A review on heavy metals, uses and its environmental health effects

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ABSTRACT

Environmental pollution is posing significant public health risks worldwide. It is becoming a major concern in developing countries because of rapid economic activities and poor waste management. It is challenging to establish an association between environmental pollution and health effects because of the nature of pathways to exposure, limited data availability and the absence of a monitoring system. Furthermore, associations between environmental pollution and health are difficult due to the occurrence of multiple exposures, and the latency period of effect. Heavy metals are hazardous contaminants in food and the environment and they are non-biodegradable having long biological half-lives. The implications associated with metal (embracing metalloids) contaminations are of great concern, particularly in agricultural production systems due to their increasing trends in human foods and the environment. Environmental contamination by heavy metals has become a worldwide problem during recent years due to the fact that heavy metals unlike some other pollutants are not biodegradable. Consequently, they are not detoxified but are bio accumulated in the environment. Heavy metals are released into the environment through man's industrial, domestic and commercial activities, industrial effluents, pesticides and fungicides as well as manure from poultry farms. There is concern about the potential harmful effects of these metals because besides affecting the productivity of ecosystems, they could also impact on animal and human health. Heavy metal contamination of agricultural soils and crops surrounding the mining areas is a serious environmental problem in many counties, Nigeria inclusive
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INTRODUCTION

Heavy metal is a member of an ill – defined subset of elements that exhibit metallic properties, which would mainly include the transition metals, some metalloids, lanthanides and actinides [1]. Many different definitions have been proposed, some based on density, some on atomic weight and some on chemical properties or toxicity. Heavy metals can include elements lighter than carbon and can exclude some of the heaviest metals [2]. The speciation and bioavailability of trace metals in water are controlled by physical and chemical interactions and equilibria [3]. These interactions are affected by many factors, including pH, redox, temperature, hardness, carbon dioxide concentrations, the type and concentration of available ligands, chelating agents type and concentrations of metal ions [4]. [5], concluded that the toxicity of heavy metals and their compounds largely depends on their bioavailability, that is, the mechanisms of uptake through cell membranes, intracellular distribution, and binding to cellular macromolecules. Biologically the mechanism of the toxic action of heavy metals usually arise from the strong affinity of the cations for sulphur which aid to ingest molecules that contain metals. The sulfhydryl group, -SH which occurs commonly in enzymes that control the speed of critical metabolic reactions in the human body. The resultant metal-sulphur bonding affects the functioning of the enzyme to act normally and as a result, human health is adversely affected or sometimes fatal. The reaction of heavy metal cations M^{2+} (where M is Hg, Pb, or Cd) with the sulfhydryl units of enzymes R-S-H to

produce stable systems such as R-S-M-S-R (where R is an alkyl or aryl group and S is sulphur) is analogous to their reaction with the simple inorganic chemical hydrogen sulfide, H_2S, with which they yield the insoluble solid MS [6, 7]. High concentration of some heavy metals has a cumulative carcinogenic health effect on human and this need to be avoided [8].

Cadmium (Cd)

Cadmium (Cd) is a silvery-white metallic element that can easily be shaped. The atomic number of Cadmium is 48; the element is one of the transition elements in group 12 (or IIb) of the periodic table. Cadmium melts at 321°C (610°F), boils at 767°C (1413°F) and has a specific gravity of 8.64; the atomic weight of cadmium is 112.41. When heated, cadmium burns in air with a bright light, forming the oxide CdO. Because of its high rates of soil-to-plant transfer, cadmium is a contaminant found in most human foodstuffs, which renders diet a primary source of exposure among non-smoking, non-occupationally exposed populations [9].

Occurrence in environment

Cadmium occurs naturally in soils as a result of the weathering of the parent rock. Sedimentary rocks have the greatest range of cadmium concentrations with the highest values found in sedimentary phosphate deposits and black slates. Large concentrations of Cd in the soil are associated with parent material (black slates) and most are man-made (burning of fossil fuels, application of fertilizers, sewage sludge, plastic waste and e-waste) which is responsible for soil contamination and also contaminates pasture. Anthropogenic sources of cadmium are much more significant than natural emissions and account for its ubiquitous presence in soil [10]. Atmospheric deposition is also an important source of cadmium pollution. The major sources of atmospheric emissions are non-ferrous metal production, fossil fuel combustion, waste incineration, and iron and steel production. A representative deposition rate to agricultural land across the European Union has been estimated to be 3g of cadmium per hectare per year [11]. The primary commercial source of cadmium is as a by-product from the processing of zinc ores including sphalerite and smithsonite. Cadmium metal, its alloys and compounds have been used in a variety of different industrial and consumer products, although most uses are now declining due to concerns about its toxicity. Adsorption of cadmium by soil depends strongly on pH, which affects mobility of cadmium but decreases with increasing alkalinity and soil organic matter (SOM) is also an important factor [12].

Uses Cadmium

Cadmium lowers the melting point of metals with which it is alloyed; it is used with lead, tin, and bismuth in the manufacture of fusible metals for automatic sprinkler systems, fire alarms, and electric fuses. An alloy of cadmium with lead and zinc is used as a solder for iron. Cadmium salts are used in photography and in the manufacture of fireworks, rubber, fluorescent paints, glass, and porcelain. Cadmium has been used as a control or shielding material in atomic energy plants because of its high absorption of low-energy neutrons. Cadmium sulphide is employed in a type of photovoltaic cell, and nickel-cadmium batteries are in common use for specialized purposes. Cadmium (Cd) occurs in electronics both as cadmium metal, in some switches and solder joints, and as cadmium compounds in rechargeable batteries, UV stabilizers in older PVC cables and "phosphor" coatings in older cathode ray tubes [13].

Health effect

According to [14] cadmium (Cd) causes damage to the lungs, kidneys and bones, and it is a known human carcinogen. Its toxicity is linked with reproduction problem because it affects sperm and reduces birth weight. It is a potential carcinogen and seems to be a causal factor in cardiovascular diseases and hypertension like lead, cadmium can accumulate in the body over time, with

long-term exposure causing damage to the kidneys and bone structure. Oral, dermal and inhalation exposures contribute to the same systemic effects on the kidney and bone [15]. Cadmium and its compounds are known human carcinogens, primarily through inhalation of contaminated fumes and dusts [16].

Nickel (Ni)

The nickel institute reported that nickel is a naturally occurring element (the 24th most abundant element in the periodic table) and as a consequence of natural and man-made processes can be found ubiquitously in the air, soil, sediments and water. As with all metals and chemicals, excessive amounts of nickel in any of these environmental compartments can result in deleterious impacts on the quality of the environment for flora and fauna. It has been reported that nickel is abundant in the crust of the earth, comprising about 3% of the composition of the earth. Nickel averages 50 mg/kg in soils and commonly varies from 5 to 500 mgkg-1 but ranges up to 24,000 to 53,000 mg/kg in soil near metal refineries or in dried sewage sludge, respectively. Agricultural soils typically contain 3 to 1000 mg/kg, whereas soils derived from basic igneous rocks may contain from 2000 to 6000 mg/kg [17].

Occurrence in the environment

Most nickel on Earth is inaccessible because it is locked away in the planet's iron-nickel molten core, which is 10 % nickel. The total amount of nickel dissolved in the sea has been calculated to be around 8 billion tons. Organic matter has a strong ability to absorb the metal which is why coal and oil contain considerable amounts. The nickel content in soil can be as low as 0.2 mg/kg or as high as 450 mg/kg in some clay and loamy soils. The average is around 20 mg/kg. Nickel occurs in some beans where it is an essential component of some enzymes. Another relatively rich source of nickel is tea which has 7.6 mg/kg of dried leaves [18].

Uses

Humans use nickel for many applications like the use of nickel as an ingredient of steel and other metal products.

