

Chapter Three

Literature review

3.1 Introduction

The effect of radioactive materials and heavy elements on environment was tackled by many researches. They classify the type and abundance of these materials in air, soil, water, beside their effects on the people plants, buildings and animals. Some of these studies are presented here in this chapter.

3.2 Research overview and motivation

Some Traces of radionuclide's are found in water, air, soil and human bodies. We inhale and ingest radionuclide's every day of our lives and radioactive material has been ubiquitous on earth since its creation. The presence of natural radioactivity in soil results in internal and external exposure to humans. Radioactive elements which can be found in nature are generally categorized in two distinct families, namely of arising from either 'Cosmogenic' or 'Terrestrial' Origin [22].

The most commonly encountered radionuclide's that irradiate the human body through external exposure (primarily by gamma radiation) are ^{235}U , ^{238}U and ^{232}Th and their subsequent radioactive decay products and ^{40}K [23].

There is currently no peer reviewed, published literature on the level of environmental, naturally occurring radioactivity in the most of populated area. A baseline value for the radioactivity concentration in soil has not yet been established to date. Measurements of the levels of natural background level of the radioactivity from ^{235}U , ^{238}U and ^{232}Th (and

their decay progeny), the activities from the primordial radionuclide of ^{40}K and the artificially created fission product ^{137}Cs are essential parameters with which to determine the natural radioactivity concentration levels and their behavior in the environment. Such data can be used to assess the biological effect of natural radiation in the environment and detect any significant future artificial release of radioactive radionuclide's [24].

Since individuals typically spend 80 percent of their time indoors, knowledge of the natural radioactivity levels in dwellings due to construction materials is an important issue in the assessment of overall human exposure to natural radiation associated with ^{226}Ra and ^{232}Th (and their decay progeny) and ^{40}K [23,25]. Such studies are also used to set national standards in the light of global recommendations. On the national level, this research will contribute to the establishment of area study national standards for the levels of natural radioactivity's of soil samples and building materials by determining the Gamma Dose Rate (D), Radium Equivalent (R_{aeq}), External Hazard Index (H_{ex}), Internal Hazard Index (H_{in}), and Annual Effective Dose Equivalent (AEDE) for individuals living in domestic dwellings.

3.3 Naturally Occurring Radioactive Material (NORM) in Soil and Buildings

Naturally occurring radioactivity can be found in certain industrial materials like ores and minerals [27]. Various names have been assigned to such materials in the past; such as Low Specific Activity (LSA), and Technologically Enhanced Naturally Occurring Radioactive Materials

(TENORM), but now are more generally described as simply "NORM", which refers to Naturally Occurring Radioactive Materials. The International Atomic Energy Agency (IAEA) defines NORM as “Radioactive materials containing no significant amounts of radionuclide other than naturally occurring radionuclides” [28].

Table 3.1 shows the typical activity concentrations in some commercial ores and minerals [29].

The radionuclides of particular interest are ^{238}U , ^{235}U , and ^{232}Th and their decay progeny, and the primordial radionuclide ^{40}K , Shaw considered soil which contains activity concentrations significantly higher than those in ordinary soil that has normal background levels as a NORM (see Table 1.1) [30]. Other authors consider soil with elevated levels of activity concentration as sources of natural radiation [30]. Since the elevated level of activity concentration in soil in some parts of the world may require taking action to protect humans living in dwellings built on these areas, soil with elevated levels of activity concentrations can be considered as NORM which requires the authorities to recommend precautions for health protection reasons. There are some human activities which can enhance radioactivity from NORM indirectly, such as the use of building materials that contain elevated levels of activity concentration in building dwellings and workplace [31].

