4.1. TRACE ELEMENTS: CONCEPTUAL BACKGROUND

Trace elements generally refer to elements that occur in natural and modified or perturbed environments in small amounts and that, when present in imbalanced (excessive or deficient) bioavailable concentrations, are harmful to the living organisms especially human beings.

Depending on the field of study, the term trace element is loosely used in literature and is known by different names as potentially toxic elements, heavy metals, micronutrients, and minor elements. The term "potentially toxic elements" is a recent term, meant to illustrate that while some elements are toxic to humans and plants, not all elements are toxic at all concentrations. In fact, micronutrients (e.g., Cu, I, Zn,) are necessary for life in small amounts (Alloway, 1995). Heavy metals are elements having densities greater than 5.0 g cm^{-3} and denote metals and metalloids that are associated with pollution and toxicity but also include essential elements. Over the past two decades, the term 'heavy metals' has been widely used… and related to chemical hazards. It is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or eco-toxicity. This term is based on various criteria (i.e., atomic weight, atomic number, density, chemical properties etc.). Chemists define trace elements, or transition metals, as those elements which fall in the center of the periodic table (between Group IIA and IIIA) and exhibit partial d-orbital filling. Other chemical definitions are based on density (greater than 5 g cm^{-3}), atomic weight (greater than that of sodium), and metallic properties. Soil fertility experts define trace elements as those elements that are essential to plant growth in small amounts, but toxic to plants at higher concentrations. Toxicologists consider trace elements those elements distributed into the environment by industrial processes that are detrimental to human health or the environment. This definition is not based on abundance in the environment, or density or metallic properties, but solely on the adverse effects of the element in the environment. Earth scientists define trace elements as those elements in rocks other than the eight most abundant rock-forming elements (i.e., O, Si, Al, Fe, Ca, Na, K, and Mg) found in the Earth's crust or natural environment. Geochemists use the term "trace elements" for the elements present in the earth's crust in concentrations less than 0.1% (<1000 mg kg^{-1}). In biochemical and biomedical research, trace elements are believed to be those elements that are ordinarily present in plant or animal including human beings tissues in concentrations less than 0.01% (<100 mg kg^{-1}) of the organism's dry weight. In food and nutrition science, a trace element may be defined as an element that is of common occurrence but whose concentration rarely exceeds 20 ppm in the foodstuffs consumed. It is to be noted here that some of the nutritive trace elements (e.g., Mn, Zn) may often exceed this concentration (Adriano, 2001).

4.1.1. Goldschmidt's Classification

It seems appropriate to briefly highlight the affinities and tendencies of trace elements in the natural phases of environment through Goldschmidt's classification of elements of the periodic table. Most of the elements of periodic table fall into the ambit of trace elements and so, this is a good place to reflect on the geochemical characteristics of the elements. Goldschmidt recognized four broad categories of elements: atmophile, lithophile, chalcophile, and siderophile (White, 2012) (Table 4.1). Atmophile elements are generally extremely volatile (i.e., they form gases or liquids at the surface of the Earth) and are concentrated in the atmosphere and hydrosphere. Lithophile, siderophile and chalcophile refer to the tendency of the element to partition into a silicate, metal, or sulfide liquid respectively. Lithophile elements are those showing an affinity and tendency for silicate phases and are concentrated in the silicate portion (crust and mantle) of the earth. Siderophile elements have an affinity for a metallic liquid phase. They are depleted in the silicate portion of the earth and presumably concentrated in the core. Chalcophile elements have an affinity for a sulfide liquid phase. They are also exhausted in the silicate earth and may be concentrated in the core. Many sulfide ore deposits originated from aqueous fluids rather than sulfide liquid. A chalcophile element need not essentially be concentrated in such deposits. As it works out, however, they generally are. Most elements that are siderophile are usually also somewhat chalcophile and vice versa.

The trace elements of copper and zinc behave as chalcophile while as iodine is lithophile in nature. Sometimes zinc also shows lithophile character.