Health effect

Food stuffs have low natural content of nickel, but high amounts can occur in food crops growing in polluted soils. Humans may also be exposed to nickel by inhalation, drinking water, smoking, and eating contaminated food. Uptake of high quantities of nickel can cause cancer, respiratory failure, birth defects, allergies, and heart failure.

Chromium (Cr)

Chromium has atomic number of 24 and electronic configuration of [Ar] $4S^13d^5$. The stable forms of Cr in the environment is the trivalent Cr (III) and the hexavalent Cr (VI) species, although there are various other valency states that are unstable and short-lived in biological systems. Chromium (VI) exists in soils as a relatively soluble anion under most conditions (CrO_4^{2-} or $HCrO_4^-$). While sodium and potassium salts of chromates are freely soluble over the pH range 1–14, calcium chromate ($CaCrO_4$) is only moderately soluble, and lead and barium chromates ($PbCrO_4$) and ($BaCrO_4$) are only sparingly soluble at near neutral pH values. In the absence of solubility-controlling solids, Cr(VI) aqueous concentrations under acidic to slightly alkaline conditions will primarily be controlled by adsorption/desorption reactions. Cr(VI) is adsorbed by mineral solids that have exposed inorganic hydroxyl groups on their surfaces, including iron and aluminium oxides, kaolinite, and, to a lesser extent,

montmorillonite [19,20]. Cr(VI) adsorption increases with decreasing pH as a result of protonation of the surface hydroxyl site (SOH^{2+}) and aqueous speciation of Cr(VI). Chromium (III) is less mobile, less toxic and mainly bound to organic matter in soil and aquatic environments Zupancic *et al.* 2008 asserted that Cr (III) in soil, is found predominantly in insoluble forms, such as sparingly soluble Cr_2O_3 and $Cr(OH)_3$ [21].

Uses

Chromium and its compounds have multifarious industrial uses. They are extensively employed in leather processing and finishing, in the production of refractory steel, electroplating cleaning agents, catalytic manufacture, etc. These anthropogenic activities have led to widespread contamination of the environment by Cr, as well as to deposition of Cr-contaminated waste [22].

Health effect on the environment

Chromium is a toxic, non-essential element to plants therefore they do not possess specific mechanisms for its uptake. This metal's toxicity in plants is observed at multiple levels, from reduced yield, through effects on leaf and root growth, to inhibition of enzymatic activities and mutagenesis. It is required for carbohydrate and lipid metabolism and the utilization of amino acids. Toxic levels are common in soils applied with sewage sludge [23].

Lead (Pb)

Lead (Pb) is a chemical element with symbol Pb and atomic number of 82 and it is a main group element belonging to group 4. It forms oxidation states +2 and +4, with +4 being achieved with highly electronegative elements (F, O). Lead has many isotopes, but four (4) are most stable ones. The four (4) stable isotopes are ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb with ^{204}Pb regarded as primordial Pb and Pb^{-206}, Pb^{-207}, Pb^{-208} are formed from decay of Uranium(U) and Th. The one common radiogenic isotope, ^{202}Pb, has a half-life of approximately 53,000 years [24].

Occurrence in the environment

LEAD Group Inc. [25], asserted that lead deposited on the ground is transferred to the upper layers of the soil surface, where it may be retained for many years (up to 2000 years). In undisturbed ecosystems, organic matter in the upper layer of soil surface retains atmospheric lead. In cultivated soils, this lead is mixed with soil to a depth of 25cm (i.e., within the root zone). Atmospheric lead in the soil will continue to move into the microorganism and grazing food chains, until equilibrium is reached. The central nervous of animals are affected by lead and this inhibits their ability to synthesis red blood cells. It is a widespread contaminant in soils and lead poisoning is one of the most prevalent public health problems in many parts of the world. It was the first metal to be linked with failures in reproduction. The metal can affect all components of the environment and can move through the ecosystem until it reaches equilibrium. Lead accumulates in the environment, but in certain chemical environments it will be transformed in such a way as to increase its solubility (e.g., the formations of lead sulfate in soils), its bioavailability or its toxicity. The effects of lead at the ecosystem level are usually seen as a form of stress [26].

Uses

[27], reported from Lead action news, that lead moves into and throughout the ecosystems in different routes. Atmospheric lead is deposited in vegetation, and ground water surfaces. The chemical and physical properties of lead and the biogeochemical processes within ecosystems will influence the movement of lead through ecosystems. The main sources of lead entering an ecosystem are atmospheric lead (primarily from automobile emissions), paint chips, used ammunition, fertilizers and pesticides and lead acid batteries or

other industrial products. The transport and distribution of lead from major emission sources, both fixed and mobile, are mainly through air [28]. Pb is widely used in electronic goods, as a major component of solders (as an alloy with tin) and its compounds have also been used as stabilizers in some PVC cables and other products.

Health effect

Lead affects the brain, causing hyperactivity and deficiency in the fine motor functions, thus, it results in damage to the brain. The nervous systems of children are especially sensitive to Pb leading to retardation. It is also cardiotoxic and contributes to cardiomyopathy (disease of the heart muscle leading to the enlargement of the heart). Lead is highly toxic to humans, as well as to animals and plants [29].

Zinc (Zn)

Zinc has an electron configuration of $[Ar]3d^{10}4s^2$ and is a member of the group 12 of the periodic table. Zinc is a metallic chemical element; it has the symbol Zn and atomic number 30. It is the first element in group 12 of the periodic table. According to Wikipedia zinc is, in some respects, chemically similar to magnesium, because its ion is of similar size and its only common oxidation state is +2. Zinc is the 24th most abundant element in the Earth's crust and has five stable isotopes. It is a moderately reactive metal and strong reducing agent. The surface of the pure metal tarnishes quickly, eventually forming a protective passivating layer of the basic carbonate $Zn_5(OH)_6(CO_3)_2$, by reaction with atmospheric carbon dioxide. This layer helps prevent further reaction with air and water. Zinc burns in air with a bright bluish-green flame, giving off fumes of zinc oxide. Zinc reacts readily with acids, alkalis and other non-metals. Extremely pure zinc reacts only slowly at room temperature with acids. Strong acids, such as hydrochloric or sulfuric acid, can remove the passivating layer and subsequent reaction with water releases hydrogen gas [30].

Occurrence in the environment Zinc(I) compounds

Zinc (I) compounds are rare and requires bulky ligands to stabilize the low oxidation state. Most zinc(I) compounds contains formally the $[Zn_2]^{2+}$ core, which is analogous to the $[Hg_2]^{2+}$ dimeric cation present in mercury(I) compounds.

Zinc (II) Compounds

Binary compounds of zinc are known for most of the metalloids and all the nonmetals except the noble gases. The chemistry of zinc is dominated by the +2 oxidation state [31]. The oxide ZnO is a white powder that is nearly insoluble in neutral aqueous solutions, but is amphoteric, dissolving in both strong basic and acidic solutions [32].

Uses

Zinc oxide is widely used as a white pigment in paints, and as a catalyst in the manufacture of rubber. It is also used as a heat disperser for the rubber and acts to protect its polymers from ultraviolet radiation (the same UV protection is conferred to plastics containing zinc oxide). The semiconductor properties of zinc oxide make it useful in varistors and photocopying products. Zinc sulfide (ZnS) is used in luminescent pigments such as on the hands of clocks, X-ray and television screens, and luminous paints. Crystals of ZnS are used in lasers that operate in the mid infrared part of the spectrum. Zinc sulphate is a chemical in dyes and pigments. Zinc pyrithione is used in antifouling paints.