Table 3.1 Ranges of the concentrations of ^{238}U , ^{232}Th and ^{40}K in typical rocks and soils [30]

Material	^{40}K (Bq/kg)	^{232}Th (Bq/kg)	^{238}U (Bq/kg)
Igneous rocks			
Basalt (crustal ave.)	30 0	10-15	7-10
Mafic	70- 400	7	7
Salic	1100- 1500	60	50
Granite (crustal ave.)	>10 00	70	40
Sedimentary rocks			
Shale sandstones	80 0	50	40
Clean quartz	<30 0	<8	<10
Dirty quartz	40 0	10- 25	40
Arkose	600- 900	<8	10-25
Beach sands	<30 0	25	40
Carbonate rocks	7 0	8	25
All rock (range)	700- 1500	7- 80	7- 60

Continental crust (ave.)	85 0	44	36
Soil (ave.)	40 0	37	22

The IAEA concluded that it is not necessary to apply regulatory control for activity concentrations below 1 Bq/g. Indeed, if the activity concentrations are at this level or even above, activity may still be exempt from regulatory controls if occupational exposure is found to be less than 1 mSv/y [32].

The global effective dose rate of public exposure from soil with weighted mean activity concentrations of 30 Bq/kg, 35 Bq/kg, and 400 Bq/kg for ^{238}U , ^{232}Th , and ^{40}K respectively is 0.460 mSv/y [26]. NORM occurs in minerals, coal, oil and gas, mineral sands and bauxite [33]. Mining and processing of ores to extract minerals can alter the radioactivity concentration of the products, by-products, residues and wastes of these materials [29]. Examples of bulk materials include: red mud (from bauxite processing) bricks [34]; sludge and scales (from oil and gas production) [33]; phosphate rocks [35]; and fertilizers [36]. Other products containing NORM include uranium glass, watch and clock dials [9]; clay bricks [37]; and glazed tiles [38]. Accumulation of by products produced from fossil fuels burning and metal refining can also lead directly to the production of NORM [27]. There are some activities which can enhance NORM levels indirectly, for example the reuse and disposal of industrial waste (e.g. phosphogypsum, fly ash and mine tailing) [39]. This means that exposures to ionizing radiation from NORM are common and that every country has to deal with estimating the risk from exposure

to ionizing radiation arising from NORM in some form.

3.3.1 NORM in the Oil and Gas Industry

Oil and gas production and processing operations sometimes accumulate naturally occurring radioactive materials (NORM) at elevated concentrations in by-product waste streams. The primary radionuclides of concern in NORM wastes are ^{226}Ra (from the ^{238}U decay series), and its decay progeny ^{214}Pb and ^{214}Bi . The first detection of NORM associated with the oil and gas production was as early 1904 in Canada [43] and [45], and its presence in oil and gas wastes has been recognized since the 1930s [43]. NORM was not recognized as a waste management issue, however, until the mid-1980s, when the industry and regulators realized that NORM occurrence was more widespread than originally thought and that activity levels could be high [44]. The initial production of an oil reservoir is usually dry. When the oil migrates, the natural pressure within the formation falls. The water present in the reservoir (formation water) which is normally produced in the oil and gas can carry up, during the extraction process, the reservoir's shale that contains dissolved mineral salts [45]. The concentration of radionuclides in the reservoirs shall varies depending on the rock type in the underlying sedimentary rocks. The highest values are normally found in black shale, while the limestone and sandstones rocks have lower levels of ^{238}U and ^{232}Th [45]. When the pressure in a mature reservoir drops down, it is normal practice to inject seawater, which is high in sulfate and barium, into the well in order to maintain the 'downhole' pressure. If there are chemical incompatibilities between the seawater and the formation

water (i.e., if the seawater is more saline than the formation water) [44] then, additional radioactive salts from the mineral present in the various geological strata may dissolve and form in the water (such as barium sulfate, calcium carbonate, and strontium sulfate).

Once the solubility product for particular pair of ions e.g. barium sulfate is exceeded, precipitate can (easily) form [45]. The temperature and pressure of the water change as the well fluids pass through the production equipment. Since radium is in the same group elements in the periodic table (II A) as calcium, strontium, and barium, the barium sulfate co-precipitates with radium sulfate to form complex, hard, insoluble salts such as barium radium sulfate, which may be produced with oil in the production waste steams as production water, scale, and/or sludge. The barium sulfate salt forms a hard scale on the metal surface which can be extremely difficult to remove [46]. Release of the production wastes to the ground can result in NORM- contaminated soil that must be disposed of. Scale typically forms on the inside of piping, filters, injection wellhead equipment, and other water handling equipment and also can form as a coating on produced sand grains [47]. In the case of sludge formation, radium can present in several forms. These include pieces of barium sulfate (BaSO_4) scale that become incorporated into the sludge. It can also co-precipitate with sulfates and carbonates which form in the sludge (CaCO_3 , SrSO_4). NORM contaminated sludge can also accumulate inside piping, separators, heater/treaters, storage tanks and any other equipment where produced water is handled [47].