Table 4.1: Goldschmidt's Classification of the Elements

Atmophile	Chalcophile	Lithophile	Siderophile
H, N, O	**Cu**, Ag, Be, Mg, Ca, Sr, Ba, Ga, In, Tl, Ge, Sn, Pb, As, Sb, Bi, S, Se, Te, Fe, Mo, Os, Ru, Rh, Pd	Li, Na, K, Rb, Cs, He, Ne, Ar, Kr, Xe, B, Al, Sc, Y, Si, Ti, Zr, Hf, Th, P, V, Nb, Ta, O, Cr, U, H, F, Cl, Br, **I**, Fe, Mn, **Zn**, Ga	Fe^1, Co^1, Ni^1, Ru, Rh, Pd, Zn, Cd, Hg, Os, Ir, Pt, Au, Re^2, Mo^2, Ge^1, Sn^1, W^3, C^3, Cu^1, Ga^1, As^2, Sb^2

1=Chalcophile and lithophile in the earth's crust
2=Chalcophile in the earth's crust
3=Lithophile in the earth's crust

Source: White, 2012

4.1.2. Trace Elements in Soils

Trace elements in soils are derived from the parent materials through the processes of weathering and may be increased substantially by man’s industrial and other activities (Kabata-Pendias and Pendias, 2001). There are generally higher quantities of trace elements in igneous and metamorphic rocks than in sedimentary rocks. They account for 95% of the earth’s crust and remaining 5% is contributed by sedimentary rocks. Of the sedimentary rocks 80% are shales, 15% sandstones and 5% limestones. Sedimentary rocks are the most important soil parent material since they overlie most igneous formations, and account for 75% of the outcrops at the earth’s surface (Wedepohl, 1991).

Trace elements in soils by and large tend to be immobile. Some transfer of trace elements in the A horizon occurs with plant uptake and nutrient cycling. However, trace elements in soils are generally insoluble and exhibit strong adsorption.

Soil is the main source of trace elements for plants as micronutrients. It is also a direct source of these elements to humans due to soil ingestion affected by “pica-soil”, geophagia, dust inhalation, and absorption through skin. The soil-plant transfer of trace elements is a part of chemical element cycling in nature. It is a very complex process governed by several factors, both natural and affected by humans.

Soils contain trace elements of various origins: (i) lithogenic – inherited from the lithosphere (parent material), (ii) pedogenic – from lithogenic sources modified due to soil-forming processes, and (iii) anthropogenic – elements deposited onto and/or into soils as results of human's activities especially agriculture, mining, industry and sewage disposal. Soil processes and anthropogenic factors control the behavior of all these elements (Table 4.2). It has been assumed that the behavior of trace elements in soils and in result their phytoavailability differ according to their origin. Several recent reports have shown that regardless of the forms of the anthropogenic trace metals, their availability to plants is significantly higher than those of natural origin (Kabata-Pendias and Pendias, 2001).

Table 4.2: Influence of Origin of Trace Elements on their Behavior in Soil

Origin	Association	Phase	Form	Bioavailability
Lithogenic	Minerals or attached to minerals	Solid	Residual	Very slight
Pedogenic	CC, SOM, OX	Solid	Fixed by CM, SOM, OX	Slight
	Simple and complex ions	Aqueous	Free ions and non-ionic forms	Easy
Anthropogenic	Minerals, SOM, PS	Solid	Mainly exchangeable and chelated	Moderate and easy
Pedogenic and anthropogenic	Simple and complexed ions	Aqueous	Free ions and non-ionic forms	Easy

Source: Kabata-Pendias and Pendias, 2001

Note: CC = clay content, SOM= soil organic matter, OX= oxides and hydroxides, PS= particle surface

Weathering is the basic soil-forming process which involves a complex set of interactions between the elements of lithosphere, atmosphere, and hydrosphere that occur in the biosphere and are powered by solar energy. The behavior of elements during weathering and pedogenic processes are highly associated with their geochemical properties, which are base for the geochemical classification (Table 4.3). The majority of elements reveal lithophilic character, which indicates a tendency to form oxygen compounds, as well as silicates, carbonates, phosphates, and sulfates.

Table 4.3: Geochemical Classification of some Trace Elements

Siderophile	Chalcophile	Lithophile
Mo, Co, Au, Os, Ni, As, Ge, Sn, Ru,	Ru, Cu, Ag, Zn, Cd, Hg, Ga, In, Tl, Pb, As, Sb,	Li, Rb, Cs, Be. Ba, Sr, Ra, Zr, Hf, V, Ta, Cr, Mo, Mn, Zn,B, Lanthanides, Actinides, Halogens

Source: Kabata-Pendias and Mukherjee, 2007.