Health effect

Even though zinc is an essential requirement for a healthy body, excess zinc can be harmful, and cause zinc toxicity. Excessive absorption of zinc can suppress copper and iron absorption. The free zinc ion in solution is highly

toxic to plants, invertebrates, and even vertebrate fish. The Free Ion Activity Model (FIAM) is well established in the literature and shows that just micromolar amounts of the free ion kills some organisms. A recent example showed 6 micromolar killing 93% of all Daphnia in water [33]. The free zinc ion is also a powerful Lewis acid up to the point of being corrosive. Stomach acid contains hydrochloric acid, in which metallic zinc dissolves readily to give corrosive zinc chloride. There is also a condition called the zinc shakes or "zinc chills" that can be induced by the inhalation of freshly formed zinc oxide formed during the welding of galvanized materials. Soils contaminated with zinc through the mining of zinc-containing ores, refining, or where zinc-containing sludge is used as fertilizer, can contain several grams of zinc per kilogram of dry soil. Levels of zinc in excess of 500 ppm in soil interfere with the ability of plants to absorb other essential metals, such as iron and manganese. Zinc levels of 2000 ppm to 180,000 ppm (18%) have been recorded in some soil samples. Zinc (Zn) is an indispensable element required by the human body within an allowable daily intake of 15 mg and 5 mg for adults and children respectively. Levels of zinc above 150 mg/day are considered to have deleterious effects in humans [34].

Copper (Cu)

Copper is a chemical element with atomic number 29 with symbol Cu. It has electronic configuration $[Ar]\, 3d^{10}4s^{1}$. It is a ductile metal with very high thermal and electrical conductivity. Pure copper is soft and malleable; a freshly exposed surface has a reddish orange colour. It is used as a conductor of heat and electricity, a building material, and a constituent of various metal alloys [35].

Copper (III) and Copper (IV)

Copper (III) is mostly characteristically found in oxides. A simple example is potassium cuprate, $KCuO_2$, a blue-black solid. The best studied copper (III) compounds are the cuprate superconductors. Yttrium barium copper oxide ($YBa_2Cu_3O_7$) consists of both Cu (II) and Cu (III) centres. Like oxide, fluoride is a highly basic anion and is known to stabilize metal ions in high oxidation states. Indeed, both copper (III) and even copper (IV) fluorides are known, K_3CuF_6 and Cs_2CuF_6, respectively [36].

Occurrence in the Environment

Copper is a very common element that occurs naturally in the environment and spreads through the environment through natural phenomena. Humans widely use copper in industries and in agriculture. Globally, production of copper has increased over the years and this has increased the copper in the environment. Rivers are depositing sludge on their banks that is contaminated with copper, due to the disposal of copper-containing wastewater. Copper evaporates into the air, mainly through release during the combustion of fossil fuels. Copper in air will remain there for an eminent period of time before it settles when it starts to rain. It will then end up mainly in soils. As a result, soils may also contain large quantities of copper after copper resulting in absorption or uptake by some plants [37].

Uses

Most copper is used for electrical equipment (60%); construction, such as roofing and plumbing (20%); industrial machinery, such as heat exchangers (15%) and alloys (5%). The main long-established copper alloys are bronze, brass, copper-tin-zinc, which is strong enough to make guns and cannons, and is known as gun metal. Copper and nickel is known as cupronickel, which is the preferred metal for low-denomination coins. Copper is ideal for electrical wiring because it is easily worked, can be drawn into fine wire and has a high electrical conductivity [38].

Health effect

Copper is an essential micronutrient required by plants, animals, and human health. It is also required for the normal functioning of aerobic microorganisms. Soils that are naturally deficient in copper often require copper supplements before agricultural crops, such as cereals, can be grown. Copper deficiencies in soil can lead to crop failure. Copper deficiency is a major issue in global food production, resulting in losses in yield and reduced quality of output. Nitrogen fertilizers can worsen copper deficiency in agricultural soils. The most effective strategy to counter copper deficiency is to supplement the soil with copper, usually in the form of copper sulphate. Sewage sludge is also used in some areas to replenish agricultural land with organics and trace metals, including copper. In livestock, cattle and sheep commonly show indications when they are copper deficient. Swayback, a sheep disease associated with copper deficiency, imposes enormous costs on farmers in many tropical countries. Toxicity from copper deficiency can be treated with a balanced diet or supplementation under the supervision of a doctor. On the contrary, like all substances, excess copper intake at levels far above World Health Organization limits can become toxic [39].

Mercury (Hg)

Mercury is a chemical element with atomic number of 80 and symbol Hg. It has electronic configuration of [Xe] $4f^{14}5d^{10}6S^2$. Mercury exists in two main oxidation states, I and II. Higher oxidation states are unimportant, but have been detected, e.g., mercury (IV) fluoride (HgF4) but only under extraordinary conditions. Azevedo *et al.* (2012) quoted in a review of phytotoxicity of mercury in plants that among metals, Hg is unique as it is found in the environment in several physical and chemical forms: for example, elemental Hg(Hg0), inorganic Hg (Hg_2+), associated with ions (SHg), mercurous chloride or calomel (Hg_2Cl_2), and organic Hg (e.g. CH_3-Hg).Mercury(II) oxide, the main oxide of mercury, arises when the metal is exposed to air for long periods at elevated temperatures. It reverts to the elements upon heating near 400 °C, as was demonstrated by Priestly in an early synthesis of pure oxygen. Being a soft metal, mercury forms very stable derivatives with the heavier chalcogens. Preeminent is mercury(II) sulfide, HgS, which occurs in nature as the ore cinnabar and is the brilliant pigment vermillion. Like ZnS, HgS crystallizes in two forms, the reddish cubic form and the black zinc blend form. Mercury(II) selenide (HgSe) and mercury(II) telluride (HgTe) are also known, these as well as various derivatives, e.g. mercury cadmium telluride and mercury zinc telluride being semiconductors useful as infrared detector materials. Mercury(II) salts form a variety of complex derivatives with ammonia. These include Millon's base (Hg_2N+), the one-dimensional polymer (salts of $HgNH^{2+}$)n, and "fusible white precipitate" or $[Hg(NH_3)_2]Cl_2$. Known as Nessler's reagent, potassium tetraiodomercurate (II) (HgI_2^{4-}) is still occasionally used to test for ammonia owing to its tendency to form the deeply colored iodide salt of Millon's base. Mercury fulminate is a detonator widely used in explosives. Organic mercury usually has a formula HgR_2, which are often volatile, or HgRX, which are often solids, where R is aryl or alkyl and X is usually halide or acetate. Methylmercury, a generic term for compounds with the formula CH_3HgX, is a dangerous family of compounds that are often found in polluted water.

Occurrence in the Environment

Almost all commercial production of mercury comes from the sulphide ore, cinnabar, which results from hydrothermal mineralization associated with volcanic activity. Anthropogenic activity is a major source of aerial emissions of mercury and a significant contributor to soil contamination. Most of the mercury in air is present as elemental mercury vapour: 90–99%, which assumed 5% occurred as inorganic mercury and 20% as methylmercury. The main sources of contamination have been mining and smelting, burning of

fossil fuels, industrial production of sodium hydroxide and chloride, and waste incineration although mercury also occurs in trace amounts in fertilizers used on farmland.

Uses

Elemental mercury was employed in hundreds of applications, many of which (e.g., electrical switches) took advantage of the unusual property that it is a liquid that conducts electricity well. Mercury is still used in some batteries and lighting components for flat screen electronic displays and was formerly used also in switches and relays. Mercury can also be used in the preservation of wood.

Health effect

Mercury is the most volatile of metals, and its vapor is highly toxic as asserted by Colin Baird. Mercury and most of its compounds are extremely toxic and must be handled with care; in cases of spills involving mercury (such as from certain thermometers or fluorescent light bulbs), specific cleaning procedures are used to avoid exposure and contain the spill. This heavy metal is toxic even at low concentrations to a wide range of organisms including humans. Mercury and its compounds are highly toxic, causing damage to the central nervous system and kidneys. Once in the environment, mercury can be converted to its organic methylated form by bacterial activity, a form, which is highly bio-accumulative, as well as being toxic. The organic form of mercury can be particularly toxic, and the methyl-and ethyl-forms have been the cause of several major epidemics of poisoning in humans resulting from the ingestion of contaminated food, e.g. fish. Two major epidemics in Japan were caused by the release of methyl and other mercury compounds from an industrial site followed by accumulation of the chemicals in edible fish. The poisoning became well-known as Minamata disease.