In the past, NORM was commercially managed by surface treatment including landfill and land spreading, through which NORM was blended with nonradioactive materials to reduce the NORM activity

below action levels and spread on the land. Nowadays, NORM waste are disposed of using other methods such as; Encapsulation and Downhole Disposal, Sludge Incineration [48] and [49] and licensed radioactive waste landfills. The primary, and the best method used for disposal of NORM wastes today is underground injection [46].

3.3.2 NORM classification

3.3.2.1 NORM Cosmogenic: It has been shown that the interaction between cosmic rays and some upper atmosphere elements may lead to reactions, which produce of a large number of nucleons (protons and neutrons). These nucleons may lead to charge exchange and the neutron capture reactions, which in turn lead to a production of ^{14}C through the (n,p) reaction on ^{14}N and ^{81}Kr following the (n, γ) reaction on ^{80}Kr . The light radionuclide ^7Be is produced in the atmosphere as a consequence of spallation on C, N and O nuclei [52].

3.3.2.2 Primordial

Primordial radionuclides have been present since the creation of the earth and have the half-lives similar or longer than the estimated age of the earth . These radionuclide's and their decays products are present in terrestrial materials that are distributed in the environment, foods, water, air, soil, the human body and building materials [50].

3.3.2.3 Terrestrial

Terrestrial radionuclides occur in three main nuclear decay chains. The ^{238}U chain contains 15 radionuclides and 99.3% of natural uranium. ^{238}U ultimately decays to the stable nucleus, ^{206}Pb by alpha decay. The products of the decay have shorter decay half- lives than ^{238}U , which means that the

Uranium decay and its products are in secular equilibrium. There is also a decay chain headed by ^{235}U , which makes up only 0.72% of natural uranium. This chain is shorter than its ^{238}U counterpart and contains 12 radionuclides. Finally, there is a chain headed by ^{232}Th , which makes up 100% of thorium in nature [53].

^{238}U heads arguably the most important primordial radionuclide chain with a half-life 4.47×10^9 years. There are other terrestrial radionuclides that have low concentration levels which arise in the natural background and include the ^{235}U series, ^{87}Rb , ^{138}La , ^{147}Sm , and ^{176}Lu . Non-series radionuclides such as ^{40}K also occur in the nature. ^{40}K (half life 1.28×10^9 years) is a which exists in the environment and human body. [51].

Man-made radionuclides play an important role in elevating the NORM levels in nature either as chemical waste products in the environment, or as soil fertilizers that have high levels of potassium. Furthermore, nuclear weapons tests which lead to radioactive fallouts in the atmosphere and may lead to traces of ^{137}Cs , ^{90}Sr , $^{239,240}\text{Pu}$ and ^{241}Am are other radionuclides that are mainly detected after any nuclear releases from a reactor or nuclear weapon, including in the incident at [54].