Clay minerals, the main products of weathering and soil development, are due to water-rock interaction processes. Two types of compounds released by organic matter or organisms are believed to be particularly involved in weathering processes: carbonic acid, formed from the CO_2 released during decay of organic matter, and organic chelates.

Pedogenic processes cannot be easily distinguished from weathering processes as they take place simultaneously and at the same sites; most often they are closely interrelated. The principal types of these processes include: (i) podzolization, (ii) alkalization, (iii) aluminization, (iv) laterization, (v) salinization, and (vi) hydromorphic processes. All these processes control the distribution and behavior of trace elements in distinct layers of soil profiles that are related to sorption and desorption and to the formation of various species of elements.

The main soil parameters governing these processes are: (i) pH and Eh values, (ii) amount and mineral composition of the fine granulometric fraction (<0.2 mm), (iii) amount and kind of organic matter, (iv) oxides and hydroxides of Fe, Mn and Al, and (v) microorganisms.

Smith and Huyck (1999) described mobility of metal ions under different environmental settings. Although it is rather difficult to predict trace element mobility in soils and other terrestrial ecosystems, the authors referred to the capacity of an element to move with fluids after dissolution in surficial environments. The following conditions and behavior of trace elements were distinguished:

- Oxidizing and acid, pH <3: *(a)* very mobile – Cd, Co, Cu, Ni, and Zn, *(b)* mobile – Hg, Mn, Re, and V, and *(c)* somewhat mobile and scarcely mobile – all other metals
- Oxidizing in the absence of abundant Fe-rich particles, pH >5: *(a)* very mobile – Cd and Zn, *(b)* mobile – Mo, Re, Se, Sr, Te, and V, and *(c)* somewhat mobile and scarcely mobile – all other metals
- Oxidizing with abundant Fe-rich particulates, pH >5: *(a)* very mobile – none, *(b)* mobile – Cd and Zn, and *(c)* somewhat mobile and scarcely mobile – all other metals

- Reducing in the absence of hydrogen sulfide, pH >5: *(a)* very mobile – none, *(b)* mobile – Cd, Cu, Fe, Mn, Pb, Sr, and Zn, and *(c)* somewhat mobile and scarcely mobile – all other metals
- Reducing with hydrogen sulfide, pH >5: *(a)* very mobile – none, *(b)* mobile – Mn and Sr, and *(c)* scarcely mobile to immobile – all other metals

Other soil minerals such as, carbonates, phosphates, sulfides, sulfates and chlorides may have important influences on the distribution and behavior of trace elements in soils developed under specific geological and climatic conditions (Kabata-Pendias and Sadurski, 2004).

The effects of soil characteristics on trace element concentrations in soils have been studied by many soil scientists. In brief, seven factors determine the fate of trace elements in soil: soil pH, cation exchange capacity (CEC), anion exchange capacity (AEC), organic matter content, clay content and type, oxide content and type, and redox potential. Trace element sorption depends on pH and whether the element occurs in anionic or cationic form. Cation sorption increases with pH showing a steep increase within a small pH range, which is known as the adsorption edge. Sorption of anions shows a maximum when the pH is equal to the pKa of the corresponding acid. This phenomenon is known as the adsorption envelope. A high CEC or AEC allows a soil to hold more cations or anions, respectively, than a soil with a low CEC or AEC. The exchange capacity of a soil is related to other soil properties, such as organic matter, clay, and oxide content. Soil organic matter retains elements both through its exchange capacity and through specific sorption, especially for elements such as Cu, Co, Mn, and B. A soil high in clay has more surface area for elements to adsorb and a higher CEC than a soil low in clay. Also, 2:1 clays usually have a higher CEC than 1:1 clays. Redox potential of a soil can change the solubility of an element. When a soil is reduced, some elements such as Fe, Cd, Ni, and Pb can form insoluble sulfide precipitates.

Soil solution: Transfer of trace elements between soil phases should be considered as the main process controlling their behavior and bioavailability. The aqueous phase of the soil (soil solution) is composed of water with a colloidal suspension, free and/or complexed, and dissolved substances of various compounds, including bio-inorganic complexes. Concentrations of trace elements in soil solution are closely correlated with their mobility and availability. In this phase, the minerals are highly bioavailable.