Iron (Fe)

Iron is a chemical element with symbol **Fe** (from Latin: *ferrum*) and atomic number 26. It is a metal, that belongs to the first transition series and group 8 of the periodic table. It is by mass the most common element on Earth, forming much of Earth's outer and inner core. It is the fourth most common element in the Earth's crust. Pure iron is very rare on the Earth's crust, basically being limited to meteorites. Iron ores are quite abundant, but extracting usable metal from them requires kilns or furnaces capable of reaching 1500 °C or higher, about 500 °C higher than what is enough to smelt copper. Humans started to dominate that process in Eurasia only about 2000 BCE and iron began to displace copper alloys for tools and weapons, in some regions, only around 1200 BCE. That event is considered the transition from the Bronze Age to the Iron Age. Iron alloys, such as steel, inox, and special steels are now by far the most common industrial metals, because of their mechanical properties and their low cost. Pristine and smooth pure iron surfaces are mirror-like silvery-gray. However, iron reacts readily with oxygen and water to give brown to black hydrated iron oxides, commonly known as rust. Unlike the oxides of some other metals, that form passivating layers, rust occupies more volume than the metal and thus flakes off, exposing fresh surfaces for corrosion. The body of an adult human contains about 4 grams (0.005% body weight) of iron, mostly in hemoglobin and myoglobin. These two proteins play essential roles in vertebrate metabolism, respectively oxygen transport by blood and oxygen storage in muscles. To maintain the necessary levels, human iron metabolism requires a minimum of iron in the diet. Iron is also the metal at the active site of many important redox enzymes dealing with cellular respiration and oxidation and reduction in plants and animals [40]. Chemically, the most common oxidation states of iron are iron(II) and iron(III). Iron shares many properties of other transition metals, including the other group 8 elements, ruthenium and osmium. Iron forms compounds in a wide range of oxidation states, −2 to +7. Iron also forms many coordination compounds; some of them, such as ferrocene, ferrioxalate, and Prussian blue, have substantial

industrial, medical, or research applications.

Occurrence in the Environment
Cosmogenesis

Iron's abundance in rocky planets like Earth is due to its abundant production by fusion in high-mass stars, where it is the last element to be produced with release of energy before the violent collapse of a supernova, which scatters the iron into space. A polished and chemically etched piece of an iron meteorite, believed to be similar in composition to the Earth's metallic core, showing individual crystals of the iron-nickel alloy (Widmannstetter). Metallic or native iron is rarely found on the surface of the Earth because it tends to oxidize. However, both the Earth's inner and outer core, that account for 35% of the mass of the whole Earth, are believed to consist largely of an iron alloy, possibly with nickel. Electric currents in the liquid outer core are believed to be the origin of the Earth's magnetic field. The other terrestrial planets (Mercury, Venus, and Mars) as well as the Moon and are believed to have a metallic core consisting mostly of iron. The M-type asteroids are also believed to be partly or mostly made of metallic iron alloy [41]. The rare iron meteorites are the main form of natural metallic iron on the Earth's surface. Items made of cold-worked meteoritic iron have been found in various archaeological sites dating from a time when iron smelting had not yet been developed; and the Inuit in Greenland have been reported to use iron from the Cape York meteorite for tools and hunting weapons. About 1 in 20 meteorites consist of the unique iron-nickel minerals taenite (35–80% iron) and kamacite (90–95% iron) [42].

Mantle minerals

Ferropericlase (Mg,Fe)O, a solid solution of periclase (MgO) and wüstite (FeO), makes up about 20% of the volume of the lower mantle of the Earth, which makes it the second most abundant mineral phase in that region after silicate perovskite (Mg,Fe)SiO$_3$; it also is the major host for iron in the lower mantle (Stark, 2007). At the bottom of the transition zone of the mantle, the reaction γ-(Mg,Fe)$_2$[SiO$_4$] ↔ (Mg,Fe)[SiO$_3$] + (Mg,Fe)O transforms γ-olivine into a mixture of silicate perovskite and ferropericlase and vice versa. In the literature, this mineral phase of the lower mantle is also often called magnesiowüstite (Ferropericlase). Silicate perovskite may form up to 93% of the lower mantle (Murakami *et al.*, 2012) and the magnesium iron form, (Mg,Fe)SiO$_3$, is considered to be the most abundant mineral in the Earth, making up 38% of its volume (Sharp, 2014).

While iron the most abundant element on Earth, it accounts for only 5% of the Earth's crust; thus being only the fourth most abundant element, after oxygen, silicon, and aluminium (Morgan and Anders, 1980). Most of the iron in the crust is combined with various other elements to form many different iron minerals. An important class is the iron oxide minerals such as hematite (Fe$_2$O$_3$), magnetite (Fe$_3$O$_4$), and siderite (FeCO$_3$), which are the major ores of iron. Many igneous rocks also contain the sulfide minerals pyrrhotite and pentlandite (Sharp, 2014). During weathering, iron tends to leach from sulfide deposits as the sulfate and from silicate deposits as the bicarbonate. Both of these are oxidized in aqueous solution and precipitate in even mildly elevated pH as iron (III) oxide. Banded iron formation in the McKinley Park, Minnesota, Minnesota. Large deposits of iron are banded iron formations, a type of rock consisting of repeated thin layers of iron oxides alternating with bands of iron-poor shale and chart. The banded iron formations were laid down in the time between 3,700 million years ago and 1,800 million years ago.

Materials containing finely ground iron(III) oxides or oxide-hydroxides, such as ochre, have been used as yellow, red, and brown pigments since pre-historical times. They contribute as well to the color of various rocks and clays, including entire geological formations like the Painted Hills in Oregon and the Buntsandstein ("colored sandstone", British Bunter). Through Eisensandstein (a jurassic 'iron sandstone', e.g. from Donzdorf) in Germany and Bath stone in

the UK, iron compounds are responsible for the yellowish color of many historical buildings and sculptures. The proverbial red color of the surface of Mars is derived from an iron oxide-rich regolith. Significant amounts of iron occur in the iron sulfide mineral pyrite (FeS_2), but it is difficult to extract iron from it and it is therefore not exploited. In fact, iron is so common that production generally focuses only on ores with very high quantities of it. According to the International Resource Panel's Metal Stocks in Society report, the global stock of iron in use in society is 2200 kg per capita. More-developed countries differ in this respect from less-developed countries (7000–14000 vs 2000 kg per capita).

Uses

The iron compounds produced on the largest scale in industry are iron(II) sulfate ($FeSO_4 \cdot 7H_2O$) and iron (III) chloride ($FeCl_3$). The former is one of the most readily available sources of iron (II) but is less stable to aerial oxidation than Mohr's salt (($NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$). Iron (II) compounds tend to be oxidized to iron(III) compounds in the air (Holleman, 1985). Iron is the most widely used of all the metals, accounting for over 90% of worldwide metal production. Its low cost and high strength often make it the material of choice material to withstand stress or transmit forces, such as the construction of machinery and machine tools, rails, automobiles, ship hulls, concrete reinforcing bars, and the load-carrying framework of buildings. Since pure iron is quite soft, it is most commonly combined with alloying elements to make steel.