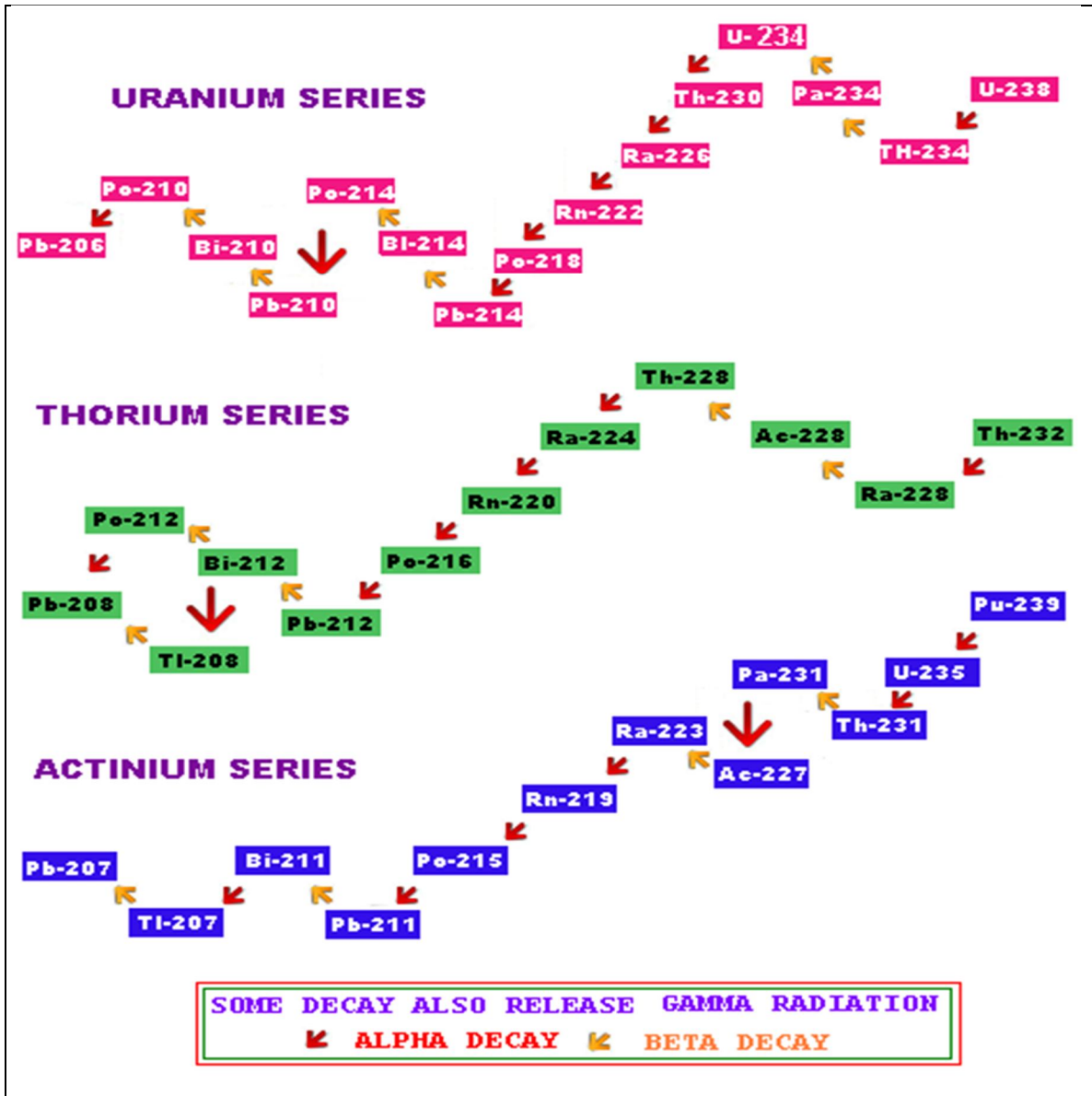


Figure 3.1 Decay chains for the three main naturally occurring radioactive decay series.

Another source of NORM is oil field operations which are created from subsurface oil and gas and transported to the surface through radioactive water sludges and scales which are produced. These scales and sludges may form thin radioactive films on the inner surface of the gas processing equipment. Then with the production of fluids these radioactive elements

are brought to surface staying within the water phase before incorporating in pipe scale, the radioactivity in oil fields is part of NORM[54].

3.4 Heavy Metal

Heavy Metals are defined as elements in the periodic table having atomic number more than 20 or densities more than 5g/cm³ generally excluding alkali metals and alkaline earth metals.

The environmental problems with heavy metals are that they as elements are destroyable and the most of them have toxic effects on living organisms when exceeding a certain concentration. Furthermore, some heavy metals are being subjected to bioaccumulation and may pose a risk to human health when transferred to the food chain. Soils, whether in urban or agricultural areas represent a major sink for metals released into the environment from a wide variety of anthropogenic sources [55]. Once in soil, some of these metals would be persistent because of their fairly immobile nature. Other metals however would be more mobile therefore the potential of transfer either through soil profile down to ground water aquifer or via plant - root uptake (bio available) is likely. When the food chain is concerned, one has to take into account the mobility and the bio availability of metals, because plant uptake of metals parallels the bio available fractions of the metals in soil. In most soil environment sorption is the dominating speciation process and thus the largest fraction of heavy metal in a soil is associated with the solid phase of that soil.

