows us to conclude that hair represents a non-invasive approach for monitoring Hg accumulation in wild terrestrial mammals and the environment.

The only study carried out on spines that stands out, the one focused on the Brandt hedgehog (*P. hypomelas*) [35], determined that animals from agricultural areas had higher Hg concentrations in comparison with those from forest areas (31 and 23 ppb, respectively). These results proved strong evidence that spines can reflect the level of exposure to Hg in areas associated with human activities, such as the massive use of pesticides. Contrary to that indicated for spines, Hg concentrations in hair have been widely described for mammals. In small terrestrial mammals, Hg concentrations ranged from 20.1 ppb (*P. Alecto*) in unpolluted areas of eastern Australia [43] to 132 ppm (*M. lucifugus*) surrounding an industrial source with historical Hg contamination in North America [42]. Moreover, the last author reported the maximum value quantified in small mammals (274 ppm). In relation to medium-sized mammals, Hg concentration in hair ranged from 0.044 ppm (*C. lupus* in Italy) [27] to 2010.4 ppm (*P. onca* living in the gold mining area of Brazil) [59], this last value being the highest ever recorded in a wild animal. In large mammals, the range was between 0.022 ppm (*Cervus elpahus* in Austria) [70] and 0.34 ppm (*R. tarandus platyrhynchus* in Norway) [72]. However, the highest Hg concentration (0.532 ppm) was detected in a *S. scrofa* individuals from Russia [69]. These ranges would reflect that the degree of exposure depends on dietary habits [94], being lower in large mammals, whose dietary habits are mainly herbivorous, and higher in species, which occupy the medium and top of the food chain, whose species are mainly omnivores and carnivores [95]. Given the importance of the diet, some researchers have shown a strong association between dietary uptake and Hg accumulation in hair. It has been established that about 20% of Hg administered in the diet will end up in hair [96]. For example, Wang et al. [97] observed that Hg was mainly excreted and incorporated into the hair of mink after 60 days of feeding experiment, exposed to a total dose of 0.676 ppm MeHg chloride, and establishing a biomagnification factor (expressed as coefficient between hair and diet) of 69.1. In other similar experiments carried out in rats for 90 days with rice containing 51.3 ppb Hg, a major proportion of Hg was primarily bioaccumulated in kidneys and secondarily in hair, Hg being excreted through feces predominantly [98]. Moreover, in the studies by Wada et al. [48] and Yates et al. [99] carried out in different species of bats, a further insight into the tight correlation between endogenous levels in blood and transfer kinetics into the hair was observed, blood representing a dynamic balance between recent dietary exposure and tissue accumulation [100].

Aulerich et al. [14] fed minks a dose of 5 ppm of MeHg for a month and established a ratio of Hg burdens in hair, liver, kidneys, muscle, and brain for mustelids of 10:5:5:2:1. Although all minks died, this experiment reflects the short-term exposure to Hg and its acute effects on the organism, the liver and kidneys being the main target organs affected by this exposure, whereas hair had the lowest Hg level, surely due to the absence of hair growth during the experiment. These results suggest that Hg levels in hair are extremely linked to dietary exposure, this heavy metal being transferred and biomagnification through the trophic web.

Among other factors, age is considered to be a key factor, which can influence metal accumulation. As Hg has a low removal rate, its concentrations in hair are expected to increase with age as previous studies have reported [101]. Adults can be assumed to have bioaccumulated higher Hg concentration in hair when compared to juveniles because of their long-term exposure. Dahmardeh Behrooz et al. [35] observed that old European hedgehogs had high levels of Hg in spines (94 ppb) in comparison with juveniles (20 ppb) or pups (2 ppb); thereby a positive correlation between Hg levels in spines and age was observed. As widely described for other mammals, this observation has also been previously shown in the fur of bats [43, 99], mustelids [38, 56, 101], and other terrestrial wild mammals [58].

Similarly, sex should be another relevant factor to be considered when contemplating metal accumulation. However, a common pattern of Hg accumulation on keratinized tissues is not established. It has been observed how females can accumulate high Hg levels in hair in comparison with male terrestrial mammals

[43, 47, 56, 89, 99, 102], while other authors have reported higher Hg concentration in hair and spines from male than females [35, 38]. These differences could be attributed to different factors, such as the foraging rate of female during the breeding season or their maternal transfer to the fetus during the gestation and lactation periods [29] as well as differences among dietary uptakes due to sexual size dimorphism (male preys on larger animals present in high levels of food chain) or some physiological differences (females are able to demethylate MeHg more efficiently than males and excretion rate) [103]. Indeed, the Hg bioavailability and toxicokinetics in terms of sex are not yet well understood due to the differences in hormonal and reproductive states, gene expression, and the metabolic rate between males and females [103]. In fact, the influence of sex on metal accumulation in hair has been investigated to a lesser extent, making it necessary to clarify the toxicokinetics of each inorganic element in males and females of different species and to consider this factor in future biomonitoring studies [104].

When focusing on hair, some researchers have concluded that the normal background level of Hg in the hair of terrestrial wild mammals ranges between 1 and 5 ppm [87]. It is known that Hg levels above 6 ppm in hair would be associated with subclinical neurological effects [105]. Thereby, a threshold of 10 ppm Hg in hair can be related to neurobehavioral disorders [106]. However, some interspecies differences are evident, and for example, neuronal effects have been described at 30 ppm in mustelids such as river otter or mink [78], this concentration being considered as the lowest observed adverse effect level (LOAEL) for terrestrial mammalian wildlife.

Lead has extensively been quantified in hair from a wide range of wild terrestrial mammals, as shown in **Table 2**, and the average including all terrestrial species is 4.06 ± 0.82 ppm between 0.19 and 34.20 ppm.

This inorganic element has high environmental relevance, being bioavailable and assimilated by terrestrial wildlife through food or water intake. Due to its potential health hazards, Pb has comprehensively been studied [80, 119–122]. When considering the elimination route, it is mainly excreted through urine (67%) and feces (33%); however, small amounts are also excreted through the hair, spines, or nails [18, 21, 122]. It has been described that Pb may be bound to cysteine and has a certain affinity for sulfhydryl contained in keratin; hence, when it is distributed by blood, lead is incorporated into the hair follicle while growing, due to its continuous contact with the bloodstream [27]. The affinity between Pb and blood should be highlighted since this matrix is the main source of metals incorporated into the hair. A large part of Pb is bound to erythrocytes (95%) because of enzymes which make up these cells [25, 122]. The strong positive association between both keratinized tissues (hair and spine) and blood has been evidenced in some wild mammals at different trophic levels [37]. Likewise, it has also been observed that a significant linear relationship exists among both keratinized tissues and internal organs such as liver, kidney, brain, lungs, and gastrointestinal tract for Pb concentrations in wild terrestrial mammals [21–23, 73, 110]. When considering biomonitoring programs in human beings, hair has also been widely used in Pb quantification [122]. Despite the fact that hair has been considered as a suitable tool for measuring long-term Pb exposure in mammals in biomonitoring studies, bones are mainly chosen as the best tissue since they provide the best estimate of body burden. Nevertheless, bone collection requires the animal to be dead; therefore, it is discarded as a non-invasive technique.

In small mammals, mean Pb concentrations ranged from 0.34 ppm (*M. myotis*) to 34.2 ppm (*P. pipistrellus*) in Germany. The higher Pb level (973 ppm) in

H. auropunctatus was quantified in a polluted area from Hawaii [107]. In medium-sized terrestrial mammals, Pb levels ranged from 0.19 ppm (*C. lupus signatus* from Italy) [27] to 2.95 ppm (*Vombatus ursinus* in a mining area from Australia) [114]. Mora et al. [49] quantified 150 ppm of Pb in hair of *Felis pardalis* from Texas (US), these authors suggesting that the animal was exposed through consumption of preys captured near busy roadsides. In large mammals, the variation between species was even larger, ranging from 0.401 ppm in *U. arctos* from Poland [76] to 13 ppm in *Camelus sp.* in polluted areas from Egypt [28]. The highest Pb level was determined

	Species	**Pb levels**		**Ref.**
Small mammals				
Hair	*Antechinus stuartii* (n = 53)	1.78–5.54	Ppm	[24]
	Apodemus sylvativus (n = 419)	0.36–14.7	Ppm	[22, 23]
	Erinaceus europaeus (n = 134)	0.4–7.6	Ppm	[13, 21, 37]
	Herpestes auropunctatus (n = 44)	1.51 (0.0585–973)	Ppm	[107]
	Lepus europaeus (n = 11)	4.5 (1.7–9.7)	Ppm	[108]
	Marmota marmota (n = 16)	1.1	Ppm	[27]
	Myotis daubentonii (n = 9)	4.26 (0.0159–20.6)	Ppm	[109]
	Myotis bechsteinii (n = 14)	5.14 (1.80–8.62)		
	Myotis myotis (n = 136)	0.39–0.763	Ppm	[106, 109]
	Oryctolagus cuniculus (n = 28)	1.80 (0.494–8.70)	Ppm	[110]
	Pipistrellus pipistrellus (n = 8)	34.2 (0.0159–519)	Ppm	[109]
	Pteropus alecto (n = 281)	1255* (172–9958)	Ppb	[43]
	P. policephalus (n = 315)	1641 (179–28,892)		
	P. conspicillatus (n = 45)	2264 (228–32,345)		
	Rattus norvegicus (n = 29)	2.16–20.6	Ppm	[24, 111]
	Rattus rattus (n = 40)	1.49–10.6	Ppm	[24]
	Rhombomys opimus (n = 25)	3.7 (3.55–4)	Ppm	[111]
Spines	*E. europaeus* (n = 43)	3.8 (0.5–13.7)	Ppm	[21]
	E. europaeus (n = 63)	0.54 (<LD-7.02)	Ppm	[13]
	E. europaeus (n = 26)	0.8–7.3 (0.2–17.2)	Ppm	[37]
Medium mammals				
Hair	*Cani lupus* (n = 225)	0.19–1.228	Ppm	[20, 27, 112]
	Cerdocyon thous (n = 14)	2.45	Ppm	[113]
	C. brachyurus (n = 10)	2.34		
	D. virginiana (n = 24)	319–524	Ppb	[47]
	F. pardalis (n = 32)	0.70	Ppm	[49]
	Lycalopex vetulus (n = 2)	1.50	Ppm	[113]
	M. meles (n = 10)	0.83	Ppm	[27]
	Vombatus ursinus (n = 5)	0.17–2.95	Ppm	[114]
	V. vulpes (n = 33)	0.33–0.642	Ppm	[27, 115]

	Species	Pb levels		Ref.
Large mammals				
Hair	*Camelus sp* (n = 20)	0.90–13	Ppm	[28]
	Capra sp. (n = 20)	0.35–12		
	C. capreolus (n = 113)	0.556–2.8	Ppm	[25, 70, 108, 116]
	C. crispus (n = 77)	0.43–0.72*	Ppm	[71]
	C. elaphus (n = 57)	0.479–0.61	Ppm	[27, 70, 117]
	Ovis arles (n = 20)	0.01–8.9	Ppm	[28]
	R. tarandus (n = 72)	3.2–5.40	Ppm	[72, 73]
	R. rupicapra (n = 19)	0.863 (0.369–9.588)	Ppm	[70]
	S. scrofa (n = 89)	0.68–8.71	Ppm	[27, 108, 117, 118]
	U. arctos (n = 50)	401 (30.3–1553)	Ppb	[76]

**Wet weight (ww).*
LD (limit of detection).

Table 2.
Concentration of lead in hair and spine of small, medium, and large terrestrial wild mammals. Levels are expressed as mean (dry weight). Ranges are given when data were available.

in *S. scrofa* from Turkey (81.80 ppm) [118]. In spines, the average Pb concentration was 3.88 ± 1.95 ppm, and the range of Pb levels in *E. europaeus* was narrower in comparison with hair, ranging from 0.54 [13] to 7.3 ppm [37]. Moreover, in the last study, it was quantified that the highest Pb concentration (17.2 ppm) existed in the hedgehog population near the nonferrous metallurgic factory.

In addition to the quantity and bioavailability of Pb exposure, as shown in these ranges, the accumulation in hair and spines relied on ecological factors such as diet and endogenous factors such as species, size, behavior, or season [123]. Small mammals represent the medium stage of the trophic webs since they have multiple diet habits (insectivorous, omnivorous, and herbivorous). Further, their high metabolic rates increase their food intake, being highly exposed to metal [5]. In addition, their high exposure is due in part to the fact that they are closely linked to soil particles during their life cycle (i.e., grooming habits, storing food in their burrow, covering, or burrowing habits) and through the ingestion of soil and invertebrates, which tend to retain great amounts of metals, such as earthworms, slugs, earwigs, or beetles [31, 37, 124]. Therefore, small mammals are expected to have the highest Pb concentrations in hair and spine from exogenous source (i.e., particles covering the outer surface) or from endogenous source (i.e., Pb assimilated mainly by the diet and incorporated through the blood) [24, 31, 40].

Attending to a range of Pb concentrations in large mammals, they are exposed to a greater extent. This may be due in part to the fact that most of them are herbivores, ingesting mainly polluted plants by atmospheric particle deposition or taking up from the soil. It is noteworthy that some plants are able to accumulate even more than 1000 ppm, thus constituting a potential risk to mammals that feed on them, especially those living near areas where fertilizers and pesticides are used [121, 125]. Some researchers have shown under laboratory condition a positive linear increase of the Pb concentration in hair from animals fed with supplemental Pb. For example, these results were observed by Choi et al. [126] in pigs fed with 200 ppm Pb for 56 days. Even in field conditions, the effect of dietary habits on Pb accumulation in hair has also been observed [127]. Besides inhalation and grooming, animals can also ingest Pb from contaminated drinking water or even small amounts of soil, which may lead to unintentional ingestion of ammunition. Moreover, it is worth highlighting that most of the large mammal species are hunted, and when the animals are not killed, the bullets are accumulated in the body for a long time [128]. However, according to Gall et al. [125], Pb concentration in hair relies on its bioavailability in the environment, individual factors such as age, and its mobility in the organism.

Age is an intrinsic biological variable, which influences Pb retention in mammal hair, older animals being exposed to longer periods of time, having a higher concentration in comparison with young animals. Hence, a clear Pb accumulation in hair has been shown in terrestrial wild mammals such as *C. lupus signatus* [20]. However, most studies have not observed an age-related influence on Pb hair concentrations. Hernández-Moreno et al. [20] and Beernaert et al. [23] attributed it to the fact that in mammals most of the Pb (90%) is well stored in bone tissues with an age-related pattern. When considering the sex factor, studies have observed differences in Pb concentrations between females and males. For examples, in the hair of *D. virginiana*, higher concentrations in females when compared to males were observed [47]. This result was confirmed in *A. sylvaticus* [23], *C. lupus signatus* [112], and *C. capreolus* [25], too. However, although females tend to retain higher Pb concentrations in hair than males, little is known about the accumulation pattern according to sex. Differences between the accumulation or excretion process, physiology, bodily growth, and the presence of specific metabolizing enzymes or sexual hormones must be assumed in biomonitoring studies [129].

Limit thresholds for Pb in internal organs such as liver or kidney have been well established; for example, a critical renal value, which cause toxicosis in mammal, is defined in 15 ppm; meanwhile, in liver it is 5 ppm [130]. However, a wide range of Pb toxic levels in different mammal species has also been established for liver, kidney, brain, urine, and blood [121]. In the last matrix, a concentration above 5 μg dL^{-1} causes neurobehavioral deficits and neurotoxicity and death when reaching 80 μg dL^{-1}. Thus, despite the toxic limit thresholds for Pb in wild mammal hair have not been well described yet, some authors have established in other keratinized tissues, such as feather, clinical sign of poisoning at a Pb concentration above 4 ppm [121]. It is noteworthy that in human, Pb background levels in hair have been established in 20–25 ppm; nevertheless, those levels have been established in 12–15 ppm by other authors [131].