4.1.3. Trace Elements in Water

Freshwater: Water plays essential functions in geochemical and biochemical processes. It is also a main carrier for all chemical elements; its amount and chemical composition control element cycling in water-air-soil systems. Thus, water is probably the most studied medium that governs the forms of trace elements of which Cr, Se, Cu, As, Pb, Cd, and Hg have been studied the most frequently (Das, *et al*., 2001 cited in Kabata-Pendias and Mukherjee, 2007).

The main ions dissolved in waters are: Na^+, K^+, Mg^+, Ca^+, Cl^-, SO_4^{2-}, HCO_3^-, and these also occur as different species and variable concentrations adsorbed by inorganic and organic colloidal particles. So-called secondary elements (C, N, P, S, and Si) as well as trace elements occur in all water systems, in highly variable concentrations, depending on several factors of which pollution plays a significant role. Water pollution by trace elements is an important factor in both geochemical cycling of trace elements and in environmental health. The water cycle of trace elements plays a significant role in each aquatic and terrestrial ecosystem. Especially cycling of trace metals in the oceans and their role in the photosynthetic fixation of carbon by phytoplankton is of great importance.

Most trace elements especially trace metals; do not remain in soluble forms in waters, for a longer period. They are present mainly as suspended colloids or are fixed by organic and mineral substances. On the other hand, easily volatile elements such as Br and I can reach higher concentrations in surface waters, from which they can easily, vaporize under favorable climatic conditions. Trace element speciation in water control their behavior and toxicological risk. The bioavailability of trace elements to both unicellular and higher organisms is the result of complex reactions between the ligands present in the aqueous medium and those of living cells. Practically, all fractions of trace elements, truly dissolved and associated with suspended particulate matter, may be bioavailable to aquatic organisms.

Ground waters: About 99% of the world's fresh, available water is groundwater that is a basic source of the domestic, industrial, and agricultural water supply (Bhattacharya and Mukherjee, 2002). The transfer of trace elements depends on several properties of the soil media as well as on the geochemical properties of an element. Thus, elements that predominate in soils in easily mobile forms are of higher hazard than those that are relatively stable in prevalent soil conditions.

The chemical quality of groundwater is of special importance, as it is a source of both drinking and irrigation waters and therefore, has a significant impact on trace element transfer into the food chain.

Drinking waters: Concentration of trace elements in drinking water is of special concern in relation to health. Several ecological studies have indicated an influence of the quality of drinking water on some diseases. Liu *et al*. (2000, cited in Kabata-Pendias and Mukherjee, 2007) have reported significantly increased levels of Ti, V, Fe, Cu and Sr in drinking water collected from areas with high incidence of gastric carcinoma.

The quality of drinking water is very important since it is consumed every day during the whole lifetime. Momot and Synzynys (2005) have calculated daily intake of several metals by inhabitants of Obninsk (Middle Russia) and assessed that it may be a risk of oncological diseases to 4 of 100 persons and of non-oncological diseases to 1 of 1, 000 persons. The daily doses of metals to this population are as follows (in $\mu g\ kg^{-1}$ BW): Ag-<1.0; Al-4.01; As-1.28; B-2.57; Be-0.04; Cd-1.03; Cr-2.1; Hg-0.17; Pb-0.43; and Zn-0.17.

4.1.4. Trace Elements in Biosphere

The biosphere is the natural environment of living organisms and is the complex biological epidermis of the Earth existing at the interface of the three major realms of the natural environment i.e., lithosphere, hydrosphere and atmosphere, characterized by continuous cycling of chemical elements and flow of energy. There is a homeostatic interrelationship between the nonliving media (abiotic compartments) and the living organisms (biotic compartments). However, a significant part of the natural environment has already been considerably modified by humans, and these processes will continue.

Most of the chemical elements for life including humans on the land are supplied mainly from the soil (Kabata-Pendias and Mukherjee, 2007) and secondly from water. The concentration of trace elements in different phases of natural environment creates several problems for plants, animals and humans associated either with their deficiency or with excess. Thus, questions of how and how much of an element is taken up by organisms and what is its concentration in the living systems have been hot topics of research in recent decades. Usually, the quantitative differences between essential or required amounts and excesses/deficiencies of trace elements are very small. The bioavailability of these elements is variable and is controlled by specific properties of abiotic and biotic media as well as by physico-chemical properties of a given element.