Pollution problem arise when heavy metals are mobilized into the soil solution and taken up by plants or transported to the surface/ground water. The properties of the soil are thus very important in the attenuation of heavy metals in the environment.

The solubility of heavy metals in soil is controlled by reactions with solid phases. Once sewage sludge is applied to soil, the heavy metal species undergo several possible fates including adsorption/desorption reactions, Precipitation/dissolution reaction, Plant uptake and a possible mobility thro' soil profile.

3.4.1 Sources of some heavy metals and their properties in soil

Mercury (Hg): Major contaminating sources of Hg are: Hg based fungicides, sewerage sludge and atmospheric fall out resulting from combustion of fossil fuels and industrial processes.

Cadmium (Cd): Cd is an element that can be found naturally in the earth's crust or used in a variety of applications, including manufacturing of batteries, paint pigments, metal coatings, and plastics. Additionally, the burning of fossil fuels can contribute to the presence of Cd in the environment. Cd can enter natural systems through deposition from air emissions, as well as through leaching or washing of contaminated sites. Sediment contamination from Cd occurs through sorption to organic matter, and through co precipitation with iron, Al, and Mn-oxides. It binds strongly to soil particles, not breaking down in the environment, but rather changing forms. Exposure to Cd occurs mainly through inhalation of contaminated air, ingestion of contaminated food sources or through contaminated water supplies. Soil contamination occurs by the addition of phosphate fertilizers. (Containing 2-200 mg Cd/kg) domestic and sewage sludge, wear of automobile tyres, lubricants and mining and metallurgical activities. The bioavailability of Cd in sediments is dependent upon pH, redox potential, water hardness, and the presence of other complexing agents. Studies have shown that animals exposed to high doses of Cd experienced lung disease

and stomach disorders. Cd ability to remain in the body for a very long time allows for levels to build up, even if exposure concentrations are low. Aquatic organisms exposed to Cd have shown various effects, including acute mortality, reduced growth, and inhibited reproduction. It is unclear whether human exposure to Cd will result in similar diseases when exposed to equal levels as in animal studies. Exposure to Cd through dermal contact has no known effect in either humans or animals. Recommendations to protect public health have been made by several governmental agencies. The United States Environmental Protection Agency (USEPA) has established limits for Cd in drinking water set at 0.005 parts per million (mg/L). The United States Food and Drug Administration (USFDA) allows up to 15 parts per million (ppm) in food colorings, while the Occupational Safety and Health Administration limits workplace air to 100 ug/m³ as Cd fumes, and 200 ug/L as dust particulate [56]. Additional guidance concentrations have been derived for use with the SQAGs, and SCTLs. SQAGs have established a TEL of 0.68 mg/kg, and a PEL of 4.2 mg/kg. The SCTLs for exposure limits are set at 75 mg/kg for residential exposures, and 1300 mg/kg for commercial exposures.

Chromium (Cr): Similar to Cd, Cr is an element that can be found occurring naturally in the environment, as Cr(III), or as by product from various industrial processes as Cr(VI). Processes involving the use of Cr include steel production, paint and dye production, leather tanning and wood preservation. Cr enters the environment through deposition from air emissions and leaching at contaminated sites, mainly in the Cr(III) and Cr(VI) forms. Once introduced to a natural system its fate depends upon the form at which it enters. In aquatic systems Cr(VI) tends to be very soluble, not readily sorbed to particulate matter. However, as anaerobic conditions