4. Conclusions

In this critical review, mercury and lead concentrations in hair and spine from wild terrestrial mammals have been summarized, in an attempt to validate the use of these two non-invasive matrices for biomonitoring purpose. In this sense, diet habit plays a key role when considering Hg accumulation, being higher in animals occupying the medium and top of the food chain (i.e., carnivores and omnivores). With respect to Pb, its concentrations are usually higher in mammals linked to the soil fraction (i.e., insectivores and herbivores). Furthermore, the endogenous factor such as age must be considered when quantifying heavy metals because of its linear relationship between time of exposure and bioaccumulation. Besides, the influence of sex should be also studied as different metal bioaccumulation patterns in hair and spine according to this factor have been observed. With these considerations, hair and spines can be suitable non-invasive tissues reflecting the internal metal levels, thus constituting a good alternative in order to avoid the sacrifice of wild mammals and at the same time providing an effective early warning system of metal pollution.

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Chapter 4

The Toxicity of Plastics

Edda E. Guareschi

Abstract

According to more than 200 scholarly publications, plastic pollution has been emerging as a major environmental concern in recent decades, and has been posing a relevant threat to ecosystems and global health. While the focus has primarily been on the physical, chemical and biological impacts of primary and secondary plastics, also for their ability to cross biological barriers within the human body, an additional hazard is represented by their association to heavy metals, used as additives. Metals are, in fact, added to plastics for their stabilizing actions. The examples of metal toxicity here reported are Antimony (Sb), Arsenic (As), Barium (Ba), Beryllium (Be), Cadmium (Cd), Chromium (Cr), Cobalt (Co), Copper (Cu), Iron (Fe), Lead (Pb), Manganese (Mn), Nickel (Ni), Selenium (Se), Vanadium (V) and Zinc (Zn). This chapter explores the toxicity of metals associated with plastic pollution in the environment, illustrating their potential consequences for the global ecological system, with prevalent focus on human health. The interdisciplinary approach, which includes environmental science, chemistry and toxicology, aims to enhance the understanding of this complex issue and highlight the urgent need for efficient mitigation strategies.

Keywords: environment, heavy metals, human health, nanoplastics, plastic pollution

1. Introduction

Plastics are synthetic organic polymers that are produced by the polymerization of monomers extracted from oil or gas [e.g., Polyvinylchloride (PVC)]. Additives are added to plastics to achieve desirable commercial properties, for example mechanical resistance. Examples of additives are antioxidants, flame retardants and ultraviolet (UV) stabilizers [1], which include heavy metals, that is, chemical elements characterized by atomic number > 20, density > 5 g cm^{-3} and toxicity at low concentrations [2–6]. Plastics are classified as primary, when they are manufactured products, or secondary, when they result from the breakdown and degradation of the manufactured products. Beside the shapes of whole manufactured objects, the shapes of plastics include fibers, beads (also known as "nurdles"), pellets, foam, agglomerates, films and irregular fragments. The size of plastics varies from bigger than 50 cm (megaplastics) to nanoplastics, that is, smaller than 0.1 μm, passing through macroplastics (between 5 and 50 cm), mesoplastics (between 0.5 and 5 cm) and microplastics (smaller than 5 mm). The mass production of plastics began in the 1940s, and until 2017 an estimated 9 billion tons of plastic had been produced [7], with 710 million metric tons of plastic waste expected to enter the natural environment by 2040 [8].

As of 2015, only 9% of the plastic waste was recycled, 12% was incinerated and 79% went to landfills or were spread out in the environment [7]. The aim of this chapter was to characterize the pollution caused by plastics and their toxicity on the human organism, with a special focus on metal additives.

2. Environmental impact of plastic pollution

In the environment, plastics are degraded by physical, chemical and biological agents, such as abrasion, thermal action, oxidization of the polymer matrix by UV radiation (photodegradation), hydrolysis and biodegradation, that is, the degradation of starch into the products made of the so-called biodegradable plastics. Plastic debris is then transported and dispersed in aquatic environments [9], sediment [10], soil [11] and air [12]. Notably, the aging of plastics increases their ability to sorb chemicals and leads to free radical formation by the dissociation of the C-H bonds [13]. Once fragmented, plastics and their associated additives can be incorporated by living organisms (biota), including plants [14], and exert their toxic effects through cumulative exposure [15]. The uptake by biota occurs through cracks at the emerging sites of new lateral roots in plants, from where plastics move up the xylem and reach the edible part, or by inhalation, ingestion and skin contact [16, 17]. In humans, who are estimated to ingest 0.10–5 g of plastics every week and inhale 26–130 airborne plastics every day, plastics can either be retained by tissues and organs, or cross epithelia (e.g., respiratory) [18] and the underlying endothelia of capillary vessels [19], reaching the pulmonary and/or the systemic blood circulation [20]. The consequence is bioaccumulation of plastics, with higher values in occupational exposures. Finally, a link between Coronavirus disease 2019 (COVID-19) and plastic particles is being investigated, both in terms of pollution increase (e.g., disposable face masks) [21] and of the potential role of airborne particles as viral carriers [22].

3. The toxicity of plastics

In nonhuman organisms, e.g., mice, polystyrene particles can modify the gastrointestinal microbiome and cause hepatic lipid disorder [23], or can be retained in the hippocampal brain region of embryos, increasing the risk of neurodevelopmental defects [24]. The number of oocytes and the sperm velocity in oysters decrease with the exposition to polystyrene particles, while other marine organisms, such as crabs, clams and worms, slow down their feeding activity [25]. In fish (*Daphnia magna*), nanoplastics can accumulate in brain tissues, causing behavioral disorders [26]. Hitherto, the physiology of more than 200 nonhuman species has shown some form of disruption when exposed to plastic particles [27]. In humans, plastic particles smaller than 20 μm in size can penetrate biological membranes, such as the blood-brain barrier, the placenta and the gut epithelium [28], and accumulate in tissues, while nanoplastics can penetrate within cells through multiple mechanisms, e.g., phagocytosis [29]. The plastics uptake, estimated as 0.1–5.0 g/week by ingestion and 26–130 particles/day by inhalation [17, 30, 31], is influenced by distinct factors, including but not limited to surface charge, hydrophobicity and the presence of a protein corona [1]. Other influencing factors are comorbidities and socioeconomic, through the increase in the permeability of the gastrointestinal epithelia in inflammatory bowel diseases (e.g., Chron, Ulcerative Colitis), diet, excessive alcohol intake, occupational exposure (e.g., synthetic textile mill workers) and the use of low-quality cosmetics with added microbeads [32].

The human health risks associated with plastic particles and their metal additives have not been completely characterized; however, multiple and diversified correlations are under continuous investigation. Examples are oxidative stress and cytotoxicity, chronic inflammation (e.g., foreign body reaction, bronchitis and interstitial pneumonitis) [17], metabolic alterations favoring obesity [16], disruption of the immune system with diabetes mellitus mediated by insulin resistance [33], beside the scarce response to infections (COVID-19 in highly polluted areas) [34], neurotoxicity due to nanoplastics crossing the blood-brain barrier and affecting neurotransmission [35], gastrointestinal dysbiosis linked to the disruption of epithelial permeability [36, 37], occlusion of capillaries, whose diameter is typically 5–8 μm [38], toxicity of the endocrine system by estrogenic activity with early puberty, breast and prostate cancer [39], decreased reproductive function supported by the crossing of the placental barrier by nanoplastics smaller than 240 nm, which can promote preeclampsia, fetal anomalies and birth defects [40], carcinogenesis [41] through chronic inflammation and DNA damage, with the altering of gene expression, induction of angiogenesis and mitogenesis favoring the formation and progression of malignant cells, transport of chemicals [e.g., bisphenol A, heavy metals] [42, 43] and microorganisms (e.g., *Vibrio* spp.) [44].

Many heavy metals are used as plastic additives [4] and pose the threat of a vast array of toxic effects on biota [45, 46]. Specifically, Antimony (Sb) oxide is used as a fire-retardant, while trisulfide is a component of pigments. Since the exposure levels of the general human population are low, toxic respiratory and cardiovascular effects originate by occupational exposure or treatment of the parasitic infections by *Schistosoma* spp. and *Leishmania* spp. [47]. The toxicity of Arsenic (As) is linked to the impairment of cellular respiration, with severe gastroenteritis as the most common acute symptom, and anemia and neuropathy in the chronic course [48]. Barium, used in a variety of industries (e.g., mining) and as a rodenticide, leads to severe hypokalemia through a complex transcellular mechanism and can progress to respiratory paralysis and cardiac arrhythmia [49]. Beryllium (Be) can cause acute pneumonitis by inhalation, although a chronic pulmonary granulomatous disease (berylliosis) is much more common, and is caused by a hypersensitivity reaction in occupational exposures [50]. Pneumonitis is also caused by Cadmium (Cd) exposure, with renal damage and cancer [51], a known toxic effect of Chromium (Cr), as well, through several molecular actions, including DNA double-strand breaks and heavy DNA adducts difficult to repair [52]. Cobalt (Co), on the other hand, holds a biologically necessary role as a cofactor of cyanocobalamin (vitamin B12), and overexposure can follow excessive nutritional supplementation. Other routes of chronic toxicity include occupational exposure or the presence of orthopedic implants (e.g., hip prostheses). The main toxic effect of Cobalt is represented by pulmonary interstitial fibrosis and cardiomyopathy [53].

Another essential element in the human physiological homeostasis is Copper (Cu), which acts as a catalytic cofactor in the redox chemistry of many proteins. The ingestion of more than 1 g of Copper, commonly used in farming as a pesticide, is toxic, with gastrointestinal, neurological and hematological adverse effects induced by oxidative stress, DNA damage and reduced cell proliferation [54]. Iron (Fe), Manganese (Mn), Nickel (Ni), Selenium (Se) and Zinc (Zn) are also essential micronutrients for humans, although overloads can result in acute or chronic toxicity. The Iron balance, which maintains the total content of the human body between 3.5 g and 5 g, relies on elaborate regulatory metabolic processes aimed to minimize the systemic effects of cell death, due to the generation of free radicals. The most common diseases linked to acute or chronic iron poisoning are gastrointestinal, cardiovascular and neurodegenerative [55]. The central nervous system is the main target of Manganese (Mn) toxicity. In fact, Manganese crosses the blood-brain barrier, the cerebrospinal fluid barrier and the olfactory nerve microstructures, accumulates in specific brain regions and causes a progressive disorder of the extrapyramidal system, known as manganism [56]. Even though the functional role of Nickel in higher organisms, such as humans, is currently being researched, it has been recognized as an essential nutrient for some plants and nonhuman species. The most known adverse effect of exposure to Nickel is contact dermatitis, a type of allergy, although prolonged exposure can result in pulmonary fibrosis and kidney diseases through mitochondrial damage [57]. The acute intoxication by Selenium (Se), a component of blueing agents, is very rare and presents with nausea and abdominal symptoms, such as vomiting, diarrhea and pain, which can progress to fatal cardiac arrythmias [58] through dehydration and related electrolyte imbalances. Chronic intoxication is much more common, usually due to environmental exposure (e.g., drinking water), and induces neurotoxicity through multiple mechanisms of molecular concentration, uptake and activity [59]. Gastrointestinal and neurological symptoms also occur with an extremely high intake of Zinc (Zn), otherwise considered to be relatively nontoxic [60]. Finally, Lead (Pb) and Vanadium (V), added to plastics for their stabilizing, hardening and pigment properties, hold no evident biological role, and exert their toxic actions through neuropsychiatric symptoms, anemia [61], hepatocyte degeneration and renal failure by glomerulonephritis [62].

4. Current analytical techniques for the detection of plastic particles and additives

The identification of plastic particles carrying metal additives in different substrates, such as water, soil and air, follows sampling with filters, mesh and sieves, which can be selective, bulk or volume-reduced depending on the research purposes, then preprocessing and extraction. After sampling, pretreatment methods commonly used include filtration, screening and density separation. Digestion by acid, alkaline or enzyme-based substances is primarily used for the pretreatment of biological samples, such as human blood [20], placenta [40] and colon [36]. Visual methods by microscopy [scanning electron (SEM), transmission electron (TEM), with the possibility of a specific configuration for nanosizes, fluorescence microscopy with stimulated emission depletion (STED)], spectrometry methods [Raman, Fourier transform infrared spectroscopy-attenuated total reflection (FTIR ATR), X-ray photoelectron spectroscopy (XPS), atomic force microscopy-infrared spectroscopy (AFM-IR, nanoIR energy-dispersive X-ray spectroscopy)] and thermal analysis by pyrolysis gas chromatography/mass spectrometry (Pyr-GC/MS) complete the identification and the quantification, including the chemical/elemental analysis [63–67]. The characterization of nanoplastics was unavailable until very recently [68], but has been actively researched with encouraging results, in spite of relevant challenges and limitations, such as low or no crystallinity and the ubiquitous distribution of the incorporated elements (C, H, N, O) [69, 70].

Since 2020, plastic particles have been identified in several human biological matrices, tissues and organs [71]. In fact, they were detected in cell cultures of human gastric adenocarcinoma [72], in colectomy specimens (331 particles per individual, or 28.1 +/− 15.4 particles per gram of tissue) [36], placenta, both on the maternal and fetal sides (with sizes smaller than 10 μm) [20], stool (a median of 20 microplastics, 50 to 500 μm in size per 10 g or 10.19 micrograms/gram (mcg/g) in another study) [73–75], lung tissue (with size smaller than 16.8 μm) [18], whole blood (with mean of the sum concentrations 1.6 μg total plastic particles/ml blood sample and size limited to 700 nm) and urine (4–15 μm size) [76]. A direct evidence of human health risk linked to the incorporation of plastic particles has not been demonstrated [77]; however, it is highly likely that chronic exposure to both the physical particles and the associated additives, including metals, will eventually cause widespread diseases, even on account of the expected global increase in plastic production related to the increase in global population.

5. Plastic pollution mitigating strategies

Strategies are urgently needed to mitigate the impact of plastics on the environment and, as a consequence, on the global health. The prevention and the reduction of plastic pollution can be achieved by supporting research toward sustainable plastic removal methods, by implementing policies and regulatory measures and by promoting recycling and waste management practices, although not free from potential contamination hazard [78]. Plastic waste might be removed physically or by physicochemical and biological methods [3], converted into hydrogen [79], recycled [80] or biodegraded by microorganisms like bacteria, algae and fungi [81–83]. The toxicity of plastics, as particles and as carriers of toxic chemicals and microorganisms, will soon embody an urgent concern, and as such should be addressed [84]. Future research on the effect of plastics particles and their additives on the human health should consider retrospective or prospective observational population studies based on samples of biological matrices, such as bronchoalveolar fluid lavages and tissues obtained from biopsies and autopsies. Methods and methodologies need standardization, and a unified quantitative analytical technique needs to be established. Furthermore, the collaboration of various institutional sectors, such as academia, industry, regulators, environmental associations and policy, is critical. Until the complex issue of plastics pollution will be efficiently dealt with, thresholds of acceptable exposure for humans need to be determined and publicized, for example, as concentrations of milligrams per gram (mg/g) of body weight.

6. Key points

- The global plastic pollution has been continuously increasing in the recent decades, and it has become a serious health concern for the whole Earth ecosystem.

- Plastic particles exert their toxicity physically and by carrying, absorbing and releasing toxic chemicals and microorganisms.

- Heavy metals, here exemplified by arsenic, cadmium, lead, and several more, are commonly used as additives to plastics.