The biochemical functions of essential trace elements have been unraveled by many great scientists. Essential trace elements are known to have a biological role, often as cofactors or part of cofactor in enzymes and as structural elements in proteins. Some of them also are used in several processes of electron transfer. Non-essential elements seem to be involved in vital processes but their biochemical functions are not yet understood. The essentiality of other trace elements, possible at very minor concentrations, may be revealed in the future. Most of trace elements that are essential to humans are also essential to plants. Unfortunately, contents of most elements that may be harmful to humans and animals are not toxic to plants. This has created an amplified transfer of some elements in the food chain.

The survival of mankind is somehow dependent on foods of different varieties. Lack of food as well as bad quality of food has created throughout the centuries serious health problems for people. Nowadays it has been found that more than 3 billion people worldwide suffer from either deficiency or toxicity of some trace elements.

It seems pertinent to remind Paracelsus' (1538) statement cited in Kabata-Pendias and Mukherjee, 2007:

"All substances are poisonous, there are none which is not a poison; the right dose is what differentiates a poison from a remedy"**.**

4.1.5. Trace Elements in Human Beings

Since the father of human beings, Aadam (AS), was created from clay and all human beings take foods (including air and water) derived from the earth system, they like other living organisms have developed their internal biochemistry in close connection to the composition of the natural environment. Humans, as well as all mammals, unlike prokaryotes and other lower organisms, are not able to adapt easily to any change in the chemical composition of their surroundings. Variations in trace element concentrations are of vital importance. The homeostatic balance of chemical elements in any organism is the basic requirement of good health. Ionic relationships within any organism are very fragile and governed by several factors. Their balance is controlled by factors such as bioavailability of an element, capability of tissues or organs to accumulate and excrete an element and by interactions among elements that might vary from antagonistic to synergistic depending mainly on their quantitative ratio.

Trace elements, both essential and non-essential, play fundamental roles in the normal development and health of humans. They commonly play the functions of metallo-enzymes. The elements that are essential for the activity of physiologically important enzymes and function as catalysts are Cu, Zn, and Fe (Kleczkowski *et al*., 2004 cited in Kabata-Pendias and Mukherjee, 2007).

Geochemical anomalies of the bedrock, variable soil properties, agricultural practices, and anthropogenic inputs influence the trace element contents of food crops and other plants resulting in a dietary intake of trace elements. Diseases and/or impaired metabolism, attributable to trace element deficiency or excess, are sometimes not easy to assess, especially at early stages of development. Moreover, effects of their imbalanced supply may be quite variable (Table 4.4).

Table 4.4: Consequences of Deficiency and Excess of Essential Trace Elements

Element	Deficiency	Excess
Iodine (I)	Goiter, cretinism, decreased fertility rate increased stillbirths, spontaneous abortion rates, increased perinatal and infant mortality	Hyperthyroidism {rapid heart rate, trembling, excessive sweating, lack of sleep, and loss of weight and strength}
Copper (Cu)	Anemia, bone fractures {osteoporosis, osteopeneisis}, hypopigmentation, prematurity growth retardation (children), fertility, hair and weight loss, menke's disease	Wilson's disease, vomiting, diarrhea, hemolytic anemia, renal & liver damage
Zinc (Zn)	Anorexia, anemia, impaired keratosis, teratogenic effects, alopecia, dermatitis, growth retardation, appetite loss, impaired wound healing and skin lesions, impaired taste/smell, diabetes	Nausea, vomiting, fever/diarrhea, epigastric pain, anemia, fatigue, dehydration, tissue lesions
Selenium (Se)	Cardiac myopathy, asteoarthropathy,	Selenosis, liver and kidney damage, cancer, fetal toxicity
Chromium (Cr)	Defective glucose metabolism, hyperlipidemia	Lesions in skin, lung cancer
Molybdenum (Mo)	Defects in keratosis, growth retardation	Molybdenosis, defect in Cu metabolism, diarrhea

Source: Kabata-Pendias and Mukherjee, 2007

Iodine deficiency occurs commonly in regions with light sandy soils developed from young geologic formations. It is not likely to occur in close-to-sea areas.