prevail, Cr(VI) reduces to Cr(III), a state which can strongly sorb onto organic particulates. Exposure to Cr contamination occurs through inhalation, ingestion, or dermal contact. Inhalation of high levels of Cr(VI) has been shown to cause nasal irritations such as nosebleeds or ulcers. Ingestion of similar levels can cause stomach, liver or kidney damage, which may result in death. Unlike Cd, dermal exposure to high levels of Cr(VI) may result into skin ulcers. Individuals with severe allergies may experience swelling and redness to exposed areas. Studies have shown Cr(VI) compounds can increase the risk of lung cancer, and the several health organizations have labeled Cr(VI) in various forms as a human carcinogen. Additional adverse effects to biological communities include death and decreased growth, particular by vegetative species. Fish do not tend to be as sensitive as humans to Cr contamination[56]. Federal regulations have been established by the EPA and OSHA to protect public health from exposure to high levels of Cr. EPA recommends Cr concentrations in water not to exceed 0.1 mg/L. In addition to drinking water standards, SQAGs and SCTLs have been derived for contamination and remediation assessments. Under the SQAGs, a TEL of 52.3 mg/kg and a PEL of 160 mg/kg have been established for aquatic biota protection. The SCTLs for residential and commercial exposures are 210 mg/kg, and 420 mg/kg, respectively.

Copper (Cu): Cu is a natural occurring metallic element in crustal rocks and minerals, released during weathering processes. Anthropogenic sources of Cu include agricultural fungicides, pesticides, sewage treatment effluent, wood preserving, and fallout from industrial sources and coal burning.

Cu can enter natural systems through weathering of minerals, release in air Emissions , and through direct exposure as in soil or water treatment devices. Inhalation, ingestion and dermal contact are the main pathways for

Cu exposures to many organisms. While Cu is considered an essential micronutrient, exposure to elevated levels in the air can cause irritations to the nose and mouth. Ingestion of high levels of Cu can lead to kidney and liver damage as well as stomach disorders. Dermal exposure to elevated Cu levels can result in an allergic reaction or rash in sensitive individuals. There is no indication that Cu exposures can lead to cancer in either humans or animals. However, Cu contamination of aquatic systems may be associated with acute and chronic toxicity in biotic organisms [56].

Human health concerns from Cu contamination have led to the establishment of federal guidelines regulating consumption and workplace exposures. Drinking water standards have been set at 1.3 mg/L. In addition to EPA and OSHA regulations, protective levels have been derived under the SQAGs and the SCTLs. The SQAGs have established a TEL of 18.7 mg/kg, and a PEL of 108 mg/kg. Residential exposure guidelines established for SCTLs has been set at 110 mg/kg, while commercial exposure limits are 76,000 mg/kg.

Lead (Pb): Pb is a metallic element that is found in virtually all parts of our environment. While it can be naturally occurring, anthropogenic sources contribute heavily to its presence. These sources include the burning of fossil fuels, mining, and the manufacturing of batteries, metal products, and ammunition. The use of Pb in many items such as paints and gasoline has been greatly reduced due to health concerns. Pb can enter natural systems through deposition with air particulates or by leaching or washing of contaminated surfaces. Once Pb comes into contact with sediments, its movement is dependent upon the type of Pb compound and soil characteristics. Pb(II) tends to be the most stable ionic species, and can be found bound to Fe and Mn-hydroxides in addition to clay and organic

matter. Oxidized sediments tend to bind closely with Pb, with its release and mobility increasing under reducing conditions. The majority of exposures to Pb occur through ingestion or inhalation.

In humans, Pb exposures to high levels have been shown to affect the organs of the body and the central nervous system. Blood disorders and male reproductive problems may also occur. Aquatic organisms also exhibit toxic effects from Pb. Plants tend to be less sensitive to exposures than fish or invertebrates. While studies involving animals indicate the possibility of Pb to be a carcinogen, there is no evidence to suggest carcinogenic effects in humans.

Federal agencies have set regulations to control Pb exposures through ingestion and workplace incidences. Drinking water standards for Pb are set at 0.015 mg/L. Additional recommendations have been made regarding Pb screening programs for children who live in areas determined to be high risk zones [56]. The SQAGs have derived a TEL of 30.2 mg/kg, and a PEL of 112 mg/kg. SCTLs set exposure limits at 400 mg/kg for residential classifications, and 920 mg/kg for commercial sites.