- The chronic exposure to plastic particles, and their associated additives including metals, holds the potential to cause widespread diseases.

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Conflict of interest

The author declares no conflict of interest.

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Chapter 5

Redox Stress Burden of Trace Metals on Environmentally Dependent Ecosystem

Kenneth Okolo

Abstract

Contamination of the environment by trace metals (TMs) has become a global health challenge. Some of these metals are found in some food substances in minute quantities as a normal part of nutrition. Excessive exposure of living organisms to these metals poses' a great risk to the health of the living organisms. Once in the environment, these metals are not biodegradable and last for a long time. Their contamination of the environment leads to contamination of the ecosystem, which intricately depends on the environment. Normal physiological processes of the living organisms in these ecosystems are distorted following the dysregulation of their redox system. An imbalance in the ecosystem's redox state led to damage to living organisms. There is an increase in mortality and morbidity, diversification is compromised, the genetic makeup of organisms is altered and over time the whole ecosystem becomes compromised. Several bioremediation techniques have been of valuable assistance in reverting this ugly trend. How well these remediation works could revert the damage and restore the ecosystems will be a measure of their survival, including all the dependent organisms and man.

Keywords: trace metals, redox balance, ecosystem, environment, ROS, RNS, remediation

1. Introduction

Trace metals (TMs), and their contamination of the environment with associated health risks is a current global environmental burden that requires urgent attention. This is a sequel to rapid urbanization, industrialization, and globalization [1]. The word TM is difficult to define and the list of metals included in this term is somehow controversial. The deleterious effects associated with TMs had been known to man since the twelfth century AD when Selenium (Se) toxicoses were recorded in livestock [2]. Before then, environmental toxicants are known, but not properly defined. For instance, the toxicities of realgar (As4S4) and orpiment (As2S3) are well known in ancient times (64–50 BC), prompting the miners to use slaves for the exploration of these metals since they know that it is associated with early death [3]. Ever since then, several environmental TM contaminations may have taken place, but not until the eighteenth century when the toxic effects of arsenic (As), lead (Pb), copper (Cu), zinc (Zn), iron (Fe) and manganese (Mn) in drinking water were established [4]. The term TM in ordinary usage refers to metals that living things (both plants and animals) require in minute (trace) amounts to maintain normal homeostasis. Chemically, TM refers to metals that are less than 100 micrograms per gram (<100 μg/g). They include approximately 47 metals, but not all are common. The most common ones that are associated with either nutrition in living things or are well known for toxicity are iron (Fe), copper (Cu), zinc (Zn), rubidium (Rb), selenium (Se), strontium (Sr), molybdenum (Mo), manganese (Mn), lead (Pb), arsenic (As), chromium (Cr), cobalt (Co), vanadium (V), and cadmium (Cd) [5]. Some sources also include nickel (Ni) and beryllium (Be). Generally, metals can be essential or non-essential. The non-essential ones like Pb, Cd, As, etc. exhibit toxicity without playing any physiological roles while the essential ones play some roles in the normal functioning of living things [6, 7]. TMs are non-biodegradable and as such last forever in the environment, exerting deleterious effects. Elements such as As, Cd, Cr, Hg, and Pb are believed to have no known physiological role either in mammals or plants. The beneficial ones only serve as nutrients in minute quantities. Excess doses beyond the requirements of living things lead to toxicity [8].

The environment in which the TMs contaminates could be divided into three parts: 1. The earth is known as the geosphere. 2. The water body is known as the hydrosphere. 3. The gaseous environment is known as the atmosphere. There is a great interaction going on between the geosphere (lithosphere), hydrosphere, and atmosphere leading to the exchange of materials and energy, TMs inclusive (**Figure 1**). TMs can occur in any form of matter, i.e., solid, liquid, or gas either as single metals or combined. Originally, every TM is found in the earth's crust as metal deposits or in

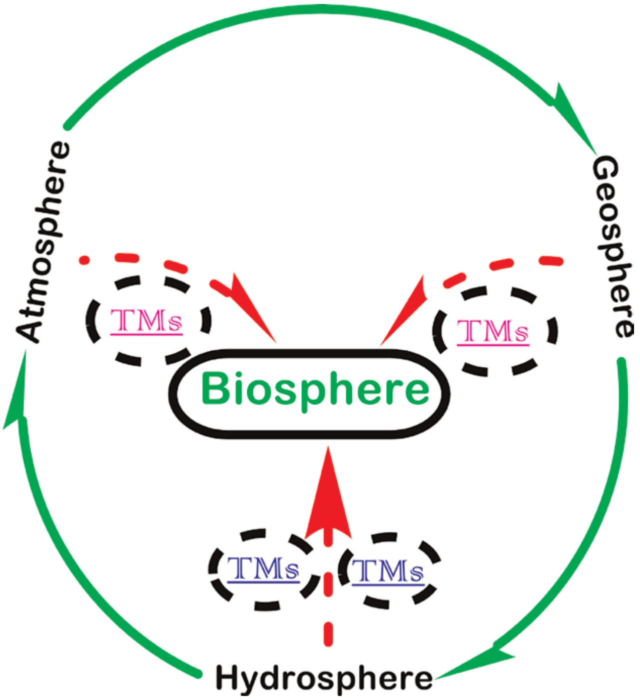

Figure 1.
Schematic description of the trace metal interaction between the geosphere, atmosphere, hydrosphere, and biosphere.

minute quantities in plants and animals. But, following anthropological activities, these TM find their way to the environment where they exist as contaminants. They get to man via food, inhalation, water, or direct contact with the body. The chemistry of TMs made it such that they are non-biodegradable, and as such once in the environment, they exist for ages. Some micro-organisms though may partially detoxify these TMs by taking them up in some of the protein moiety that has an affinity for TMs and storing them there for long periods [9].

1.1 Trace metals: a source of environmental contamination

Contamination of the geosphere, hydrosphere, and atmosphere ultimately leads to contamination of the biosphere, the dwelling place of living things. The biosphere is the primary environment where humans, animals, plants, and microorganisms dwell, live, work and interact within themselves and with the environment [10]. The last millennium saw an upsurge in the anthropological activities of the earth's crust as a way of meeting up with the increasing demand for products involving metals as raw materials or used in their manufacturing process. Other sources like poorly maintained vehicles, volcanic eruptions, and agricultural chemicals like pesticides, insecticides, and fertilizers also contribute to the TMs source [1]. While increasing care in metal exploitation following legislation has reduced the level of contamination, careless disposition and unintended contamination had increased metal flux in the environment [11]. The resultant effect is an environment defiled with TMs, leading to disruptions in natural habits and its dependent ecosystem. The forces of inter and intra-compartmental exchange of TMs make exchange between one compartment to another easy. The chemistry of these TM is such that they easily form covalent bonds with organic materials leading to the formation of secondary compounds with lipophilic properties. They also form compounds with non-organic materials resulting in increased toxicity to living things. Because of this ability to form different compounds of different chemical classes, toxicity arising from the TM in the biosphere differs from simple surface allergies to complex distortions in enzymes, and proteins and damage to DNA [12, 13]. Compounds like tributyltin oxide and methylated As are easily found in the environment and are very toxic to the ecosystem. TMs like Hg or Pb has a very high affinity for sulfhydryl groups of thiol proteins [9].

Following contamination of the biosphere, movement from one area to another depends on the interplay of the water body and air movement, the temperature of the environment, polarity, partition coefficient, pressure, and stability of the element [14]. Contamination of the soil with TMs can lead to entrance into the ecosystem by way of plant absorption and magnification and subsequent transfer to higher troughs of the ecosystem which will eventually get to the man. TMs can also alter the chemistry of other environmental pollutants that hitherto were more degradable, making them less degradable and increasing both the lifespan in the environment and the duration of toxicity [14, 15]. Contamination of the water body from industrialization and urbanization ends up in bigger water bodies like the ocean where aquatic dependent species accumulate these TMs and pass them along the ecosystem. The toxicity to aquatic organisms depends on the chemistry of the TM, the physiological role of the TM, the nature of the organism, the duration of exposure, and the health state of the organism [16]. TMs even at very low dose in the aquatic system is deleterious to aquatic animals since factors like salinity, pH, and other concomitant pollutants in the water bodies like microplastics affect their toxicity [17]. Once an edible aquatic animal is contaminated, it passes it along the food chain until it eventually gets to man, the ultimate sufferer of the poison because of bioconcentration. Some TMs like Cd, nickel, arsenic, beryllium, and chromium are known for their mutagenicity, carcinogenicity, and teratogenicity [18]. Since there is usually a high level of TMs in the sewage leading to contamination of water bodies, proper treatment of the sewage to remove TMs leads to healthier water bodies and their associated ecosystem. This can be achieved with stringent regulations using improved technology [19]. TMs can settle on the surface of water or form a solution with water or settle to the bottom of the water along with particulate matter (PM). Urbanization and industrialization have also affected greatly TMs contamination of the air especially latching to particles where the wind can convey it long distances away from the primary source of contamination [6]. TMs can get adsorbed on particles to form a metal-particulate complex that can be transported by wind to the non-contaminated area [20]. The atmosphere is made up of different layers and each can be affected differently. The troposphere and the stratosphere are the worst hit since they are the ones above the immediate earth with a lot of swirl wind exerting mixing pressure within it [21]. TMs distribution in the air of a particular area depends on the predominant activity in that area. For instance, a high vehicular traffic area is usually dominated by Pb, while the ceramic industrial area is contaminated with As [22, 23]. Furthermore, Cr is common in mining areas while Hg comes with coal burning, and Zn and Cu come with the incineration of biomass [24, 25]. The PM size forming complex with the TM is also an important factor since finer metal-particulate complexes of less than PM 2.5 μm (≤PM2.5) are known to have more health hazards [26]. There could be direct consequences of TMs in the air like faster infrastructural decay, acidification of rain, and formation of smooth [27]. The time of assessment of TM in the atmosphere is important since there had been a dynamic shift in the metal composition of air today relative to 30 years ago [28].

1.1.1 Ecosystem and its intricate dependent on the environment: redox implications along the trough

An ecosystem describes a community of living (biotic) and non-living (abiotic) things interacting with each other in a dynamic and evolving environment (**Figure 2**). Over time, the equilibrium of survival forces tends to shape the environment, as a result of conquest for nutrition and the pressure of population growth [29]. Considering the fact that different states of the environment can serve as an ecosystem of their own, contamination of the environment may be seen as contamination of different ecosystems since boundaries may or may not exist [30]. The ecosystem is valuable to man because of the economic and possible esthetic values. The functional system of an ecosystem involves activities of different organisms, their different life processes ranging from production, consumption, and excretion, and how all these affect the environment [30]. Humans benefit as a major source of food, fuel, and fiber, as natural cycling of both water and gases. The distortion of an ecosystem by man is assuming a catastrophic dimension by altering the land for his purposes and over-harvesting biological resources like forest damage and excessive fishing [31]. Estimates have it that man uses up to 40% of the ecosystem for economic ventures which has altered the ecosystems leading to the extinction of species, replacement of high biological diversities with lower ones, and ecosystem contamination [32]. These distortions will result in reduced ecosystem biomass as a result of alteration in the process of converting solar radiation to chemical energy; the first trough in the energy matrix [33].

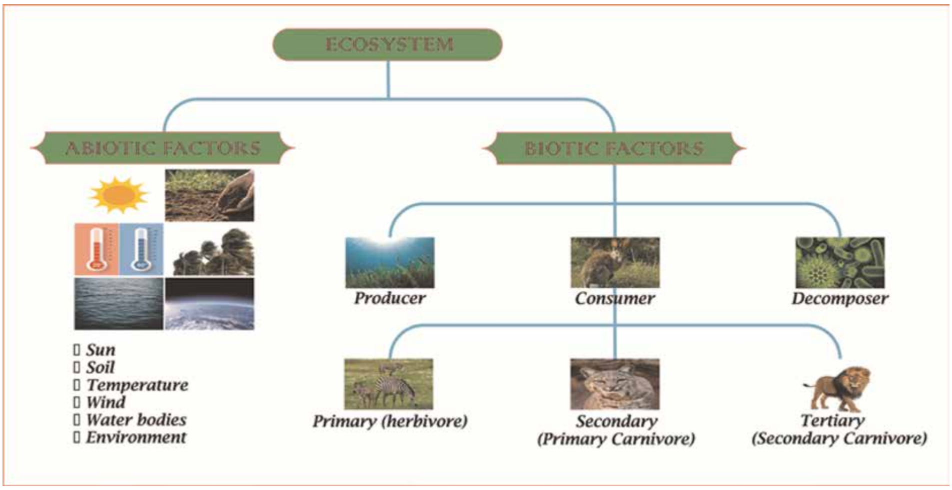

Figure 2.
Schematic representation of the relationship between biotic and abiotic components of an ecosystem and how they relate to each.

Pollution of ecosystems with TM has generated a lot of environmental concern and comes with severe global health implications. Some TMs that plants and micro-organisms require will enhance the growth of such an ecosystem so long as the concentration is not up to the threshold that elicits toxicity. TMs in the environment do not last forever as mono-metals but undergo several chemical processes which will result in the modification of their bioavailability and mobility within different compartments [9]. Such chemical processes include: 1. Complexation; 2. Desorption; 3. Adsorption; 4. Dissolution; and 5. Precipitation. The first sufferer in terms of TM ecosystem contamination is the soil micro-organisms [34]. TMs induce these damages by either direct intoxication of biotic producers (plants) or altering the physiological and biochemical properties of micro-organisms resulting in a reduction in soil arability. TMs like Cr, Cd, and even high levels of Zn are known for such, possibly via the generation of oxidative stress [35]. These metals affect not only microbial growth but also alter genetic variation, morphology, and metabolism. Proteins are denatured, cell membranes peroxidized, and enzymes and DNA distorted leading to altered decomposition capacity and reduced nutrients for plant growth [34]. TMs could attack plants directly destroying their cell membranes and subsequently chlorophyll, resulting in decreased photosynthetic activity and plant growth. Either by attacking plants directly or indirectly via distortion of the soil micro-organism community, TMs result in a decrease in plant production. Because plants are the first in the trophic level, any decrease in plant availability for nutrition will affect plant-dependent herbivores [36]. The catastrophic consequences of altering a plant's biodiversity start with damage to photosynthesis-dependent cascades. In addition to TMs damage to chloroplast membrane, there could be damage to essential enzymes involved in photosynthesis. This results in inability of plants to generate enough energy (sugars and starch) since it loses the ability to convert CO_2 and H_2O from air and soil to give O_2 and glucose (electron transport process). Thus, plants are at the heart of CO_2 sink and O2 generation that the consumers and decomposers depend on (**Figure 3**) [37].

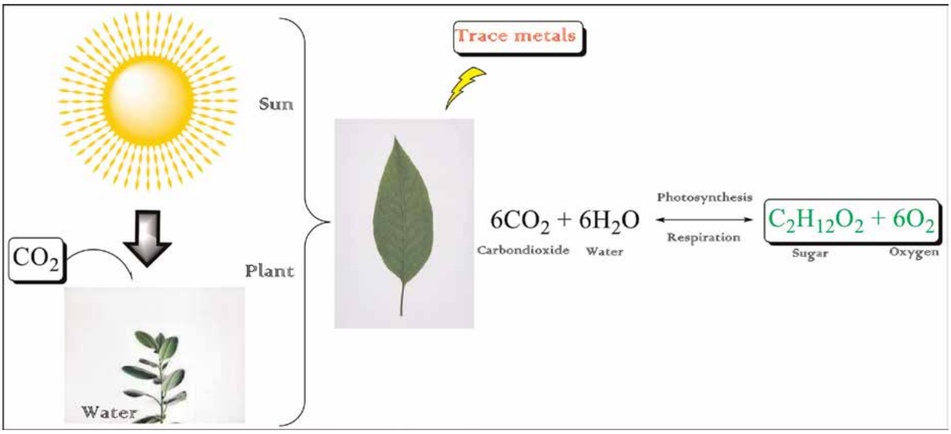

Figure 3.
Schematic representation of the interactive effect between sunlight, carbon dioxide water, and plant during photosynthesis to generate sugar and oxygen.