Contents of trace elements in the human body vary greatly, and are controlled by several external (local environment and foods grown) and internal (habits and diseases) factors.

Exposure sources: The general population is exposed to trace elements mainly by ingestion of drinking water and food and by inhalation of air. Adults inhale daily approximately 20 m^3 of air and intake about (above) 2 L of water. Human beings take trace elements from various sources by three absorption pathways:

- Gastrointestinal tract, from: food, water, drugs, soil, and aerosols
- Respiratory tract, from: aerosols, and gases
- Skin, from: soil, water, aerosols, gases, and others

The food chain is considered the main tract for transfer of trace elements to humans. There are several possible routes of their (TE) transfer from soil to human via food chain:

- Soil→plant→animal→human
- Soil→plant→human
- Soil→animal→human
- Soil→microbiota, mezobiota→human
- Soil→airborne dust→animal, human
- Soil-geophagia→human
- Soil→groundwater→drinking water→animal, human
- Soil/sediment→surface water→aquatic biota→human

A special source of some trace metals is associated with various orthopedic and stomatological metallic implants. Various alloys are used for orthopedic surgery. The most commonly are the alloys of Co, Cr, Mo, Ni and W. Metals are released into body tissues, due to the corrosion (in some cases due to the abrasion) of alloys

Trace element intake due to soil ingestion both involuntary and deliberate may be significant especially for children. Ingested mean amounts of some metals by children, 1–4 years of age, were as follows (in mg d^{-1}): Al-136; Ti-208; V-148; Zr-113; and Y-97 (Calabrese and Stanek cited in Abrahams, 2005). Significantly, however, the most often unrecognized sources of ingested metals are those released from kitchen utensils. It has been reported that cookware, especially enamel and stainless steel, may be a source of Cr, Ni, Zn, and Fe in popular soups.

The appreciation of the recommended dietary allowance (RDA) of essential trace elements is very important for the human health. It refers to the average daily dietary intake level that is sufficient to meet the nutrient requirement of nearly all (97-98 percent) health individuals in a particular life stage and gender group (ICMR, 2010). A group of experts of ICMR modified RDA of Indians taking into consideration the guidelines given by FAO/WHO. The table 4.5 gives the RDA for Indians of three important trace elements as:

Table 4.5: Recommended Dietary Allowances of I, Cu and Zn for Indians

Trace Element	Group	RDA
Iodine	Infants and Children (up to 5 years)	90 µg d^{-1}
	School Children (6-11 years)	120 µg d^{-1}
	Adolescents and Adults	150 µg d^{-1}
	Pregnant/Lactating Women	200 µg d^{-1}
Copper	Adults	1.35 mg d^{-1}
Zinc	Adult Man and Lactating/Pregnant Woman	12 mg d^{-1}
	Adult Woman	10 mg d^{-1}
	Children (1-9 years)	5-8 mg d^{-1}
	Boys and Girls (10-17 years)	9-12 mg d^{-1}

Source: ICMR, 2010.

4.2. HUMAN HEALTH: CONCEPT

Human health is a very complex topic to be dealt with. Many scholars have defined it differently. Herein, only the definition of human health is given that has been adopted by WHO in its World Health Assembly held in 1948. According to W.H.O., "Health is a state of complete physical, mental and social well-being and not merely the absence of disease or infirmity". It is a very comprehensive definition that covers two primary aspects of health: i) physical health and ii) mental health. It also takes into account social well being of the people wherein different socio-economic, cultural and religious factors exercise their role on human health.

Physical fitness is achieved through proper nutrition in the daily diet and regular exercise that is determined by geo-environmental factors and socio-cultural and economic set-up of the society/individual. Mental stability depends on psychological well-being that is partially dependent on nutrition and socio-religious factors. Likewise, social fitness and stability is conditioned by the ability to operate comfortably within the expectations of the society the individual lives. Though these health aspects are explained separately, but in practical they are highly interlinked with one another and change in one aspect of human health leads to change in another aspects as well.

Human health is conditioned by a multitude of factors involving geo-physical, social, cultural, religious and economic. Human beings are so complex that they have interdependence on all the above mentioned factors. The soil, water and air quality and quantity, the climatic phenomena, the socio-cultural set-up and economic standard, all determine directly or indirectly the health of people settled at a place.