Nickel (Ni): Ni is an element found abundantly in the earth's crust, primarily combined with oxygen and sulfur. The following information on metal toxicity was obtained through the Agency for Toxic Substances and Disease Registry (ATSDR) website, located at www.atsdr.cdc.gov [56]. Ore deposits often contain Ni with Fe or Cu. While Ni is used in a variety of manufacturing and industrial industries, the major anthropogenic sources include fossil fuel combustion, batteries, Ni ore mining, smelting and refining activities, and electroplating [57]. Anthropogenic sources of Ni may enter environmental systems as small deposits in air particles, or through the washing and leaching of surfaces containing Ni. As anthropogenic sources

are introduced to sediments they become bound as Fe or Mn oxides or they sorb with organic matter. Release of Ni from sediments may decrease under anaerobic conditions as they form insoluble complexes with sulfides. Human and animal exposures to Ni can be through inhalation, ingestion or dermal contact. Ni is considered a required element for maintaining good health, but, exposures to high levels can cause adverse health effects.

The most severe exposures for humans and animals in terms of health related concerns appear to be through dermal contact and inhalation. Allergic reactions from contact with Ni, in the form of skin rashes, are the most common types of health effect seen. Workplace exposure to air particles containing Ni compounds have been linked to lung and nasal cancers. In terms of adverse effects on aquatic organisms, increased mortality rates, decreased growth and avoidance reactions have been observed. With certain Ni compounds determined to be carcinogenic, federal agencies have established recommendations regarding ingestion of water containing these compounds [56]. In addition to drinking water standards of 0.04 mg/L, occupational exposure levels have also been established to reduce concerns from inhalation. For the protection of aquatic organisms the SQAGs have derived a TEL of 15.9 g/L, and a PEL of 42.8 g/L. SCTLs have been determined to be 110 ug/L for residential considerations, and 28,000 ug/L at commercial sites.

Zinc (Zn): Zn is an abundant element, found in air, soil, and water. As a crustal element it is present commonly as a sulfide, carbonate, or silicate ore. Zn has a number of different production uses, including dry cell batteries, rust preventatives, and as a mixture with other metals to form alloys. Release of Zn into the environment can occur through natural processes. Anthropogenic inputs from air deposition and leaching also contribute to its

presence. Much of the Zn entering the environment stays bound to soil with Fe and Mn-oxides, clay minerals and organic matter. Adsorption rates of Zn have been determined to be pH dependent, showing a decrease in aquatic systems with pHs below 6. Sorption to organic matter in fine grained sediments is controlled by reducing conditions, which form insoluble sulfides (FDEP, 2000). Health concerns over exposure to Zn arise from ingesting contaminated food or water supplies, or from breathing aerosolized Zn particles near manufacturing plants.

Zn is an essential element to the diet of humans, requiring an appropriate balance to be effective. Since our bodies require Zn, low inputs to our systems can be just as harmful as exposures to high levels. Ingestion of high levels of Zn may lead to short-term stomach and blood disorders and possibly pancreas damage. Inhalation of Zn at high concentrations may cause lung irritations and body temperature fluctuations on a short term basis. Long-term effects for Zn inhalation have not been determined. Effects on aquatic organisms appear to be minor as they can experience a wide range of sensitivity to Zn exposure. Zn is currently not listed as a possible carcinogen [56].

Federal agencies have established recommendations for human exposures to Zn contamination through drinking water of 0.005 mg/L, and workplace exposure guidelines. To protect aquatic organisms, the SQAGs have recommended a TEL of 124 mg/kg, and a PEL of 271 mg/kg. SCTLs have been established at 23,000 mg/kg for residential sites, and at 560,000mg/kg for commercial clean up designations.

The accumulation of heavy metals in soils is of increasing concern due to food safety threat and potential health risks as well as detrimental effects on soil ecosystems [57].

There are two sources of heavy metals in the soil namely, the anthropogenic and natural activities. The natural sources of metals in soil include flooding, weathering of rocks and volcanic eruptions.

Previous Studies have reported that heavy metals such as arsenic (As), mercury (Hg), aluminum (Al), Iron (Fe), lead (Pb), magnesium (Mg), cadmium (Cd), copper (Cu) and zinc (Zn) are produced when volcanic eruptions occur [58]. Out of these As, Hg, Cd and Pb are considered as toxic while Mg, Cu and Zn are essential in low concentrations only[59]. Volcanic eruptions produce ash, dust and lava which are emitted, sometimes in large quantities, into the environment. The volcanic dust flies long in air with wind and spread over large distances and then falls onto the ground and migrates to the soil [60]. These heavy metals from the volcanic eruptions are normally transported from the volcanic mountain and settle on the soil [61]. Heavy metals in soil may dissolve in water and be up taken by plants and vegetations to enter the food chain.