The catastrophic consequences of dysregulation of the balance between CO_2 and O_2 will be the termination of all respiratory-dependent species, including man [38]. Green plants are endowed with innate repair mechanisms to keep a natural balance in check. However, it is worth mentioning that some TMs participate at one point or another in the photosynthetic process. Metals like Fe, Cu, and Mn serve as co-enzyme in the photosynthetic process since they serve as cofactors of metalloproteins during the electron chain process in photosynthesis. The concentration of metals needed is minute, and any slight increase beyond this amount becomes deleterious and damaging to the ecosystem's redox balance [39]. Following the disruption of the plant's energy process, all other living things higher in energy trough suffers deprivation. There will be decreased species diversity and abundance, leading to a shortfall in the quality and quantity of nutrients for herbivorous animals [40]. Animals from higher troughs will suffer a similar fate, scampering for food with higher-than-usual competition and adaptation for survival. Man too will have less nutrition to depend on, increasing their propensity for diseases, with decreased immunity, poor growth, and development [41]. Also, the disruption of the ecosystem by TM affects both biotic and abiotic-dependent processes. Animals like birds that use trees as shelter will become excessively exposed to both predators and environmental conditions that may be inimical to their survival. Some of the abiotic factors that have a symbiotic balance with plants like soil will be exposed to excessive erosion and there may be dysregulation of the climate and environment [42]. Another major issue with TMs exposure to plants is that of absorption by plants, passing it up along the energy chain with possibility of bioconcentration and biomagnification of these metals. Higher animals, including man that depends on these plants or other animals indirectly consume more TMs than lower animals (**Figure 4**).

The consequences of TMs on higher animals cannot easily be quantified. Most TMs like Cd, As, Pb, etc. are multi-organ toxicants; affecting every part of the body [43]. Organ damages lead to decreased morbidity and mortality, and the effect on the gonads particularly will lead to decreased population and congenital abnormalities [44]. Ultimately, all these toxicological milieus will lead to further distortion of the ecosystem.

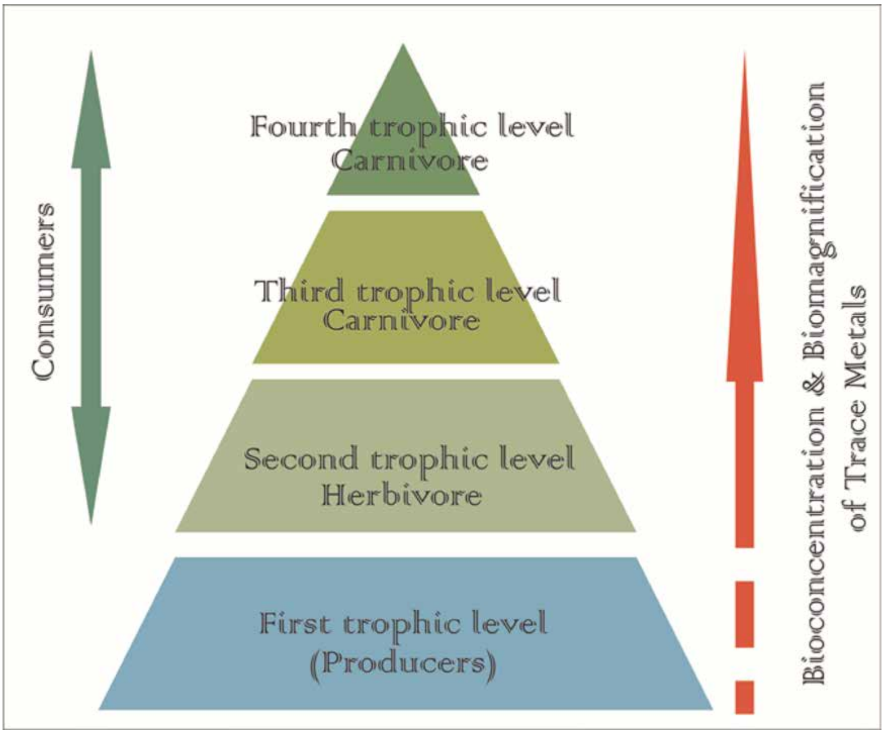

Figure 4.
Schematic representation of different energy levels in an ecosystem and how trace metals can become concentrated and magnified along the chain.

1.1.2 Acceptable limit of trace metals in the environment (ecosystem)

Due to the deleterious nature of TMs, acceptable limits in the environment had been set to forestall decreased mortality arising from accidental consumption. Of particular health importance is the preponderance of TMs to induce carcinogenicity. Studies on the occupational effect of exposure in humans and long term animal studies had been used to classify TMs based on their carcinogenic risk by the International Agency for Research on Cancer (IARC) (**Table 1**). This represents the first and primary step in carcinogenic risk assessment.

Groups	Criteria
Group I	Agent is carcinogenic to humans
Group 2A	Agent is probably carcinogenic to humans
Group 2B	Agent is possibly carcinogenic to humans
Group 3	Agent is not classifiable as to its carcinogenicity to humans
Group 4	Agent is probably not carcinogenic to humans

Table 1.
Criteria for assessment of the carcinogenicity of a chemical (TMs).

The second step in the assessment of chemicals including TMs involves establishment of the threshold for toxicity to manifest. A tolerable daily intake (TDI) gives an idea of daily exposure via the ecosystem that can manifest in toxicity using a sensitive end-point.

$$\mathrm{TDI} = \frac{\text{NOAEL or LOAEL or BMDL}}{\text{UF and/orCSAF}}$$

where NOAEL—no observed adverse effect level; LOAEL—lowest observed adverse effect level; BMDL—lower confidence limit on the benchmark dose; UF—uncertainty factor; CSAF—chemical specific adjustment factor.

The guideline value can be derived from the TDI based on the formula;

$$\mathrm{GV} = \frac{\mathrm{TDI} \times \mathrm{bw} \times P}{C}$$

where bw—body weight; P—fraction of TDI allocated to that ecosystem; C—daily consumption of either food or water from that ecosystem.

World Health Organization (WHO) had set guidelines for permissible levels of some TMs in water which can guide the levels in an ecosystem (**Table 2**).

1.2 Mechanism of trace metal's alteration of the ecosystem redox balance

TMs are believed to have a similar but complex mechanism of action in carrying out whatever toxicity that is associated with it. In living organisms, some of these metals are the fulcrum of homeostasis which involves oxygen-hypoxia sensing and therefore contribute to the intricate processes of metal absorption and storage. This homeostatic function is under strict control, but any imbalance leads to the activation of other biochemical pathways like the Haber Weiss/Fenton reaction pathway. This will lead to a generation of reactive oxygen species (ROS) and reactive nitrogen species (RNS) [43, 45]. Some TMs like Cd, As, Pb, etc. that do not participate in

Trace metal	Guideline value (mg/l)
Selenium	0.01
Nickel	0.07
Molybdenum	0.07
Mercury	0.006
Manganese	0.4
Lead	0.01
Chromium	0.05
Copper	2
Cadmium	0.003
Barium	0.7
Arsenic	0.01

Table 2.
Values of TMs as guidelines from WHO.

biological reactions also generate ROS and RNS indirectly, possibly by stimulating nicotinamide adenine dinucleotide phosphate oxidases (NADPH oxidases), or by competing for the metal binding site of an enzyme or protein and taken over the active site, or by attacking the sulfhydryl moiety of proteins [46]. ROS and RNS are not entirely a nuisance in cell homeostasis as they play a role in the growth of microorganisms, cell cycle and stress response, defense, cell signaling, and apoptosis [47]. These metals indirectly generate ROS and RNS also has the potential to displace metals like Fe, Cu, Co, etc. from their active sites, making them available for catalysis, which can result in the further formation of ROS and RNS (**Figure 5**) [48]. Living things are endowed with an efficient system for removing excess ROS and RNS in their cells to avoid injury. There is an efficient antioxidant system that is innate in all living organisms for stress control. Most cells possess stress-sensing techniques that ring a bell once the oxidative and nitrative stress levels go beyond a threshold [49]. Glutathione is the first line of defense in this regard having the ability to neutralize most free radical species like lipid peroxides, peroxynitrites, hydroperoxides, superoxide, nitric oxide, and carbon radicals resulting in the protection of essential body parts [50]. Furthermore, there are other enzymatic and non-enzymatic components of the antioxidant armamentarium available to living organisms for protection. Non-enzymatic antioxidants include vitamins C and E, polyphenols, carotenoids, flavonoids, etc. that can donate electrons and neutralize free radicals, thereby preventing pathological injury [51]. Enzymatic antioxidants, on the other hand, include superoxide dismutase (SOD) which causes the dismutation of superoxide radical to produce oxygen and hydrogen peroxide (**Figure 5**), and catalase which catalyzes the

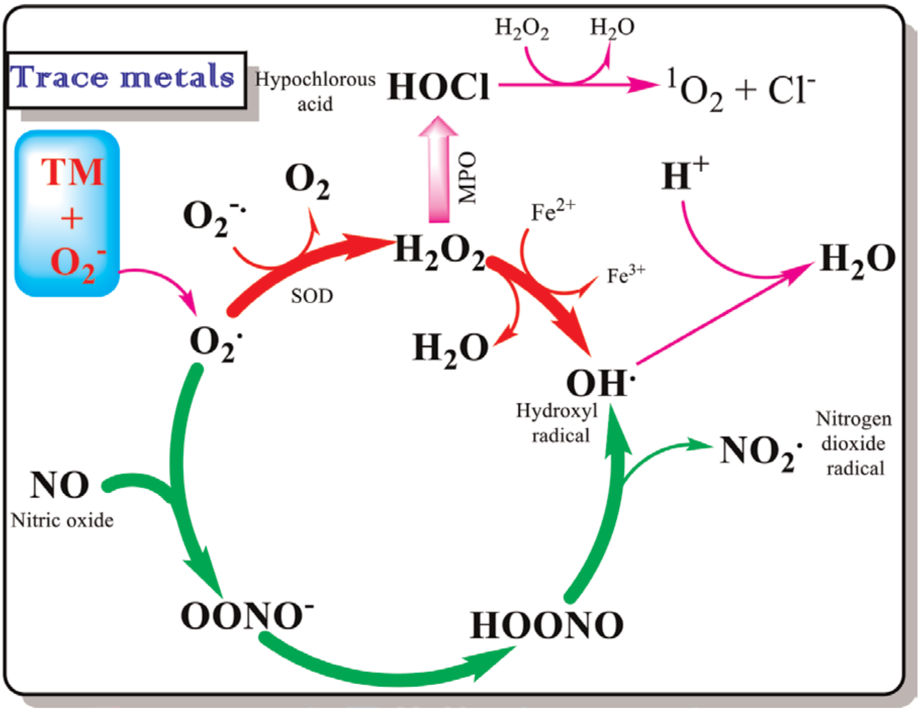

Figure 5.
Schematic representation showing the generation of reactive oxygen species (ROS) by trace metals via the formation of superoxide radicals. MPO is myeloperoxidase and SOD is superoxide dismutase.

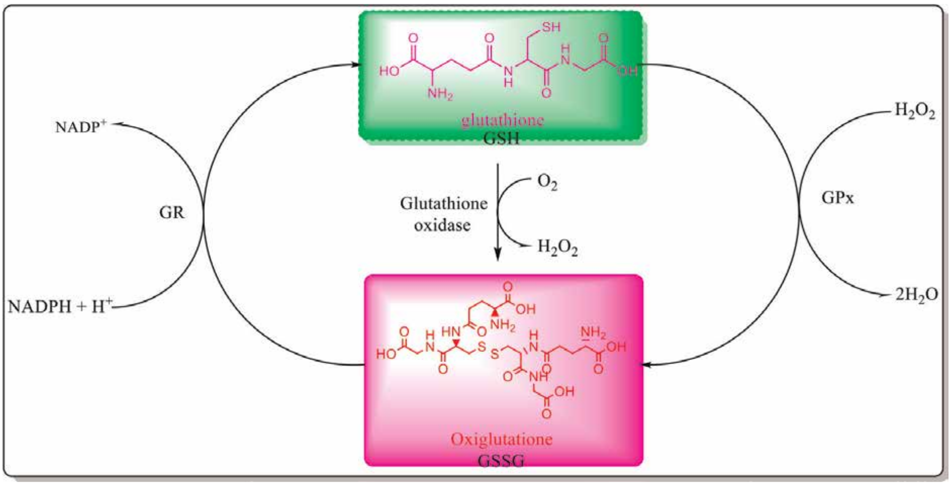

Figure 6.
Schematic diagram showing the conversion of glutathione (GSH) from the reduced form to the oxidized form (GSSG) by glutathione peroxidase (GPx) and the regeneration back to the reduced form by glutathione reductase (GR). GSH could also get oxidized by glutathione oxidase.

decomposition of hydrogen peroxide to water and oxygen. By removing peroxide radicals, these two enzymes work in tandem to keep ROS from going beyond optimal level [52]. Some enzymes are involved in maintaining the level of glutathione in living organisms.

Glutathione exists in both reduced and oxidized forms with the reduced form being more in amount. The reduced form (GSH) can convert hydrogen peroxide (ROS) to water in a reaction catalyzed by glutathione peroxidase (GPx) while in itself becoming oxidized (GSSG) [53]. GSSG can become reduced back to GSH by glutathione reductase (GR), thereby regenerating GS to participate in another round of reaction (**Figure 6**). There is always a balance between the pro-oxidant forces and the antioxidant forces for the optimal health of living organisms in any ecosystem. Where the pro-oxidant forces dominate, oxidative stress ensues with its consequential damages. By increasing the prooxidant forces and creating redox imbalance, TMs compromise the health of the ecosystem from the producers (plants) to the consumers. If this redox imbalance is unchecked, the world as a global ecosystem will be in peril [43, 54]. This redox imbalance will cause the activation of adaptive cellular responses in the organisms along the food chain. Plants will increase the expression of genes that will support both extracellular and intracellular sequestration. Organic anions like malate, oxalate, etc. will lead in the extracellular sequestration while polymers like pectin, cellulose, lignin, and hemicellulose lead the internal.

In the animal kingdom, activation of the adaptive cellular mechanisms leads to interference with immune homeostasis resulting in inflammation. Pro-inflammatory cytokines and chemokines like nuclear factor kappa B (NF-κB), tissue necrosis factor (TNF), interleukins 1B, 6, 8, etc. (IL-1B, IL-6, IL-8) get activated [55]. Activation of the inflammatory pathways will also lead to other cascades of activations like the cell death pathways. There will be an increase in the expression of genes mediating apoptotic pathways like caspase 3, 8, 9, and 10 resulting summarily in death and damage to the ecosystem [56].