Health effect

Iron uptake is tightly regulated by the human body, which has no regulated physiological means of excreting iron. Only small amounts of iron are lost daily due to mucosal and skin epithelial cell sloughing, so control of iron levels is primarily accomplished by regulating uptake. Regulation of iron uptake is impaired in some people as a result of a genetic defect that maps to the HLA-H gene region on chromosome 6 and leads to abnormally low levels of hepcidin, a key regulator of the entry of iron into the circulatory system in mammals. In these people, excessive iron intake can result in iron overload disorders, known medically as hemochromatosis. Many people have an undiagnosed genetic susceptibility to iron overload and are not aware of a family history of the problem. For this reason, people should not take iron supplements unless they suffer from iron deficiency and have consulted a doctor. Hemochromatosis is estimated to be the cause of 0.3 to 0.8% of all metabolic diseases of Caucasians. Overdoses of ingested iron can cause excessive levels of free iron in the blood. High blood levels of free ferrous iron react with peroxides to produce highly reactive free radicals that can damage DNA, proteins, lipids, and other cellular components. Iron toxicity occurs when the cell contains free iron, which generally occurs when iron levels exceed the availability of transferring to bind the iron. Damage to the cells of the gastrointestinal tract can also prevent them from regulating iron absorption, leading to further increases in blood levels. Iron typically damages cells in the heart, liver and elsewhere, causing adverse effects that include coma, metabolic acidosis, shock, liver failure, coagulopathy, adult respiratory distress syndrome, long-term organ damage, and even death [43]. Humans experience iron toxicity when the iron exceeds 20 milligrams for every kilogram of body mass; 60 milligrams per kilogram is considered a lethal dose. Overconsumption of iron, often the result of children eating large quantities of ferrous sulfate tablets intended for adult consumption, is one of the most common toxicological causes of death in children under six (Toxicity, iron). The Dietary Reference Intake (DRI) sets the Tolerable Upper Intake Level (UL) for adults at 45 mg/day. For children under fourteen years old the UL is 40 mg/day (Dietary Reference Intake [44].

Cobalt (Co)

Cobalt is a biological and chemically active chemical with potential of forming numerous compounds [40]. It does not occur as a free metal but as a component of minerals [41]. It's presence in the Earth's crust and in natural waters is of relatively low abundance [42]. The background level of cobalt in soil is 8 mg/kg but can be as low as 0.1 mg/kg and as high as 70 mg/kg [43]. It supports the growth of blue-green algae (cyanobacteria) and other nitrogen fixing organisms [44]. It is also essential to animals (in low concentration) as it is important in Vitamin B_{12} [40].

Occurrence in the Environment

Cobalt is not an abundant element but is widely diffused in rocks, sea and mineral waters, coal, meteorites, the sun and stellar atmospheres, soils, plants and animals. Relatively little cobalt ore is mined for the cobalt content, and most of the metal is recovered as a by-product of ores treated for their copper or nickel content.

Uses

Cobalt is being added to pigments to produce a distinct blue color. Lithium ion batteries contain cobalt. In the medical field, cobalt-60 is used in radiotherapy and for sterilizing medical equipment. Hip replacements are also made of cobalt.

Health Effect

Industrial plants may leak cobalt and other toxic metals into the environment. Once cobalt particles enter the atmosphere, they settle to the ground and enter the food and water supply; most of the population is exposed to cobalt through food, water, and air. Cobalt makes its way through the environment and cannot be destroyed. People working in industrial settings have an increased risk of exposure to toxins, including cobalt. Also, it's been reported that hip replacements containing cobalt have caused problems due to nano particles of cobalt breaking away and contaminating the body.

Manganese (Mn)

Manganese is a chemical element with the symbol Mn and atomic number 25. Manganese is a transition metal with important industrial alloy uses, particularly in stainless steels. Historically, manganese is named for pyrolusite and other black minerals from the region of Magnesia in Greece, which also gave its name to magnesium and the iron ore magnetite. By the mid-18th century, Swedish-German chemist Carl Wilhelm Scheele had used pyrolusite to produce chlorine. Scheele and others were aware that pyrolusite (now known to be manganese dioxide) contained a new element, but they were unable to isolate it. Johan Gottlieb Gahn was the first to isolate an impure sample of manganese metal in 1774, which he did by reducing the dioxide with carbon.

Occurrence in the Environment

It is not found as a free element in nature; it is often found in minerals in combination with iron.

Uses

Manganese is essential to iron and steel production by virtue of its sulfur-fixing, deoxidizing, and alloying properties, as first recognized by the British metallurgist Robert Forester Mushet (1811–1891) who, in 1856, introduced the element, in the form of Spiegeleisen, into steel for the specific purpose of removing excess dissolved oxygen, sulfur, and phosphorus in order to improve its malleability. Steelmaking, including its iron making component,

has accounted for most manganese demand, presently in the range of 85% to 90% of the total demand. Manganese is a key component of low-cost stainless steel. Often ferromanganese (usually about 80% manganese) is the intermediate in modern processes. The second largest application for manganese is in aluminium alloys. Aluminium with roughly 1.5% manganese has increased resistance to corrosion through grains that absorb impurities which would lead to galvanic corrosion (Chemical properties of 2024 aluminum alloy). The corrosion-resistant aluminium alloys 3004 and 3104 (0.8 to 1.5% manganese) are used for most beverage cans [9]. Before 2000, more than 1.6 million tonnes of those alloys were used; at 1% manganese, this consumed 16,000 tonnes of manganese [20].

Health Effect

Excessive exposure or intake may lead to a condition known as manganism, a neurodegenerative disorder that causes dopaminergic neuronal death and symptoms similar to Parkinson's disease. Waterborne manganese has a greater bioavailability than dietary manganese. According to results from a 2010 study, higher levels of exposure to manganese in drinking water are associated with increased intellectual impairment and reduced intelligence quotients in school-age children.

Heavy Metals in Soil

In Soil Heavy metals occur naturally in soil environment from the pedogenetic processes of weathering of parent materials at levels that are regarded as trace (<1000 mg/kg) and rarely toxic. The uptake of metals from the soil depends on different factors such as their soluble content in it, soil pH, plant growth stages, types of species, fertilizers and soil. The worldwide Pb concentration for surface soils averages 32 mg/kg and ranges from 10 to 67 mg/kg. Tiruchirappalli, an open dumpsite in Tamilnadu receives 400-470 tonnes of municipal solid waste [7]. The heavy metal concentration in soil samples collected from the solid waste found in the order of Mn> Pb>Cu>Cd in the ranges of 0.1605-1.7962, 0.7655-5.1485,0.546-2.6886 and 0.1641-1.0372 mg/l, respectively. The presence of heavy metals in soil samples indicates that there is appreciable contamination of soil by leachate migration from this dumping site [14]. The concentrations of heavy metals from different sites ranged from a minimum of 42.400 to a maximum of 137.858, 25.500-108.325, 4.800-32.283 and 2.28313.725 for Zn, Cu, Pb and Ni, respectively [15]. Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem through direct ingestion or contact with contaminated soil, the food chain, drinking of contaminated ground water, reduction in food quality via phytotoxicity, reduction in land usability for agricultural production causing food insecurity and land tenure problems. Distribution and forms of Cu, Zn, Cd, Fe and Mn in soils were studies near a copper smelter in Washington which revealed that the mobility of Cu, Zn, and Cd in the soils was limited, as evidenced by a sharp reduction in concentrations of the three elements with depth [8]. Comparing subsoil concentrations of these elements with those from areas relatively unpolluted by smelter fallout revealed that Cd was more leachable than Cu or Zn [15]. Metal bearing solids at contaminated sites can originate from various anthropogenic sources like metal mine tailings, disposal of high metal wastes, lead based paints, compost, pesticides, petrochemicals and atmospheric deposition. There was significant correlation between distance from the main chimney of the smelter and the levels of a number of metals in soil. Accumulation of Heavy Metals in Soil and their Transfer to Leafy Vegetables was studied in the Region of Dhaka Aricha Highway, Savar, Bangladesh. Higher concentrations of Cu (137.7 µg/g) and Zn (139 µg/g) were reported in the soils collected from industrial areas of Surat, Western India. Cr, Ni and Pb concentrations in the soils of Jagi road paper mill area, Assam, India, mainly originated from paper mill effluent and soil Cd was associated with natural concentration. Most accumulation of heavy metals was

observed in the surface layer of the soil. However, through shrink-swell cracks heavy metals can penetrate into the subsoil layers and consequently contaminate the surface groundwater. Long term irrigation with effluent and sludge increased heavy metal contents in soil and plants and made this practice unsafe to be applied by man [8].