The exposures to poisonous elements such as Pb, Cd, Ni and As have been linked with significant health risk to human body [62]. Heavy metals in soils may be of natural or anthropogenic origin. Natural sources include volcanic emissions, Aeolian dusts and weathering of rocks (Ernst, 1998). However, the major contamination is usually of anthropogenic origin due to mining and smelting, application of metal-containing pesticides and fertilizers in agriculture, combustion of fossil fuel, waste disposal, as well as military activities [63]. Cu, Ni, Cd, Zn, Cr, Pb are the most important inorganic soil pollutants. Because soils have limited capacity to inactivate or to attenuate these inputs, heavy metals can persist in soil for very long times, with little decrease in their biological potency [64]. Ample evidence now exists that chemically degraded soil may not only imperil our life support system, i.e.

the soil, but also may threaten the whole food chain and consequently humans . In addition, soil degradation may impact economic development by limiting the marketing of agricultural products and reducing the profitability of the agricultural industry[65].

Barium (Ba): Barium is not an extensively used element. Most is used in drilling fluids for oil and gas wells. It is also used in paint and in glassmaking. All barium compounds are toxic; however, barium sulfate is insoluble and so can be safely swallowed. A suspension of barium sulfate is sometimes given to patients suffering from digestive disorders. This is a ‘barium meal’ or ‘barium enema’. Barium is a heavy element and scatters X-rays, so as it passes through the body the stomach and intestines can be distinguished on an X-ray[66,69].

Zirconium (Zr): Zirconium does not absorb neutrons, making it an ideal material for use in nuclear power stations.. Nuclear reactors can have more than 100,000 meters of zirconium alloy tubing. With niobium, zirconium is superconductive at low temperatures and is used to make superconducting magnets.

Zirconium metal is protected by a thin oxide layer making it exceptionally resistant to corrosion by acids, alkalis and seawater. For this reason it is extensively used by the chemical industry[66,67]. Zirconium (IV) oxide is used in ultra-strong ceramics. It is used to make crucibles that will withstand heat-shock, furnace linings, foundry bricks, abrasives and by the glass and ceramics industries. It is used in cosmetics, antiperspirants, food packaging and to make microwave filters. Zircon is a natural semi precious gemstone found in a variety of colours. The most desirable have a golden hue. The element was first discovered in this form, resulting in its name. Cubic

zirconia (zirconium oxide) is a synthetic gemstone. The colourless stones, when cut, resemble diamonds.

Zircon mixed with vanadium or praseodymium makes blue and yellow pigments for glazing pottery [68,69].

3.4.2 Soil contamination by heavy metals in Europe

In Switzerland It is estimated that in Western Europe, up to 1.4 Mio. Sites are polluted, many of them with heavy metals such as Zn, Cd, Pb and Cu . Accumulation of these metals continues as inputs exceed the outputs in many European soils [70].

3.4.3 Impact of heavy metals on soil functions

Plant roots and most soil organisms depend on energy derived from assimilates produced above ground by photosynthesis. The mineralization of organic residues by bacteria and fungi, i.e. "microorganisms", releases inorganic nutrients such as nitrate, sulphate and phosphate that can then be utilized again by plants and other organisms. Microbial biomass and activity are generally much higher in the rhizosphere than in the bulk soil due to the much larger availability of substrates such as root exudates [71]. Because of their role in organic matter decomposition, microorganisms are of utmost importance for the fertility of soil as well as for the recycling of nutrient elements. Poisoning of soil microorganisms can thus have dramatic consequences for the functioning of the entire ecosystem. Soil contamination by heavy metals is one of the problems threatening soil fertility and element cycling most seriously in many areas. If present in sufficiently high concentrations, heavy metals have been found to reduce the size of the microbial populations, to disrupt their community structure and to reduce

their activity. Heavy metal pollution may therefore result in severe ecosystem disturbance [72].