1.3 Remediation and restoration of the ecological redox imbalance

Bioremediation is the scientific approach usually used to remove and or convert damaging environmental contaminants like TM into less harmful ones. It involves physical, chemical, or biological processing like adsorption, precipitation, ion exchange, electro-dialysis, complexation, electrostatic attraction, redox process, etc. [57]. It is an eco-friendly, effective, and cost-effective technique for the treatment of soil and water contaminated with unwanted and hazardous chemicals [58]. Ion exchange has recorded some level of success as it can remove TMs even at low concentrations. The major setback to its use is the high cost associated with it and the fact that pH usually affects its efficiency [59, 60]. Recently, interest in the use of adsorption has been on the increase because of the low cost involved. Nanomaterials, industrial biowastes, metal organic frameworks (MOF), microbes and nanocomposites are being used for adsorption purposes [61]. Precipitation is ideal, especially in TM-contaminated effluent-like water. It is cost-effective and requires fewer technicalities than ion exchange and the precipitate comes out as carbonates, hydroxides, and sulfides which are removed by sedimentation and filtration [62]. Electrodialysis (ED) is a promising and emerging technique for removing and recovering TMs from mixtures and matrices. Its major merit is that it can be combined with other methods for improved efficiency [63]. Complexation involves establishing a coordination complex between macro ligands and coordinating atoms of TMs in other to increase their size and molecular weight. It is ideal for the removal of TMs in industrial setups like paper mills, textiles, pulp, water treatment, agriculture, etc. with moderate cost [64]. Recently, attention regarding TMs removal from contaminated water has shifted to the use of electrically charged ions for attraction. This involves the use of materials that attract TMs ions to adsorb and remove it from the contaminating environment [65]. A relatively new trend in the removal of TMs involves the redox process which is the redox technique. So many other bioremediation processes involve redox reactions such as electrokinetics, the use of nanotechnology, ultrasonication, etc. Biological techniques in bioremediation use mainly organisms like fungi, bacteria, plants, or plant parts to degrade, reduce, remove or recover TMs in soil and water [66]. Use of microbes in bioremediation could be by bioaugmentation, bioventing, bio-sparging, land farming, bio-stimulation, bio-piling, or composting. Bio-augmentation involves the use of organisms to speed up the rate of degradation of a TM. This requires information on the diversity of micro-organism present before the introduction of additional organisms [67]. In bioventing, there is increased aeration of contaminated water or soil to promote increased bioactivity of the indigenous micro-organisms as a way of metabolizing TM [68]. In bio-sparging, oxygen is injected and made to become saturated in the contaminated area to aid biodegradation and bio-transformation [69]. Furthermore, land farming involves the mixing of contaminated soil with soil amendment substances like nutrients and bulking agents and tilling back into the soil with occasional tilling to aid aeration [70]. Bio-stimulation is an ideal technique for water contaminated with TM and involves supplying the contaminated water with growth-limiting nutrients like phosphorus and nitrogen as a way of facilitating the interaction of micro-organisms in the fluid [71]. The technology of bio-piling encompasses mixing excavated soil with soil amendment that is in compost piles and enclosed for decontamination [72]. Compost bioremediation of TM-infested areas involves a process where both fungi and bacteria are used to break down these contaminants in water and soil [73]. The bottom line in all these biological techniques is the use of organisms that can metabolically use these TMs as an energy source while converting it to less toxic forms [74]. Proper bioremediation is the first step in bio-restoration of TM dysregulated redox imbalance in a contaminated environment.

2. Conclusion

TMs contamination of the environment is of global dimension with its associated risk in terms of threat to biotic and abiotic components of the environment. These TMs are naturally found in the crusts of the earth but contaminate the environment following anthropological activities. Some TM can be found in some food, where minute quantities could aid the normal homeostatic functions of living organisms. In large amounts, they cause potential damage to the ecosystem that supports life, including that of man. Scientists believe that the unifying mechanism of environmental distortion is the formation of free radicals which cause damage via chemical electron abstraction. Bioremediation of soil and water contaminated with TMs has offered some relief in terms of mitigation and holds promise for a balanced redox ecosystem.

Conflict of interest

No conflict of interest to declare.

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Section 2

Trace Elements in Water

Chapter 6

Heavy Metals in Wastewater Effluent: Causes, Effects, and Removal Technologies

Evans Odumbe, Sylvia Murunga and Jackline Ndiiri

Abstract

Heavy metal contamination is one of the fundamental ecological problems of new instances. These heavy metals are very tricky as they without delay have an effect on residing organisms and human health. These contaminations typically occur as a result of herbal and human activities. Technological development and business improvement have brought about an upward push in heavy metallic pollution inside the surroundings. Indiscriminate discharge of toxic wastewater into the encompassing surroundings regularly are reasons for severe environmental and health impacts. The heavy metal particles are nonbiodegradable and could popularly amass inside the dwelling organisms, accordingly are carcinogenic and teratogenic. Elimination of heavy metals has therefore become a problem of first-rate difficulty. Various technology and traditional techniques were utilized in heavy metallic elimination. This review paper is therefore geared toward assessing some of the reasons and results in addition to diverse strategies for the elimination of heavy metals in wastewater effluent.

Keywords: adsorption, carcinogenic and teratogenic, contamination, heavy metals, nonbiodegradable, wastewater

1. Introduction

Water is a key resource for survival of all living organisms all over the world. With an increase in population and human activities such as urbanization, development of industrial parks, recreation facilities, and agricultural practices, there is reduced access to water resources as all these activities require water. These human-induced activities require the use of water resource. This in turn increases on water consumption and the water demand, thus putting a strain on the ever diminishing water resources. The various water uses often results in high levels of pollution that usually find their way to the environment through indiscriminate wastewater disposal. These pollutants include organic and inorganic compounds as well as heavy metals. Since the freshwater resource is continuously decreasing, there have been high advocacy for water reuse to try and address on the ever-increasing demands for freshwater resources. This further elevates the water contamination problem as some of these pollutants find their way to the environment and affects living organisms.

For instance, reuse of wastewater in irrigation tends to increase the prevalence of health infections [1–3]. Heavy metals are components with atomic density that is greater than 5 g/cm^3 and a relative atomic mass that ranges from 63.5 to 200.6 are viewed as the major contaminations for freshwater resources due to their direct effect on living organisms and human health [4–6]. They are nonbiodegradable and have been reported to cause environmental pollution worldwide due to their persistence in wastewater [4, 6].

Industrial and municipal effluents are considered to be the main sources of heavy metal pollution [7]. Increased industrial activities leads to deposition of large wastes and wastewater pollution with heavy metals content [8]. Discharge of heavy metal ions to the environment as a result of industrial development and springing of urban centers has posed a great problem globally [9]. This has made heavy metal ions to be one of the most problematic issue of environmental concern of the recent time [2, 10]. Therefore, there has continuously been an increased focus toward the disposal of heavy metals, since they are increasingly becoming an environmental threat because of their unfavorable impacts on human health [7, 9, 11]. Elimination of metal ions from wastewater effluent has also been an issue of great conversation because of their interaction with health risk for all living things, for their toxicity and nonbiodegradable nature [2, 7].

2. Causes and effects of heavy metals in wastewater effluent

Water pollution is a worldwide problem and needs to be controlled [12]. The main sources of heavy metals in wastewater are natural and man-made activities [6, 11]. The natural factors include weathering and soil erosion, precipitation runoffs, volcanic eruptions from active volcanos, particulate matter such as aerosols, while the human sources are quite numerous [4, 5, 11]. They include effluents resulting from industrial and municipal waste. The industrial effluents results from processes such as metal smelting and electroplating processes, leather tanning and textile, mineral extraction, and nuclear power, whereas municipal effluent are from residential and municipal discharges [4, 5, 13]. Municipal and industrial effluents contain organic matter, water contaminants, and heavy metals ions. Heavy metals mainly emanates from various industries [13]. These heavy metals are nonbiodegradable and require to be removed from the wastewater effluent before disposal since their presence in water deteriorates water quality [4, 11]. They are a major concern due to their toxicity effects, bioaccumulation tendencies, and threat to human life and the environment [8, 13]. Agricultural activities consisting of irrigation with wastewater effluent can also end in regular pollutants with heavy metals to soil and groundwater, consequently posing a threat to human health. Similarly, the accumulation of heavy metals usually by using vegetable plants is deemed to be of extreme environmental trouble in regions where wastewater irrigation has come to be significant [1–3, 14].

Metal ions including lead, nickel, cadmium, and chromium are additives from the earth crust and are usually related to high degrees of toxicity [10, 15]. These metals, however, have various uses in consumer products and fundamental engineering works, paper and pulp industries, leather tanning, plastic stabilizers, photographic substances, fertilizers, pigments, batteries, metal plating, mining, jua-kali, radiator production, smelting, and alloy industries [11, 13, 15]. Pollution occurs when wastewater resulting from these industrial processes find their way in to the environment [16]. Since these metal ions are nonbiodegradable, they can undergo transformation that can have health, environmental, and economic impacts [11]. Untreated and poorly treated heavy metal contaminated wastewater often results in health and environmental impacts [4]. If these heavy metals are ingested, they generally tend to build up within the essential organs of dwelling organisms and vegetation [4, 5, 8, 11]. These can result in damage of the human nervous system, liver, brain cells, and bone marrow. Similarly, they can block some of the functional groups of essential enzymes thus disrupting the metabolic processes of the body [4, 5, 8]. Because heavy metals tend to accumulate in the living organism, they are carcinogenic and teratogenic [6]. Cadmium and lead, even as trace levels, are known to have toxicological effects and have adverse effects on human health and other living organisms [11]. Exposure to a few metals, including mercury and lead, may motive development of autoimmunity, in which a person's immune device attacks its very own cells. This can cause joint illnesses inclusive of rheumatoid arthritis, and sicknesses of the kidneys, circulatory gadgets, worried system, and unfavorable of the fetal mind. At higher doses, heavy metals can cause irreversible mind damage [4, 5]. On the other hand, zinc and copper ions are rather not harmful to human health and animals at low concentrations as they may be required for various sports for residing organisms. However, exposure to high concentrations are extremely harmful [11].

3. Heavy metals removal technologies

Numerous traditional methods and technologies have often been used for the elimination of heavy metals ions from wastewater. They include chemical precipitation, ion change, opposite osmosis, oxidation-discount, solvent extraction, adsorption, electrochemical remedy, evaporation recuperation, membrane era, biological remedy, and coagulation, among other methods [7–13]. However, some of these methods are rather too expensive or very complex for treatment of heavy metals [15]. The important downside of these technologies is the manufacturing of toxic sludge whose disposal is intricate and now not green [9, 12]. For instance, metal extraction of less than 100 ppm tend to be very costly [9]. Bioremediation, on the other hand, is a new technology which employs the use of enzymes, micro-organisms, eco-friendly plants, and agricultural by-products [4, 9].

Adsorption has proven to be economical and is vastly accepted in the environmental treatment processes globally [8, 10, 17]. Adsorption has shown many advantages over physicochemical methods [15]. It is always considered better among other methods due to convenience, easy operation, and simplicity of design as well as low cost of the initial materials used as adsorbents [6, 8, 10, 18]. Adsorption of heavy metals on conventional adsorbents such as activated carbon is one of the methods that have been widely studied. However, activated carbon has a cost implication that is not sustainable [16]. Activated carbon shows a high adsorption capacity, but its expensive nature presents a major drawback for practical applications especially in industrial effluent treatment [7, 8, 13]. Activated carbon requires chelating agents to enhance their performance [7, 8, 16]. The activating carbon is commonly used as industrial sorbents. Other materials include silica gel and alumina since they present a great surface area per unit weight [10, 18].

These commercially available adsorbents are expensive and therefore, there has always been the need to study alternative substitute which has high adsorption efficiency and is low in cost [16, 18]. This need for safe and economical method has necessitated research interest toward production of low-cost alternatives to commercially available activating carbon [8, 13, 17]. These research works have employed the use of agricultural wastes, clay, cooked tea dust, zeolites, cashew nut shells, fly ash activated carbon, sawdust, peat, sewage sludge, fruit wastes, diatomite, and rice husk [8, 15]. Agricultural by-products such as rice husk, fly ash, sugarcane bagasse, palm oil shell, and coconut husk have yielded some promising results in the adsorption of heavy metals from wastewater effluent [9, 13, 19]. Agricultural resources has therefore been found to be an alternative due to their low cost (cost efficiency) and abundance [13, 16, 20]. Most investigations on agricultural by-products such as fruit wastes have asserted that they can act as a good sorbent for hazardous material and heavy metals [7, 9, 12].

4. Conclusion

This paper review was aimed at discussing heavy metals in wastewater effluent, with a great focus on some of the causes, effects and removal technologies in wastewater effluents. It revealed the main causes of heavy metal pollution as a result of natural and human activities. However, metal ion contaminations have been catalyzed by human activities such as technological advancements and industrial developments. Affluent and inadequately treated effluents polluted with heavy metals poses a great challenge to the environment as well as human health.

In order to ensure adequate and proper protection of human health and environmental sustainability, numerous treatment technologies have been studied and applied. Application of these methods depends on the pollution load, cost implications, efficiency and simplicity in the design, effectiveness, and sustainability. Adsorption have been singled out as a better alternative to the physicochemical methods.

In particular, the use of agricultural by-products and wastes has majorly been investigated for use as low-cost adsorbents. This has therefore created a new spectrum in the remediation of heavy metals polluted wastewater and sludge. However, the use of a blend of various agricultural wastes and anaerobically digested agricultural wastes have not been zealously explored in this endeavor. Therefore, there is need for more studies in this area in order to fill this gap.

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Chapter 7

Water Quality Assessment in Terms of Major and Minor Elements in Surface, Ground and Sea Water and Correlating the Presence with Associated Problems

Ajay Kumar and Rakesh Kumar Singh

Abstract

The major and minor elements and their salts are the targeted investigation of surface water, ground water and sea water by the scientists worldwide. The presence of such elements depends on the nature of rock, soil, weathering phenomenon, pH value, water soluble salts etc. Other than the natural source, many contaminants are introduced into water by the domestic or industrial activities of that region. The heavy metals have a tendency to accumulate in animal and human bodies through this water system. Moreover, the accumulation of these heavy metals beyond permissible level has harmful effects on biotic components. These metals also get accumulated in water-sediment and percolate down in to ground water that effects food chain and biomagnification. The mobility of metal or its salt in water depends upon chemical forms in which it exists in water. Major components (Na^+; Ca^+, Mg^+, K^+, Cl^-, NO^{3-}, HCO_3^- etc.) and minor elements (Al^+, F^-, Cd^+, Co^+, Cu^+, Cr^+, Fe^+, Mn^+, Ni+, Pb^+, $Sr.^+$, Zn^+ etc.) are present in surface water, ground water and sea water. The present chapter deals with the water quality of surface water, ground water and sea water assessed by the authors and their team of scientists, where, the distribution of major and minor element concentrations in the surface and ground was evaluated in one of the districts of India, Moradabad Uttar Pradesh, whereas, seawater from Southern ocean and glacial lake water from Proglacial and Epishelf lakes of Antarctica. Major and minor elements beyond the permissible limits causes severe health problems such as liver cancer, diabetes, cirrhosis of liver, diseases related to heart and central nervous system, infertility etc. and thus needs to be monitored on regular basis.

Keywords: surface water, sea water, ground water, drinking water, water quality, water pollution

1. Introduction

Water is one of the natural resources which is found in an adequate amount. About 70% of the earth's surface is covered with water. It is essential for the existence of life on the earth. It is also being widely used for various purposes such as drinking, washing, bathing, cooking, irrigation, industrial uses etc. [1]. Most of the water on earth is present in sea and oceans and accounts for 96%. This water is unfit for human consumption due to high salt content. Around 2% of water is locked up in polar icecaps, icebergs, mountain glaciers, snow cover etc. Water found on land is categorized as surface water (river, lakes, ponds) and ground water accounting as 0.02 and 1.40% respectively. **Table 1** shows the global water reserves and their distribution as surface water; rain water; ground water; sea water, ocean water etc. [2]. The human life on earth is dependent on surface water that meets the livelihoods for a large number of people all over the world. Surface water is a water body found on the earth surface, which can persist throughout the year or a part of the year and includes the rivers, streams, lakes, ponds etc. Surface water is more accessible than ground water. Man-made surface water reservoirs are also found in structures such as dams, bridges etc. They are used for renewable energy generation by hydropower, irrigation and recreational purposes.