Soil metal concentrations decreased with depth, suggesting anthropogenic sources of contamination. The concept of pollution index (PI) of soils gives important information on the extent and degree of multi-element contamination and can be applied to the evaluation of soils prior to their agricultural use and remediations [12]. The analysis of plant available metal content in the soil showed the highest level of Fe, which ranged from 529.02 to 2615 microg $g^{(-1)}$ dw, and lowest level of Ni (3.12 to 10.51 microg g(-1) dw [8]. Cd uptake in sludge amended and Cd salt treated soils maintained at high and low soil pH was studied. Cd uptake by plants grown in sludge amended soils was significantly lower than Cd uptake by plants grown in the Cd-salt treated soils at low and high pH. Zinc phytotoxicity in most leafy vegetables occurs when Zn accumulates to an average tissue concentration of 500 mg/kg dry weight than twice the concentration of Zn found in the vegetables at the Pension site. The total of Cd concentration in most of the soil samples exceeded the suggested Swiss thresholds (0.8 mg/kg). Most of the plants grown on the soils of Isfahan province, Iran, were contaminated with heavy metals and pose a major health concern [12]. Vegetables, especially those of leafy vegetables grown in heavy metal contaminated soils, accumulate higher amounts of metals than those grown in uncontaminated soils because of the fact that they absorb these metals through their leaves.

Soil Concentration Ranges and Regulatory Guidelines for Some Heavy Metals

The specific type of metal contamination found in a contaminated soil is directly related to the operation that occurred at the site. The range of contaminant concentrations and the physical and chemical forms of contaminants will also depend on activities and disposal patterns for contaminated wastes on the site. Other factors that may influence the form, concentration, and distribution of metal contaminants include soil and ground-water chemistry and local transport mechanisms. Soils may contain metals in the solid, gaseous, or liquid phases, and this may complicate analysis and interpretation of reported results. For example, the most common method for determining the concentration of metals contaminants in soil is via total elemental analysis [9].

The level of metal contamination determined by this method is expressed as mg metal kg−1 soil. This analysis does not specify requirements for the moisture content of the soil and may therefore include soil water. This measurement may also be reported on a dry soil basis. The level of contamination may also be reported as leachable metals as determined by leach tests, such as the toxicity characteristic leaching procedure (TCLP) or the synthetic precipitation-leaching procedure, or SPLP test (USEPA Method 1312). These procedures measure the concentration of metals in leachate from soil contacted with an acetic acid solution (TCLP) or a dilute solution of sulfuric and nitric acid (SPLP). In this case, metal contamination is expressed in mgL^{-1} of the leachable metal. Other types of leaching tests have been proposed including sequential extraction procedures [9] and extraction of acid volatile sulfide. Sequential procedures contact the solid with a series of extractant solutions that are designed to dissolve different fractions of the associated metal. These tests may provide insight into the different forms of metal contamination present. Contaminant concentrations can be measured directly in metals-contaminated water. These concentrations are most commonly expressed as total dissolved metals in mass concentrations (mgL^{-1} or gL^{-1}) or in molar concentrations ($molL^{-1}$). In dilute solutions, a mgL^{-1} is equivalent to one part per million (ppm), and a gL^{-1} is equivalent to one part per billion (ppb).

Heavy Metals in Irrigation/Drinking Water

Disposal of sewage water and industrial wastes is a great problem. Often it is drained to the agricultural lands where it is used for growing crops including vegetables. These sewage effluents are considered not only a rich source of organic matter and other nutrients but also, they elevate the level of heavy metals like Fe, Mn, Cu, Zn, Pb, Cr, Ni, Cd and Co in receiving soils. Concentration of Pb, Cr and Fe were found to be higher than the standard limit indicating imperilled state of canal water of Chittagong city, Bangladesh [12]. All water samples from farming sites in Accra (Ghana) contained detectable concentrations of each of the seven heavy metals except for irrigation water which had no detectable chromium, cadmium and cobalt [15]. Most of our water sources are gradually becoming polluted due to the addition of foreign materials from the surroundings. The lakes have a complex and fragile ecosystem, as they do not have self-cleaning ability and therefore readily accumulate pollutants. Bellandur lake in Bangalore is 130 years old and sewage from residential areas near Bangalore International airport is directly allowed into this lake. The water samples were analysed which showed that the average concentrations (µg/l) for Fe (1087), Zn (132),Cu (12), Ni (3), Cr (6), Pb (9) and Cd (0.7) were 2,9,4,6,6,9 and 23-fold higher than the natural element levels 500 (Fe), 15 (Zn), 3 (Cu), 0.5 (Ni), 1 (Cr), 1 (Pb) and 0.03 (Cd) in freshwater respectively. Increasing pollution has given rise to concern on the intake of harmful metals in humans. These metals enter the human body through inhalation and ingestion. The intake through ingestion depends on food habit. Dareta Village is a mining community with so many mining mills in operation within the village.

The trace metal levels of water from hand dug wells around Dareta Village were determined. Water samples were collected from 12 wells scattered around the village. The metals studied include Cd, Pb, Cu, and Zn. The mean trace metal concentrations and their ranges were Pb 0.279(0.25-0.869) ppm; Cd 0.0177(0.0112- 0.0256) ppm; Zn 0.512 (0.248-1.842) ppm; Cu 0.182 (0.110-0.729) ppm [14]. Jannapura lake, a perennial fresh water body located in Bhadravathi town of Karnataka state, India is used for irrigation purpose. This lake receives untreated domestic wastewater from residential areas. Water samples collected during October 2004 to June 2005 were analysed using Atomic Absorption Spectrophotometer for Cu, Zn, Pb, Cd and Ni. The concentration of all the heavy metals of concern in the water exceeded the permissible limits as per WHO Standards.

The study indicated that the water of the lake was not suitable for drinking purpose. The concentration of Zn for irrigation and livestock watering are 1.0 and 0-20 mg/l respectively. High concentration of Zn in water is unsuitable for the sustenance of the aquatic life. But could be used for irrigation and livestock watering. Although Zn has been found to have low toxicity to human, prolonged consumption of large doses can result in some health complications such as fatigue, dizziness and neutropenia. Nigeria's industrial cities are resulting in an increased quantity of discharge and a wide range of pollutants reaching water bodies. Urbanization and industrialization have contributed to the large scale of pollution currently observed in most Nigerian cities notably those swarming with industries viz. Lagos, Kano and Kaduna states. There are no incentives for implementing pollution reduction measures. Wastes are disposed indiscriminately especially from small and medium scale industries [25].

The lack of information on pollution is a serious hindrance to pollution directly or remotely. Thus, in addition to treatment of wastewater before disposal, appraisal of water resources would offer proficient information to indicate areas of main concern. This would prove useful in detection of threats to human and environmental health [23]. Wastewater from urban area is being used profitably to irrigate crops near cities from the time unknown. Wastewater is still considered rich in plant nutrients and organic matter [25].