In fact, surface water, ground water and sea water are all important for survival of human being, plant and animals living on this earth planet. Surface water participates in the water cycle, which involves the movement of water vapors to and from the earth's surface. Evaporation and seepage of water into the ground cause water bodies to lose water. Surface water and groundwater are reservoirs that can feed into each other. The surface water can seep underground becomes groundwater and also can resurface on land to replenish surface water, lakes, river, pond etc. [3].

Ground water is the second largest store of fresh water on this earth. The sustainability of the ecosystem is largely dependent on groundwater availability. For the last few decades, the groundwater has been under tremendous pressure to fulfill human needs owing to human activities around the world. Moreover, rapid rise in population and human activities such as agriculture, industry and infrastructures also cause increase or alter the natural composition of water or concentration of several major and trace elements in water, which results in deterioration of the water quality [4].

The physical and chemical composition of water plays a key role in assessing the quality of water. In unpolluted systems, major ions in water are provided by soil and rocks. The quality of water is dependent on several factors such as geology, weathering, quantity of recharge water, water-rock interaction etc. In ground water,

S. No.	Particulars	Distribution Area (10^3 km^2)	Global Reserves (%)
1.0	Sea and Ocean	361,300.00	96.00
2.0	Ground Water	134,800.00	1.40
3.0	Polar icecaps, Glaciers, Icebergs, Snow Cover	16,227.00	1.55
4.0	Lake, pond, river	2228.70	0.02
5.0	Others (biological, swamp, atmospheric etc.)	748.00	0.01

Table 1.
Global water distribution and reserves.

metal salts may enter into many ways; natural rocks, weathering, irrigation and also by human activity. The accumulation of metal through food chain is called bio-magnifications. The concentration of metal gets increased at every level. The metal concentration can cause harmful effects on agricultural soil, human beings and livestock by alteration in biochemical reaction in body cells [5].

Thus, the water resources play an important role both at national and international level. However, the human activities witnessed in terms of climate change, global warming, industrialization, pollution has altered the constitutional changes in water resources. Therefore, a regular water quality assessment of surface water, ground water and sea water are essential in terms of major and minor elements composition [6].

1.1 Macro and micro elements in water

Macro and micro elements or their salts are naturally present in the water bodies. They come primarily from various sources such as rock weathering, soil erosion, dissolution of salts etc. Naturally occurring metals move through aquatic, biotic and abiotic environments [7]. Human beings also intake essential nutrients, elements or salt through water and food that are essential to human health. Some major metals such as sodium, potassium, magnesium, calcium, iron etc. are found in water. The industrial activities have affected on water quality. The metals can become toxic or undesirable when their concentrations are higher than permissible limits. Therefore, a better understanding of elemental/or metal sources and their presence in the water is essential [8].

The metal and metal salts enter in to the ecosystem and may lead to geo-accumulation, bioaccumulation and bio-magnifications. Major components like (Ca^{2+}, Mg^{2+}, Fe^{2+} Cl^{-}, SO_4^{2-}, Na^{+}, NO_3^{+} etc.) and other trace elements (F^{-}, Mn^{2+}, Co^{2+}, Ni^{2+}, Al^{3+}, Zn^{2+}, Cr^{6+}, Mo^{6+} etc.) are important for biological systems and their deficiency or excess could lead to a number of diseases. The element or its salt like chloride, calcium, iron, molybdenum, manganese, zinc, fluoride etc. have been linked to human life development. Several heavy metals like cadmium, lead, mercury, arsenic, iron etc. are toxic at low concentrations in water [9] that can accumulate in body tissues over long periods of time. The contamination by element has become a cause of concerns in recent years because of their accumulation in food chain, soil and sediment. Therefore, quality control of water is regularly needed from time to time [10].

1.2 Sea water

Sea water makes up the oceans and covers more than ~70% earth's surface. Surface sea water is slightly alkaline and have an average pH 8.0. Sea water is a mixture of 97.0% water, 2.5% salts and smaller amounts of other substances ~0.05%. **Table 2** shows the macro and minor elements or salt present in sea water [11].

Sea water vary in their chemical compositions. Dissolved mineral originates from earth crust, rock weathering, biotic components. Sea and ocean are dominant by sodium and chloride ions, followed by sulphate, calcium and magnesium [12, 13]. The samples of sea water were analyzed for the major elements and trace metal concentrations in surface sea water [13, 14].

However, the concentration of major and minor element in sea water varies with depth and location. Organisms living on the surface of sea water and below are also involved in changes in its chemical composition. Dissolved element such as ion present in sea water is principal as electrolytes [9]. The average composition of sea water is made up of dissolved salts as shown in **Table 2**.

S. No.	Particulars	Sea water	River water	Rain water	Surface water
1.0	Chloride as (Cl^-), mg/L	19,345.00	66.75	3.79	5.30
2.0	Sodium as (Na^+), mg/L	10,752.00	6.30	1.98	4.50
3.0	Potassium as (K^+), mg/L	390.00	2.30	0.30	1.30
4.0	Sulphate as (SO_4^{-2}); mg/L	2700.00	8.25	0.58	33.40
5.0	Calcium as (Ca^{+2}), mg/L	416.00	66.40	0.09	48.60
6.0	Magnesium as (Mg^{+2}),mg/L	1295.00	3.35	0.27	8.00
7.0	Bicarbonate as (HCO_3^{-1}) mg/L	145.00	60.00	0.12	—
8.0	Bromide as (Br^-); mg/L	67.00	0.02	—	—
9.0	Strontium as (Sr^{+2}); mg/L	0.70	0.03	—	0.04
10.0	Silica as SiO_2, mg/L	6.40	13.10	—	1.34
11.0	Boron as B, mg/L	4.50	0.01	—	0.025
12.0	Fluoride as (F^-), mg/L	1.30	0.10	—	0.083
14.0	Arsenic as (Ar), mg/L	0.02	0.002	—	0.0014
15.0	Cadmium as (Cd), mg/L	—	0.0001	—	0.00002
16.0	Copper as (Cu), mg/L	—		—	0.00075
17.0	Iron as Fe, mg/L	—	0.67	—	0.0055
18.0	Aluminum as Al; mg/L	0.50	0.03	—	0.0035
19.0	Fluoride as F; mg/L	1.30	0.10	—	0.08
20.0	Nitrate as NO_3; mg/L	—	16.30	—	4.55
21.0	Barium as (Ba); mg/L	—	0.018	—	0.09

Table 2.
Elemental composition of variety of water.

1.3 Rain water

Rain water has a chemical composition that varies from place to place, shower to shower and season to season in the same place. Rain water contains some constituents of local origin, and some that have been transported by winds from other place. Even during rainless periods there is precipitation of mineral and dust. The chemical constituents in rain are also added continually to any area of the earth's crust to become part of the environment (**Table 2**) [15].

Rain water is a mixed electrolyte that contains varying amounts of major and minor ions. Sodium, potassium, magnesium, calcium, chloride, bicarbonate, sulfate ions are major constituents. They also contain nitrogenous compounds. Minor constituents are iodine, bromine, boron, iron, alumina, silica etc. Dust particles are added locally. The main sources of rain water are from evaporation of sea, oceans, fresh water lakes and their condensation phenomenon [10].

1.4 Ground water

Ground water is found in earth aquifers, which is an essential and vital component of our life. In the last seven decades, the ground water resources are being continuously utilized for drinking, irrigation, industrial purposes etc. However, due to rapid growth of population, urbanization, industrialization and agricultural activities, ground water resources are under stress. There is also growing concern on the deterioration of ground water quality due to ongoing human activities [5].

The sodium, magnesium and calcium content of ground water is a function of weathering of rocks containing calcium and magnesium. Most of the ground water contains sodium, calcium and magnesium. This is due to metallic ions present in earth crust and rocks. It is also derived from biotic components. On the other hand, trace elements can be divided into essential and non-essential categories [16].

Inorganic salts such as sulphate, chloride, nitrate etc. along with Na, K, Mg, build up dissolved solids. The combination of carbonates and bicarbonates along with Ca and Mg make hard water. Hard water creates stomach and gastrointestinal problems in human being, if consumed as drinking water [17].

Dissolved nitrate is most common contaminant in groundwater. High level can cause blue baby syndrome in children. It can also accelerate eutrophication in lakes, ponds, river etc. The main sources of nitrates include sewage, fertilizers, landfills, industry effluents etc.

In the recent years, the contamination of ground water by major and trace elements in excess has received attention due to their toxicity and bio-accumulation. Many of the heavy and trace elements are not biodegradable. The major sources of toxic elements in ground water include discharge of sewage and waste effluents. Although, some trace elements are essential for human beings but larger quantities of them may cause psychological disorders. Heavy metals like cadmium, chromium, lead, iron etc. are highly toxic to humans at even low concentrations [18].

1.5 Drinking water

Drinking water is water intended for drinking and cooking purposes. It includes untreated or treated by any means for human consumption. Drinking water comes from a variety of sources including public water systems, lakes, wells, bottled water etc. [19].

Table 3 shows the limits of drinking water prescribed by World Health Organization (WHO), United States Environment Protection Act (USEPA) and Indian standard. Ground water represents 30% of the world drinking water. Therefore, monitoring and analysis of the water is an important requirement specifically the measurement of major and minor elemental concentrations in water.

2. Major factors affecting the water quality

2.1 Pollution

Human activities of rise in population, industrialization, infrastructure development etc. demands on exploitation of natural resources affecting water in many ways. The water resources are getting polluted due to addition of effluents generated in these activities including organic matter from plant and animal, washing and bathing discharge etc. [6].

The polluted water has undesirable color, odor, taste, turbidity, organic matter, chemicals, metals, salt, pesticides, oil sludge, high TDS, sewage etc., which may be bio-degradable or non-biodegradable [14].

S. No.	Parameters	Drinking Water		
		WHO	USEPA	IS Standard
1.0	Color, Hazen Units	5.00	5.00	5.00
2.0	Odor	Essentially free	Essentially free	Essentially free
3.0	Turbidity (NTU), max	—		5.00
4.0	pH value	6.5–8.0	6.5–8.5	6.50–8.5
5.0	Total Hardness as ($CaCO_3$), mg/L, max.	500.00	300.00	300.00
6.0	Iron as (Fe^{+2}), mg/L, max.	0.10	0.30	0.30
7.0	Chloride as (Cl^-), mg/L, max.	200.00	250.00	250.0
8.0	Total Dissolved Solids, mg/L, max.	500.00	500.0	500.0
9.0	Calcium as (Ca^{+2}), mg/L, max.	75.00	—	75.0
10.0	Magnesium as (Mg^{+2}), mg/L, max.	50.00	50.00	30.0
11.0	Copper as (Cu), mg/L, max.	1.00	1.30	1.00
12.0	Sulphate as (SO_4^-), mg/L, max.	—	250.00	200.0
13.0	Nitrate as (NO_3^-), mg/L, max.	50.00	1.00	45.0
14.0	Fluoride as (F^-), mg/L, max.	1.50	4.00	1.00
15.0	Cadmium as ($Cd^{+)}$, mg/L, max.	0.005	0.005	0.003
16.0	Lead as (Pb^+), mg/L, max.	0.05	0.01	0.01
17.0	Zinc as (Zn^+), mg/L, max.	5.00	5.00	5.00
18.0	Chromium as Cr^+, mg/L, max.	0.05	0.01	0.05
19.0	Arsenic as (As^+), mg/L, max.	0.01	0.05	0.01
20.0	Aluminum as (Al^+), mg/L, ma	0.20	—	0.03
21.0	Barium as (Ba^+), mg/L	0.07	0.02	0.70
22.0	Mercury as (Hg^+), mg/L	0.001	0.002	0.001
23.0	Selenium as (Se), mg/L, max.	0.01	0.05	0.01
24.0	Boron as (B) mg/L, max.	0.50	—	0.05
25.0	Manganese as (Mn), mg/L, max.	—	—	0.05
27.0	Nickel as (Ni) mg//L, max.	—	—	0.02

Table 3.
Physical and chemical characteristics of drinking water.

Groundwater resources are also under increasing pressure from over abstraction making it a serious threat to this natural resource. Removing pollutants from ground water is not easy as it requires lot of efforts to purify the water aquifer. Different uses of water affect quality of the water and thus the water management is required urgently [20].

2.2 Effect of climate change and global warming on water

Due to climate change and global warming, ice and glaciers are melting contributing to the rise in sea levels. As a result, salt water is beginning to infiltrate in water aquifers contaminating coastal area. It is affecting surrounding ecosystems as it places stresses on the life in those areas.

Climate change has a direct connection with the water hydro-cycle. Global warming and rise in temperature increase evaporation and decrease precipitation, runoff water aquifer and soil moisture. This has altered surface water levels of river, pond, lakes etc. [8].

Climate change may affect water quality through pollution and over utilization. For example, if an aquifer is over-abstracted, the concentrations of elemental or metal nutrients and chemicals may increase, because pollutants will be more or less diluted. Over-abstraction in water stressed areas can also cause ground water quality deterioration if salt or polluted water are drawn into the aquifer.

The quality of water is heavily affected with the presence of metals and their salts. When the water is polluted due to human activity, it alters the chemistry and composition of the water that needs systematic water management against contaminants. The methods used and standards adopted for quality testing of water are summarized in the **Table 4**.

Parameters	Methodology/procedure	Protocol guidelines
Color	Color of the water sample was determined by Hazen method. Reference standard of 500 Hazen units on Platinum-Cobalt scale was prepared by dissolving 1.20 g of K_2PtCl_6 and 1.00 g of $CoCl_2.2H_2O$ in distilled water. It was made up to 1000 ml in volumetric flask. Color measurement was made by visually using different standards by diluting the stock solutions of different standards and was compared with samples.	IS 3025 (Part 4), 2002; Standard Method for the Examination of Water & Waste Water, Ed.21, 2005, Part 2120, 2–1 to 2–8. Published by APHA
Turbidity	A standard turbidity solution was prepared by Hexamethylene Tetramine and hydrazine sulphate in 100 ml distilled water. The instrument was calibrated with different turbidity standards. Water sample was passed through filter pore size of 0.45 micron. Turbidity of collected water sample was made by turbidimeter meter (NTU)	IS 3025 (Part 10), 2002; Standard Method for the Examination of Water & Waste Water, Ed.21, 2005, Part 2130, 2–8 to 2–11, Published by APHA
Odor	Approx. 500 ml of water sample was taken in glass bottle. It was shaken vigorously for ~3 minute. The odor of water was observed after warming the water at 60°C. It was compared with standard physical sensory observation.	IS 3025 (Part 05), 2002; Standard Method for the Examination of Water & Waste Water, Ed. 21, 2005, Part 2150, 2–11 to 2–15. Published by APHA.
pH value	pH of the water sample was measured using pH meter (indicator electrode). Preparation of standard solution was done by dissolving the standard pH buffer tablet (2, 4, 7 & 10) in distilled water. For measuring the pH, first the pH electrode was calibrated by using solution of standard buffer. The electrode was then dipped in the water sample and the pH observed.	IS 3025 (Part 11), 2002; Standard Method for the Examination of Water & Waste Water. Ed.21, 2005, Part 4500, 4–90 to 4–94, Published by APHA
Total Dissolved Solids (TDS)	Gravimetric method was used for the determination of total dissolved solids in water. An approx. 200 gram of the water sample was	IS 3025, Part 15–18), 2002 and 2003. Standard method for Examination of Water & Waste Water, Ed. 21, Part

Parameters	Methodology/procedure	Protocol guidelines
	taken in a glass beaker. It was evaporated in steam bath without bumping. The residue was then dried in an oven at temperature 150°C. It was completely dried till the sample achieve constant weight. Weight of the dried residue sample was taken and TDS calculated.	2540, 2–55 to 2–59. Published by APHA.
Chloride (Cl)	An approx. 10 ml of water sample was taken a conical flask. 2–3 drops of K_2CrO_4 indicator (~ 5%) was taken. It was titrated against standard silver nitrate to 1 reddish yellow color point.	IS 3025 (Part 32), 2003. Standard method for Examination of Water & Waste Water, Ed. 21, 2005, Part 4500, 4–70 to 4–76. Published by APHA
Metal Analysis (Mn, Al, Sb, Ni, Fe, Ch, Hg etc).	Mixed metal element stock solutions was made prepared and a calibration curve method. Water sample was filtered through a 0.45 m membrane filter. Water sample 10 ml was taken in 1 Ltr volumetric flask. About 50 ml dilute nitric acid was added and volume made up to water. Analyze the instrument check standard and the calibration blank. Run condition employed for ICP-OES; RF power 1150; replicate 3; pump speed 11 rpm; Uptake delay 15 sec.; read time 5 sec; View made redial and axial.	IS 3025 (Part 2), 2004; Standard Methods of Sampling and Test (Physical and Chemical) for Water and Waste Water Part 2 Determination of 33 Elements by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP)
Sulphate	Sulphate in water sample was determined by gravimetric method. About 20 g of water sample was taken in acidified water. 10 ml of barium chloride was added and boiled. Sulphate is precipitated as $BaSO_4$. It was then filtered through Whatman filter paper (no 42). The filter paper was ignited in furnace at 800°C and residue is weighed	IS 3025 (Part 24), 2003; Standard method for Examination of Water & Waste Water. Ed.21, 2005, Part 4500, 4–186 to 4–192. Published by APHA.
Boron (Br)	About 10 ml of water sample was taken in beaker and acidifed. It was boiled to remove carbon dioxide. It was cooled and pH adjusted to 7. About 5 gram Mannitol was added. It was then titrated against 0.005 N sodium hydroxide (NaOH) solution. Volume of NaOH consumed was recorded and boron determined	IS 3025, Part 57, 2005. Potentiometric Water Analysis. By Midgley & Torrecc.
Total hardness as $CaCO_3$	EDTA method was used for determination of hardness of water. Accurately 100 ml of water was taken in conical flask and was buffered to pH 9. It was titrated against with EDTA using Eriochrome Black T indicator. The color changed from red to blue end point recorded.	IS 3025 (Part 21), 2002; Standard method for Examination of Water & Waste Water. Ed. 21, 2005, Part 2340, 2–37 to 2–39. Published by APHA

Table 4.
Methodology used for water testing.

3. Field study 1- Water quality at moradabad district, UP (India)

The district of Moradabad lies between 28°21′ to 28°16′ north latitude and 78°4′ to 79° east longitude in the state of Uttar Pradesh, India. The city is an industrial hub for its brass and aluminum handicrafts and known as Peetal Nagri [21].

Figure 1.
Blocks of moradabad district (UP, India).

A field survey was conducted in district Moradabad (UP) and water samples were collected from all over the Moradabad district covering all eight blocks (**Figure 1**) while interacting with the local population to find out the status of ground water quality and associated problems. The primary objective of this work was to determine major and trace elements in groundwater. The samples of groundwater were collected from wells in the Moradabad (1) Badi Masjid Area and (2) Bhojpur Area. To assess the water quality of ground water, samples were analyzed for major and trace elements by using Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

The test results are presented in **Table 5**. The chloride concentration was found to be 117.00 (Badi Masjid area) and 126.75 mg/L (Bhojpur area). The nitrate concentration was found to be 53.03 (Badi Masjid) and 60.13 mg/L (Bhojpur) in the study area. The concentration of fluoride in the study area is 0.16 and 0.15 mg/L which is below the prescribed limit of drinking water. The sodium concentration was found to be 63.00 mg/L (Badi Masjid area) and 79.30 mg/L (Bhojpur area).

The total dissolved solid at Badi Masjid and Bhojpur area of Moradabad was found to be 523.00 and 620.00 mg/L respectively. This is higher than the desired limit of water and found unfit for human consumption. The potassium content was found to be 5.00 mg/L in Badi Masjid and 8.30 mg/L Bhojpur area. No significant differences were reported for Br, Sr., Cu, Zn, Se, etc. between the two.

Out of the water samples collected, arsenic, iron, copper, lead and sulphate content were found above the permissible limits of drinking water. The iron concentrations were found to be 1.46 and 1.70 mg/L, exceeding the permissible limits of the drinking water in the samples collected from the aquifers.

S. No.	**Particulars**	**Desirable Limit**	**Ground Water of Moradabad**	
			Badi Masjid (Site I)	**Bhojpur (Site II)**
1.0	Color, Hazen	5.00 max	4.00	4.00
2.0	Odor	Essentially Free; (Un Objectionable)	No smell (UN)	No smell (UN)
3.0	Turbidity (NTU), max	5.00	4.00	4.50
	pH	6.5–8.5	8.00	8.40
1.0	Chloride as (Cl$^{-)}$, mg/L, max	250.00	117.00	126.75
2.0	Sodium as Na^{+}, mg/L, max	200.00	63.00	79.30
3.0	Potassium as K^{+} mg/L	—	5.00	8.30
4.0	Sulphate as SO_4^{-2}; mg/L, max	200.00	256.00	220.20
5.0	Total Dissolved solid, mg/L, max	500.00	523.00	620.00
6.0	Calcium as (Ca^{+2}), mg/L, max	75.00	181.00	134.0
7.0	Magnesium as (Mg^{+2});,mg/L, max	300.00	245.00	331.00
8.0	Bicarbonate as HCO_3^{-1}; mg/L, max	150.00	221.00	190.10
9.0	Nitrate as NO_3^{-}; mg/L, max	45.00	53.03	50.03
11.0	Bromide as Br$^{-;}$ mg/L	—	0.01	0.02
12.0	Strontium as Sr. + 2; mg/L	—	1.00	1.13
13.0	Silica as SiO_2, mg/L	—	37.00	23.10
14.0	Boron as B, mg/L, max	0.05	0.04	0.03
15.0	Fluoride as F$^{-;}$ mg/L, max	1.50	0.16	0.15
16.0	Lead as (Pb)$^{;}$ mg/L, max	0.10	0.46	0.55
17.0	Total hardness as Carbonate ($CaCO_3$), mg/L, max	500.00	625.00	725.00
18.0	Arsenic as (Ar), mg/L, max	0.10	0.16	0.15
19.0	Cadmium as Cd, mg/L, max	0.0005	0.01	0.05
20.0	Copper as Cu, mg/L, max	0.30	0.0001	0.0001
21.0	Iron as (Fe), mg/L, max	0.30	1.46	1.70
22.0	Aluminum as Al; mg/L, max	0.03	0.07	0.05

Table 5.
Major and minor elements in groundwater of Moradabad (UP).

The boron content was found to be 0.04 and 0.03 mg/L. The silica content was found to be 37.00 and 23.10 mg/L. The nitrate content was found to be 53.03 (Badi Masjid area) and 50.11 00 mg/L (Bhojpur area) that are much above the desired limit.

All the major components (Ca, Fe, Pb, SO_4, NO_3 etc.) exceed the drinking water guideline limits in both samples. This could be due to rock characteristics in aquifers and pollution. Cadmium concentration was also above permissible limits. The bicarbonate concentrations were found to be 221.00 (Badi Masjid) & 190.00 mg/L in Bhojpur area exceeding the desirable limit of 150 mg/L maximum. The high manganese concentrations are with metal processing industries in the region. In fact, the high concentration of manganese are combined effects of industrial activity and the use of fertilizers in agricultural practices. Maximum iron level in groundwater sample was found to be 0.46 and 0.70 mg/L that may cause severe health problems such as cancer, diabetes, cirrhosis of liver, heart diseases and central nervous system, infertility etc. Besides, the presence of high concentration of iron further leads to adverse changes in color, odor and taste of the water available for the drinking.

Studies performed on groundwater of Moradabad (India) have indicated a decrease in the water quality. The groundwater samples of the study area indicate a slightly higher solid content due to presence of calcium, magnesium and iron content in the water collected. The hard water is possibly due to the presence of calcium and magnesium in the aquifers. The hard water may require chemical treatment before use for drinking or any other use. The overexploitation of groundwater by aluminum and brass industry of the region resulting into loss in the water quality. The ground water of Moradabad district in this study is found not suitable for use as drinking water due to its excessive hardness and the health risks involved due to presence of the contaminants such as As, Cd, Cr, Fe, Pb.

4. Field study II assessment of Glacial Lake water quality at Antarctica

Antarctica is a snow-white desert and is unique among continents. It is coldest, windiest, driest, thickest and most isolated place on this earth. More than 98% of its surfaces is composed of ice comprising more than 70% of the world's fresh water. The combination of ice, wind and cold make the life difficult to survive at low temperature. However, there are little patches during austral summer, where temperatures rise above freezing temperature over the rocks. These are known as oasis in an icy continent. One such oasis is in Antarctica with a number of glacial lakes of different sizes known as Schirmacher Oasis. (**Figure 2**) It is about 70 km south of Prince Astrid Coast and forms a part of Dronning Maud Land [22].

The Schirmacher Oasis area is about 100 km inside Princes Astrid coast of Queen Maud Land between the ice shelf and the continental ice. The Schirmacher Oasis has width of 3.5 km and length of about 20 km. The coordinates of the oasis are: Latitude 70°44′33″S-70046′30″S; Longitude 11°22′40″E-ll054′00″E [23].

The aim of this study is to assess the water quality of glacial lake of Antractica. Two lakes at Schirmacher Oasis, Antarctica were selected and surveyed during the austral summer. These included (a) Epishelf lake and (b) Pro-Glacier-fed lake. Water samples were collected from two lakes (**Figure 3**) and analyzed for physico-chemical parameters.

The results are presented in **Table 6** and were compared with prescribed specification of drinking water. The physical parameters like color, odor was found within the prescribed limit of standards for drinking water. Turbidity in all samples was below the prescribed limit of 5 NTU. No odor and objectional smell have been observed in water sample with no turbidity in both the Epishelf lake and Proglacial lake water.

Total dissolved solids were found to be 10 mg/L in one of the Epishelf lakes and 27 mg/L in post-glacial lake, which are much less than maximum limit prescribed for drinking water 500 mg/L. pH values of lake were found to be 6.5 and 7.5 and were within standard value. Calcium in Epishelf and Pro-glacial lake was found to be 2 and 1.5 mg/L (Pro-glacial lake).

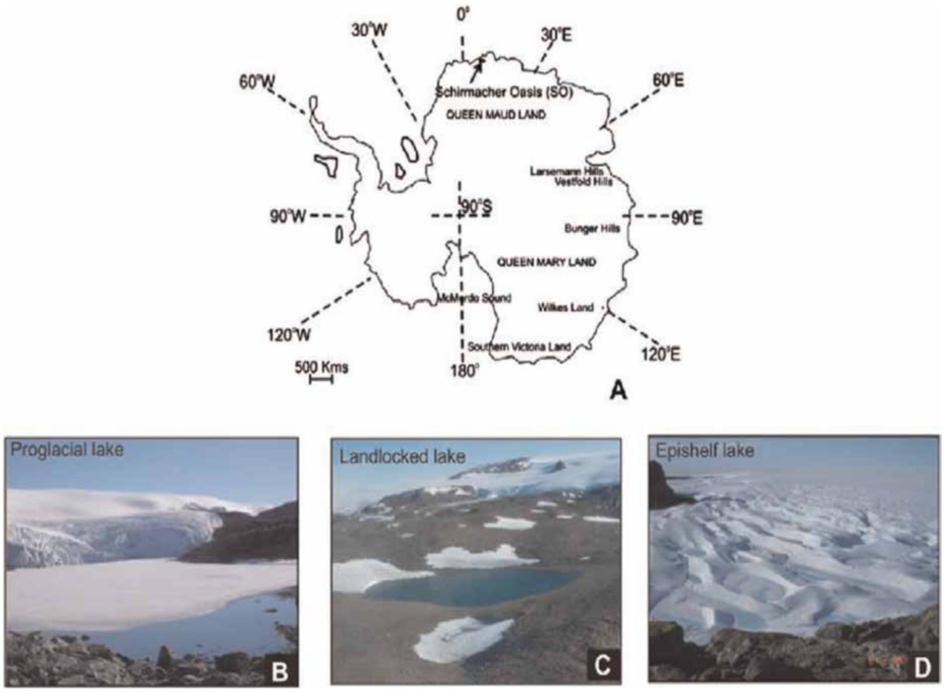

Figure 2.
Schirmacher Oasis and its lakes. (A) Map of Antartica, (B) Proglacial lake, (C) Land locked lake, (D) Epishelf lake.

Figure 3.
Water Sampling at Antarctica Lake.

S. No.	**Parameters**	**Desirable Limit**	**Antarctica Lake**	
			Epishelf Lake	**Pro-glacial Lake**
1.0	Color, Hazen, max	5	<5	<5
2.0	Odor	Un Objectionable	Un Objectionable	Un Objectionable
2.0	Turbidity NTU, max	5	2.00	4.00
3.0	pH	6.5–8.5	6.5	7.5
4.0	Total Dissolved Solids, mg/L, max	500	10.00	27.00
5.0	Chloride as Cl, mg/L, max	250	10.00	27.00
6.0	Nitrate as $NO_3^{-,}$ mg/L, max	100.00	30.00	50.00
7.0	Sulphate as $SO_4^{-2,}$ mg/L, max	200.00	1.00	6.00
8.0	Iron as (Fe), mg/L, max	0.3	0.07	0.08
9.0	Magnesium as (Mg), (mg/L), max	50.00	0.10	0.12
10.0	Calcium as (Ca), mg/L, max	75	2.0	1.5
11.0	Copper as (Cu), (mg/L), max	0.05	0.01	0.03
12.0	Manganese as (Mn), mg/L, max	0.1	0.01	0.03
13.0	Mercury as (Hg), mg/L, max	0.001	0.001	0.001
14.0	Cadmium as (Cd), mg/L, max	0.001	<0.001	<0.001
15.0	Selenium as (Se), mg/L, max	0.01	<0.005	<0.005
16.0	Arsenic as (Ar), mg/L, max	0.01	0.01	0.01
17.0	Lead as (Pb), mg/L, max	0.10	0.08	0.01
18.0	Zinc as (Zn), (mg/L), max	5.00	0.05	0.01
19.0	Chromium as (Cr), mg/L, max	0.005	0.01	0.01
20.0	Aluminum as (Al), mg/L, max	0.03	0.02	0.02
21.0	Boron as (Br), mg/L, max	15	<1.0	<1.00

Table 6.
Properties of Glacial Epishelf and pro-glacial lake water.

Nitrate was found to be 30.0 mg/L in case of Epishelf lake to continental ice and as high as 50.00 mg/L in case of Post glacial lake. Difference of the metal concentrations in Antarctic Lake (Fe, Mg, Cu, Hg, Cd, Se, Ar) was negligible and their concentrations were well within limit. The results indicate that the concentration of other metals in lake were found uniform where calcium, magnesium, boron, iron metals were found within the desired limits.

Aluminum (0.02 mg/L each in Epishelf Lake and Pro-glacial Lake), zinc (0.05 Epishelf Lake and 0.01 mg/L Pro-glacial Lake), copper (0.01 Epishelf Lake and 0.03 Pro-glacial Lake mg/L) were also found in low concentrations in all the water samples collected from these lakes.