However, the situation is changed now because, in many cities and towns the wastewater is sold for secondary use and it is a good source of income to municipalities. Drinking water samples of industrial area of Sheikhupura, Pakistan that is swarming with small and large industries were analysed. Samples were collected from the twelve different sites of the mentioned area for six months at frequency of once per fifteen days and were analysed under strict quality control conditions and ASTM (American Standard Testing Methods) methods were employed for strictly precise and accurate results. Four sites showed bacterial contamination, five sites indicated high level of TDS (Total Dissolved Solids) and conductivity. Only one site indicated elevated chromium level (0.6 mg/L) l, two depicted increased level of arsenic but five sites gave idea about the high level of manganese (highest average value 1.2 mg/L) in the study area [26]. The use of treated and untreated wastewater for irrigation has increased the contamination of Cd, Pb and Ni in edible portion of vegetables causing potential health risk in the long term from this practice. Consumption of heavy metal and minerals by adult women through food in sewage and tube-well irrigated area was studied around Ludhiana city in Punjab, India.

Wastewater irrigation is known to contribute significantly to the heavy metal contents of soils. The city of Ludhiana (Punjab, India) has large number of industries like cycle, cycle parts, sewing machine, textiles, dyeing etc. and effluents from these units is thrown into sewage system without much treatment. Municipal sewage is partly used for irrigation purposes in fields of nearby villages. The crops grown in such areas are vegetables and among these leafy vegetables and root crops accumulate large amounts of Zn, Cu, Pb and Cd than those from tube well irrigated soils. There was significant increase in the nickel content of soil irrigated with paper mill effluent whereas in the soil irrigated with sewage, chromium, iron and cadmium contents were increased appreciably. Among various metallic concentrations, maximum concentration of Fe was observed in leaves (400.12±11.47 mg/kg) and root (301.41±13.14 mg/kg) of Spinacia oleracea after irrigation with effluent of paper mill whereas it was (400.49±5.97 mg/kg) in leaves and (363.94±11.37 mg/kg) in root after irrigation with sewage after 60 days [28].

Air Pollution

Atmosphere is a gaseous layer surrounding the earth. It is the transparent layer through which life-sustaining solar radiation passes and reaches the earth's surface or into the water. However, the emergence of particulate matter and heavy metals due to industrial revolution has made present-day atmosphere to be quite different from the natural atmosphere. Rapid industrialization and urbanization during this time led to increase in anthropogenic emissions from both fossil fuel and biomass combustion. Particulate matter refers to the solid and liquid particles that are dispersed into ambient air. Particulate matter is composed of a mixture of particles directly emitted into the air (primary particles) and particles formed in the air from the chemical transformation of gaseous pollutants (secondary particles) [8].

There are two major categories of particulate matter (PM): PM10 and PM2.5. The principal types of directly emitted particles are soil related particles and organic and elemental carbon particles from the combustion of fossil fuels and biomass materials. The concentration of primary particles depends upon their emission rate, transport and dispersion and removal rate from the atmosphere. Situation with secondary particles is much more complex. As a result, it is considerably more difficult to relate ambient concentrations of secondary particles to sources of precursor emissions than it is to identify the sources of primary particles. Heavy metals are metallic elements which are toxic and have high densities, specific gravities or atomic weights. They constitute important class of pollutants which have received the attention of researchers all over the world, mainly

due to their harmful effects on living beings. Heavy metals enter into the environment mainly via three routes: deposition of atmospheric particulates; disposal of metal enriched sewage sludge and sewage effluents; and by-products from metal mining processes. Metals in the atmosphere result from processes both natural (dust re-suspension, foliage emissions, volcanic activity and bubble bursting from water bodies) and anthropogenic (primarily industrial and automotive emissions. Resuspension of roadside dust and soil is another potential source of heavy metals. Iron is a metal present in significant concentration in most emission sources of air pollution particles while sources of lead were linked to vehicles, re-suspended soil and oil burning.

Air Quality Management and Pollution Control of Particulate Matter

a. Use of source apportionment method

For the effective management of air quality, great importance is attached to the identification of the sources of suspended particulates. Source apportionment can be achieved by using a variety of air quality models. Among these, receptor-oriented modelling is one of the conventional techniques and has been in broad use for source apportionment studies in the past decades. The framework for using receptor models to solve air quality problems consists of: formulating a conceptual model; identifying potential sources; characterizing source emissions; obtaining and analyzing ambient particulate matter samples for major components and source markers; confirming source types with multivariate receptor models; quantifying source contributions with the chemical mass balance; estimating profile changes and the limiting precursor gases for secondary aerosols; and reconciling receptor modelling results with source models, emissions inventories and receptor data analyses.

b. Air quality surveillance method

Air quality surveillance is the procedure for assessing the concentrations of atmospheric contaminants and other properties of the air so that air quality management requirements can be met. Environmental regulators have access to a large set of policy tools and instruments to create incentives for industrial facilities to abate pollution. Command and control is one approach where pollution standards for emissions or effluence are set, and fines and penalties are assessed against non-compliant facilities. Other options include pollution charges, tradable permits, voluntary participation programs, as well as environmental performance rating and public disclosure programs.

c. Use of geographic information system (GIS) and global positioning system (GPS)

Other identified means of managing air quality include geographic information systems (GIS) and global positioning system (GPS). GIS are systems of hardware, software, data, people, organizations and institutional arrangements for collecting, storing, analyzing and disseminating information about areas of the earth. GIS helps in the assessment of quality of life (QOL) which is emerging as a major indicator to monitor citizen's livelihood and well-being at the grassroots level and thus inform local people and organizations of their living environment and optimize the allocations of resources to improve the community development [14]. Global positioning system (GPS) receivers are another invaluable useful tool that can be used by state and local government agencies to address spatial coordinate deficiencies of inventory data of point sources. It consists of satellite, control and receiver segments in which the GPS receivers can be used to obtain emission release point locations if site access is available.

d. Remote sensing technique

Remote sensing is another technique of immense application in environmental pollution and involves collecting information about the earth without taking a physical sample of the earth's surface or touching the surface using sensors placed on a platform at a distance from it. A sensor is used to

measure the energy reflected from the earth and information gotten can be displayed as a digital image or as a photograph. It was based on the fact that the atmosphere affects satellite images of the earth's surface in the solar spectrum and signal observed by the satellite sensor was the sum of the effects from the ground and atmosphere.

e. Meteorological and air pollution dispersion models

There are many meteorological models available for weather prediction and the mainly used are Weather Research and Forecasting (WRF) modeling system, MM5 modeling system software and Regional Atmospheric Modeling System (RAMS). MM5 is a limited-area, nonhydrostatic, terrain-following sigma-coordinate model designed to simulate or predict mesoscale atmospheric circulation. RAMS is a highly versatile numerical code developed by scientists at Colorado State University for simulating and forecasting meteorological phenomena, and for depicting the results (http://rams. atmos.colostate.edu/rams-description.html). Other applicable air pollution dispersion models for atmospheric air pollution assessment include photochemical modelling, plume rise models, particle models, deposition modules, odour models and statistical models [8].

Previous studies on collection and assessment of particulate matter and heavy metals

Generally, sources of metals and particulate matter in the atmosphere had been traced to originate either from anthropogenic activities or natural phenomena such as dust re-suspension, foliage emissions, volcanic eruption and bubble bursting from water bodies. However, different methodologies had been proposed in collecting samples of heavy metals and particulate matter; and assessing their quantities in the atmosphere.

a. Collection methods and measurement techniques

Lovett and Lindberg, 1984 estimated dry deposition of metal containing particles from inert surface fluxes using an empirical model of coarse particle dry deposition to the full canopy developed from measurements of through fall chemistry. Many researchers had measured concentrations of heavy metals in particulate matter using graphite furnace atomic absorption spectrophotometry using the method of standard additions. In a different approach, a mathematical approach was used based on the Monin–Obukhov similarity theory to predict wind speed, friction velocity and drag coefficient which were then introduced into a well-known deposition model of [16] to calculate dry deposition of heavy metals into North Sea. Elemental composition of particulate matter had also been determined using particle-induced X-ray emission (PIXE) method [23], atomic absorption spectrophotometer, benzene-soluble organic fraction method, wet sieving method and inductively coupled plasma quadrupole mass spectrometer. Determination of particle number concentration using condensation particle counter, particle size distribution using electrical aerosol spectrometer and absorption coefficient using filter reflectance in particulate matter had been investigated. In another development, results obtained from an organic speciation analysis had been used in a chemical mass balance (CMB) model, along with organic emissions profiles and key organic tracers typical of urban sources, to quantify the primary source contributions to PM2.5 mass concentrations in four major cities of India. In a related work [24] modelled chemical composition data using factor analysis with Varimax orthogonal rotation to determine five and four particle source categories contributing significant amount of PM2.5 and PM10 mass, respectively. Statistical multivariate method and deterministic method had been applied as source apportion ate methods for determining particulate matter sources whose chemical composition is stable and well defined. Gaussian predictive model had been applied for model prediction of particulate dispersion from a cement mill stack [8]. [21] used Gaussian puff dispersion and regional-scale transport models for air quality modelling of

Warsaw Metropolitan Area, Poland. In recent time [23] utilized a remote sensing method to retrieve PM10 concentration during health risk assessment of inhalable particulate matter in Beijing based on thermal environment.