In spite of the severe climatic conditions, such isolated, unaltered, and unpolluted polar ecosystems have been investigated by many research workers and found both the lakes free from any kind of pollution. Total dissolved solids are also very low conforming to the theory of poor solubility of metal salts in water at low temperature. The fresh water glacial lakes of Schrimacher Oasis, Antarctica, Epishelf lake and Pro-glacial lake, represent the standard physical and chemical properties of the lake water ideal for drinking purpose.

5. Field study III quality of sea water from Indian Bay to Bharti station at Antartica

The surface sea water samples were collected from Indian Bay (Maitri station, Queen Maud Land) to Bharti station (Larsemann Hills, Ingrid Christenson Coast) (**Figure 4**) in the Southern Ocean during the Indian Scientific Expedition to Antarctica. Eight sampling points were selected at various locations namely S-41, S-43, S-45, S-47, S-49, S-51, S-53 and S-55 from Indian bay to Larsemann hills in east Antarctica. (**Figure 5**).

Sea water samples collected from eight sampling location in Southern Ocean from latitude S 67°16′10.9″ and longitude E 28°39′64.5″ to latitude S 69°17′42.9″ and longitude E 76°13′23.3″ [23] were analyzed for various metals like copper (Cu), lead (Pb), cadmium (Cd), zinc (Zn), nickel (Ni) and chromium (Cr). The concentration of heavy metals and other major elements like sodium, potassium, calcium, magnesium, boron were measured in sea water samples [24].

Sodium, potassium, calcium, magnesium, boron and iron metals were found to be the dominant constituents among the sea water contents (**Tables 7–9**). Maximum sodium was found to be 54750.45 μg/cc at S-45 site and minimum was 39670.45 μg/cc at S-49. Maximum potassium was found to be 2619.17 μg/cc at S-45 site and minimum was 2072.29 μg/cc at S-49 sampling point. Maximum calcium was found to be 2258.12 μg/cc at S-45 site and minimum was 1642.15 μg/cc at S-49.

The magnesium was found to be 5987.13 μg/cc at S-45 sampling station and 4398.0 μg/cc at S-49. The boron was found to be 109.23 μg/cc at S-47 site and 8.96 μg/cc at S-49. The iron concentration was found to be 30.69 μg/cc at S-43 site and 1.3 μg/cc at S-55 near Bharti station at Larsemann Hills.

Besides these, aluminum (0.397–15.03 μg/cc) and zinc (0.273–1.9 μg/cc) were also present in significant quantities in all sea water samples. Cadmium was found only in

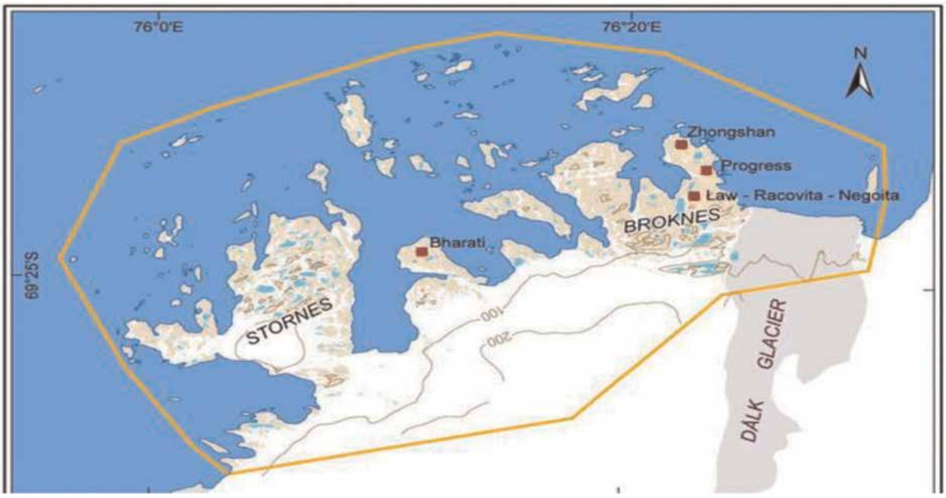

Figure 4.
Larsemann Hill, Ingrind Christern, Antarctica.

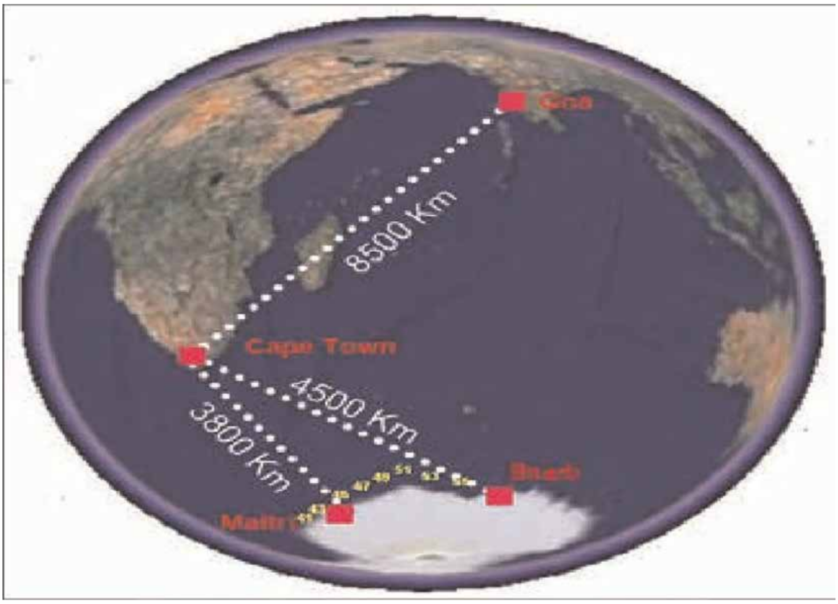

Figure 5.
Location and sampling in Southern Ocean.

one sample near Maitri station as well as in one sample near Bharti station, which shows the heterogeneous distribution concept over cadmium introduction into sea ecosystems. Maximum cadmium was found to be 0.061 μg/cc at S-43 site and 0.036 μg/cc at S-53, whereas it was found below detection limit in all remaining samples (**Tables 7–9**). Similar trend was observed for cobalt metal in sea water samples collected from coastal regions of Southern Ocean.

Maximum cobalt was found to be 0.123 μg/cc at S-43 site and 0.032 μg/cc at S-53, while it was found below detection limit in all remaining samples. Chromium concentration was below detection level in all seawater samples. Selenium was also below detection level in all samples. Lead was present in only two samples collected from S-51(1.24 μg/cc) and S-55 (1.128 μg/cc). Nickel was also one of the rarest metals in seawater as it was detected in only one sample at site S-55 (0.16 μg/cc). Beside these,

S. No.	Sample Code	Latitude	Longitude	pH	Temperature (C)
1.0	S-41	S 67°16′10.9″	E 28°39′64.5″	8.0	−0.8
2.0	S-43	S 66°14′27.6″	E 36°41′36.9	7.8	−0.5
3.0	S-45	S 65°21′29.3″	E 43°21′01.7″	7.7	−0.6
4.0	S-47	S 63°42′10.9″	E 52°11′64.5	8.0	−0.8
5.0	S-49	S 65°32′41.7″	E 58°05′56.5″	8.0	−1.5
6.0	S-51	S 66°11′32.0″	E 68°49′03.6″	7.3	−0.6
7.0	S-53	S 67°23′12.0″	E 73°29′50.5″	7.8	−.10
8.0	S-55	S 69°17′42.9″	E 76°13′23.3″	7.2	−0.9

Table 7.
Sea water samples collected from Southern Ocean.

S. No.	Sample Code	Al	B	Ca	Fe	K	Mg	Na	Zn
1.0	S-41	15.031	22.839	1874.151	14.708	2294.668	5161.877	47149.200	1.178
2.0	S-43	3.291	24.392	2149.401	30.695	2596.668	5947.127	52554.200	1.113
3.0	S-45	0.922	12.759	2258.138	16.770	2619.168	5987.127	54750.450	0.465
4.0	S-47	1.592	109.22	1767.65	13.845	2248.543	4972.377	45400.450	0.813
5.0	S-49	1.055	8.966	1642.151	10.445	2072.293	4398.002	139670.450	0.315
6.0	S-51	0.397	11.500	2022.901	10.195	2530.043	5620.627	52916.700	0.273
7.0	S-53	0.844	26.642	2128.526	14.820	2539.418	5740.3775	3267.950	1.900
8.0	S-55	4.944	13.723	1652.026	1.258	2128.543	4761.377	43052.950	0.503
	Detection Limit	0.018	0.025	0.015	0.010	0.010	0.02	0.015	

Table 8.
Major constituents in seawater samples collected from Southern Ocean (In µg/cc).

S.No.	Sample Code	Cd	Co	Cr	Cu	Mn	Mo	Ni	Se
1.0	S-41	BDL	BDL	BDL	0.235	0.059	0.103	BDL	BDL
2.0	S-43	0.061	0.123	BDL	0.206	0.074	0.186	BDL	BDL
3.0	S-45	BDL	BDL	BDL	0.088	0.030	0.338	BDL	BDL
4.0	S-47	BDL	BDL	BDL	0.043	0.030	0.363	BDL	BDL
5.0	S-49	BDL	BDL	BDL	0.073	0.023	0.541	BDL	BDL
6.0	S-51	BDL	BDL	BDL	0.1091	0.011	0.416	BDL	BDL
7.0	S-53	0.036	0.032	BDL	0.163	0.032	0.771	BDL	BDL
8.0	S-55	BDL	BDL	BDL	0.02	0.002	0.516	1.160	1.5
	Detection Limit	0.027	0.06	0.022	0.02	0.002	0.016	0.08	1.5

Table 9.
Quantities of major constituents in Seawater samples (in µg/cc).

S. No.	Sample Code	As	Ba	P	Sr
1.0	S-41	BDL	0.712	BDL	31.875
2.0	S-43	BDL	0.136	BDL	22.875
3.0	S-45	BDL	BDL	BDL	53.000
4.0	S-47	1.571	0.027	BDL	29.625
5.0	S-49	BDL	0.090	BDL	29.375
6.0	S-51	BDL	0.041	BDL	34.500
7.0	S-53	BDL	0.017	0.213	33.625
8.0	S-55	BDL	BDL	BDL	33.875
	Detection Limit	1.50	0.02	0.04	0.01
Remarks: BDL Below Detection Limit.					

Table 10.
Major constituents in seawater samples collected from Southern Ocean (in ug/CC).

copper (0.043–0.235 μg/cc), manganese (0.011–0.074 μg/cc) and molybdenum (0.103–0.771 μg/cc) were also present in all the collected sea water samples in trace quantities. However, strontium was found in seawater samples of Southern Ocean [23] ranging from 22.87 – 53.00 μg/cc (**Table 10**).

6. Comparative study of ground, glacial and sea water

The water quality of various kinds of water collected during the field study are summarized in **Table 11**. The water quality of groundwater was found satisfactory in terms of copper, arsenic, lead and chromium concentrations at Moradabad district. Iron concentration was observed beyond permissible limit in more than 50% of the samples collected. Maximum iron level in groundwater sample was 3820 ppb and that in surface water sample 6294 ppb whereas the permissible limit is 300 ppb.

S. No.	Parameters	Field Water		
		Ground Water	**Glacial lake**	**Southern Ocean**
1.0	Color, Hazen, max	4.0	<5	<5
2.0	Odor	Un Objectionable	Un Objectionable	Un Objectionable
2.0	Turbidity NTU, max	2.00	4.00	—
3.0	pH	8.00–8.40	6.5–7.5	7.2–8.0
5.0	Chloride as Cl, mg/L, max	117.00–126.00	10.00–27.00	750.00–1345.00
7.0	Sulphate as $SO_4^{-2,}$ mg/L, max	220.20–256.00	1.00–6.00	650.00–700.00
8.0	Iron as (Fe), mg/L, max	1.46–1.70	0.07–0.08	0.001–0.003
9.0	Magnesium as (Mg), (mg/L), max	245.00–331.00	0.10	295.00–594.00
10.0	Calcium as (Ca), mg/L, max	134.00–181.00	1.5–2.00	0.00016–0.00020
11.0	Copper as (Cu), (mg/L), max	0.0001	0.01–0.03	0.04–0.235
12.0	Manganese as (Mn), mg/L, max	—	0.01	0.0005
13.0	Mercury as (Hg), mg/L, max	< 0.001	0.001	—
14.0	Cadmium as (Cd), mg/L, max	0.01–0.05	0.001	BDL
15.0	Selenium as (Se), mg/L, max	<0.005	0.005	0.00015
16.0	Arsenic as (Ar), mg/L, max	0.15–0.16	0.01	BDL
17.0	Lead as (Pb), mg/L, max	0.46–0.55	0.01–0.08	0.0001
18.0	Zinc as (Zn), (mg/L), max	0.05	0.03	0.0004
19.0	Chromium as (Cr), mg/L, max	0.01	0.01	—
20.0	Aluminum as (Al), mg/L, max	0.05–0.07	0.02	0.0001
21.0	Boron as (B), mg/L, max	0.03–0.04	1.00	0.002
23.0	Potassium as (Ka), mg/L, max Potassium	5.00–8.30	—	0.0002

Table 11.
Comparative properties of water samples collected during the field study.

The glacial lakes fresh water of Schrimacher Oasis, Antarctica, Epishelf lake and Pro-glacial lake, represent the standard physical and chemical properties of the lake water ideal for drinking purpose as the physical parameters like color, odor was found within the prescribed limit of standards for drinking water. Turbidity in all samples was much below the prescribed limit of 5 NTU. Total dissolved solids were found to be 10 mg/L in one of the Epishelf lakes and 27 mg/L in Post-glacial lake, which are much less than maximum limit prescribed for drinking water 500 mg/L. pH values of lake were found to be 6.5 and 7.5 and were within standard value. Calcium 1.5–2.0 mg/L, Nitrate 30.0–50 mg/L and the metal concentrations in (Fe, Mg, Cu, Hg, Cd, Se, Ar) were well within limit. The concentration of other metals in lake were found uniform where calcium, magnesium, boron, iron metals were found within the desired limits. Aluminum (0.02 mg/L each in Epishelf Lake and Pro-glacial Lake), zinc (0.05 Epishelf Lake & 0.01 mg/L Pro-glacial Lake), copper (0.01 Epishelf Lake & 0.03 Pro-glacial Lake mg/L) were also found in low concentrations in all the water samples collected from glacial lakes of Antarctica.

In southern ocean water, the concentrations of heavy metals Cu, Pb, Cd, Zn, Ni, Cr, were found uniformly in entire selected stretch of Southern Ocean. Sodium, potassium, calcium, magnesium, boron and iron metals were found as the dominant constituents among the sea water. Aluminum (0.3–15.0 μg/cc), zinc (0.27–1.9 μg/cc), copper (0.04–0.23 μg/cc) and molybdenum (0.10–0.77 μg/cc) were also found in sufficient concentrations in all the seawater samples. Strontium was also one of the dominant alkaline earth metals in sea water. However, the concentration of strontium (22.8–53.0 μg/cc) was found to be evenly distributed from Indian Bay to Larsemann Hills in east Antarctica. Selenium and chromium were the rarest metals in seawater as these were below detection limit in all samples.

The overload of the major and minor elements beyond the permissible limits causes severe health problems such as liver cancer, diabetes, cirrhosis of liver, diseases related to heart and central nervous system, infertility etc. and thus needs to be monitored on regular basis.

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High levels of toxic elements have harmful effects on all aspects of the environment (water, air, plants, etc.). Trace elements, many of which are heavy metals, can compromise soil quality, cause toxicity to plants, and ultimately contaminate the food chain. This book summarizes the effects of trace elements in the environment. Section 1 discusses the influence of trace elements on soil and the ecosystem and Section 2 examines the influence of trace elements on water. The book also discusses microplastics, which accumulate trace elements and pollute the oceans, harming both aquatic and human life.

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