Instrumental Methods of Analysis for Heavy Metal in Soil, Water and Plant

Pollution accumulation in soil, water, and plants is a significant environmental issue that can have severe consequences on human health and ecosystem functioning. The detection and quantification of pollutants in environmental samples is critical in identifying the sources of contamination and the extent of pollution. In recent years, several analytical techniques have been used to detect and quantify pollutants in environmental samples, including gas chromatography-mass spectrometry (GCMS), microwave plasma-atomic emission spectrometry (MP-AES), and neutron activation analysis (NAA).

Gas chromatography-mass spectrometry

GCMS Gas chromatography-mass spectrometry (GCMS) is a powerful analytical technique that has been used extensively for the detection and quantification of organic and inorganic compounds in environmental samples [21]. GCMS combines the separation power of gas chromatography with the detection sensitivity and specificity of mass spectrometry. The technique is capable of detecting and quantifying a wide range of organic and inorganic compounds in environmental samples, including volatile and semi-volatile organic compounds, polycyclic aromatic hydrocarbons (PAHs), and heavy metals [23].

Microwave plasma-atomic emission spectrometry

MP-AES Microwave plasma-atomic emission spectrometry (MP-AES) is a modern analytical technique that has been increasingly used for the analysis of environmental samples [23]. MP-AES uses a microwave-induced plasma to vaporize and excite the sample, producing an emission spectrum that can be used to identify and quantify the elements present in the sample. The technique has several advantages over traditional analytical techniques, including the elimination of the need for flammable and toxic gases and the reduction of instrument maintenance requirements

Neutron Activation Analysis

Neutron activation analysis (NAA) is a nuclear process used for determining the concentrations of elements in a vast amount of materials. NAA relies on excitation by neutrons so that the treated sample emits gamma-rays. It allows the precise identification and quantification of the elements, above all the trace elements in the sample. NAA has applications in chemistry but also in other research fields, such as geology, archaeology, medicine, environmental monitoring and even in the forensic science [24]. NAA Neutron activation analysis (NAA) is a highly sensitive analytical technique that has been used extensively for the analysis of environmental samples [24]. NAA uses neutron irradiation to activate the sample, producing gamma rays that can be detected and quantified. The technique is capable of detecting and quantifying a wide range of elements, including heavy metals and non-metals, in environmental samples.

Basic Principles

The sequence of events occurring during the most common type of nuclear reaction used for NAA, namely the neutron capture or (n, gamma) reaction, is creation of a compound nucleus forms in an excited state when a neutron interacts with the target nucleus via a non-elastic collision. The excitation energy of the compound nucleus is due to the binding energy of the neutron with the nucleus. The compound nucleus will almost instantaneously de-excite into a more stable configuration through emission of one or more characteristic prompt gamma rays. In many cases, this new configuration yields a radioactive nucleus which also de-excites (or decays) by emission of one or more characteristic delayed gamma rays, but at a much lower rate according to the unique half-life of

the radioactive nucleus. Depending upon the particular radioactive species, half-lives can range from fractions of a second to several years. In principle, therefore, with respect to the time of measurement, NAA falls into two categories: (1) prompt gamma-ray neutron activation analysis (PGNAA),

where measurements take place during irradiation, or (2) delayed gamma-ray neutron activation analysis (DGNAA), where the measurements follow radioactive decay [26].

Inductively Coupled Plasma Optical Emission Spectrometry

Inductively coupled plasma optical emission spectroscopy (ICP-OES) is a recent and powerful instrument for the analysis of metals in a variety of different sample matrices. It is an electrode less source, so there is no contamination from the impurities present unlike electrode material. In this technique, the sample is subjected to temperatures high enough to cause significant amounts of collisional excitation (and ionization) of the sample atoms. Once the atoms or ions are in their excited states, they can decay to lower states through thermal or radiative (emission) energy transitions. In OES, the intensity of the light emitted at specific wavelengths is measured and used to determine the concentrations of the elements of interest. Single element measurements can be performed effectively with a simple monochromator/photo-multiplier tube (PMT) combination, and simultaneous multi element determinations are performed for up to 70 elements with the combination of a polychromatic and an array detector. The analytical performance of this systems is competitive with most other inorganic analytical techniques, especially with regards to sample throughput and sensitivity. This technique has low background emission, relatively low chemical interference, less noise, high stability leading to excellent accuracy and precision, and excellent detection limits for most elements (0.1 –100 mg/mL).

Basic Principle:

The principle used in the inductively coupled Plasma Optical Emission Spectroscopy is when plasma energy is employed to an analyze sample. Plasma are produced by inductive heating in an inductively coupled plasma (ICP) torch. Discharge of a high voltage from a Tesla coil through flowing argon will provide free electrons which will 'ignite' the gas to a plasma. If the conducting plasma is enclosed in a high frequency electromagnetic field, then it will accelerate the ions and electrons and cause collisions with the support gas, argon, and the analyte. The plasma has high electron density and temperature (10,000K) capable of exciting refractory elements, and renders it less prone to matrix interferences and this energy is used in the excitation-emission of the sample. At such temperatures, energy transfer is efficient, and the plasma becomes self-sustaining. It is held in place by the magnetic field in the form of a fireball plume, which contains the sample elements as atoms or ions, free of molecular association. As they cool to around 6000-7000 K, they relax to their ground state and emit rays (spectrum rays) and the emission rays that correspond to the photon wavelength are measured. The element type is determined based on the position of the photon rays, and the content of each element is determined based on the ray's intensity. This technique is known as ICP-Optical Emission Spectrometry (ICP-OES).

Other Instruments

ICP-MS, XRF, and FTIR Spectroscopy Inductively coupled plasma-mass spectrometry (ICP-MS), X-ray fluorescence (XRF), and Fourier-transform infrared (FTIR) spectroscopy are other analytical techniques that have been used for the analysis of environmental samples [7]. ICP-MS is a powerful analytical technique that is used to detect and quantify trace and ultra-trace elements in environmental samples. XRF is a non-destructive analytical technique that is used to detect and quantify the elemental composition of a sample. FTIR spectroscopy is a versatile analytical technique that is used to identify and quantify organic and inorganic compounds in environmental samples. The detection and quantification of

pollutants in environmental samples is critical in identifying the sources of contamination and the extent of pollution. GCMS, MP-AES, and NAA are powerful analytical techniques that have been used extensively for the analysis of environmental samples. ICP-MS, XRF, and FTIR spectroscopy are other analytical techniques that have been used for the analysis of environmental samples. The selection of the appropriate analytical technique depends on the specific research question and the characteristics of the samples being analyzed. The continued use and development of these analytical techniques are critical in ongoing efforts to monitor and mitigate environmental pollution and protect public health [12].

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